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Metal-organic framework DUT-67 (Zr) for adsorptive removal of trace Hg^{2+} and CH_3Hg^+ in water

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ABSTRACT

A Zr-based stable metal-organic frameworks DUT-67 (Zr) was successfully synthesized as an adsorbent to remove trace mercury and methylmercury ions in aqueous solution. The removal efficiency of 90% and 55% of Hg^{2+} and CH_3Hg^+ was respectively achieved at pH 6 and 55°C. The S in thiophene has a relatively weak adsorption capacity for mercury and there could be the slight π-complexation between thiophere ring of DUT-67 (Zr) and Hg^{2+} besides physical absorption, while there only was physical adsorption between DUT-67 (Zr) and CH_3Hg^+. The developed methods were applied to remove trace Hg^{2+} and CH_3Hg^+ in the real water samples, and the removal efficiency was from 69% to 90% and from 30% to 77% respectively; when the concentrations of Hg^{2+} was lower than 20 μg L^{-1} in the samples, the remaining mercury concentration was lower than 1 μg L^{-1}, which can meet the standard of the World Health Organization.

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KEYWORDS
Metal organic framework; mercury ions; methylmercury ions; adsorption

1. Introduction

Mercury is one of toxic heavy metal pollutants because it seriously damages to the human body [1,2]. With the implementation of the Minamata Convention, people increasingly concern about its hazard and the control of the global mercury emission becoming an emergency [3]. In aqueous solution, mercury exists in various species, such as inorganic mercury and organomercury, and its toxicity and bioavailability mainly depend on its different chemical forms [4]. Among them, mercury with oxidation state 2 valence can easily penetrate biological membranes and cause serious kidney, digestive, endocrine and central nervous system complications [5]. And the most toxic form of organomercury is methylmercury because of its bio-accumulation and concentration with food chains and it consequently causes permanent damage to the nervous systems and brains of human being [6,7]. The studies showed that it can cause toxic effects even though at ultra-low-concentration of μg L^{-1} (part per billion) [8]. As a result, the World Health Organization (WHO) recommends 1 μg L^{-1} as the maximum concentration of total mercury in drinking water [9]. Therefore, removing trace mercury from the natural water is an urgent matter.

At present, many methods have been developed to remove mercury in water, such as chemical coagulation [10], adsorption [11], electrocoagulation [12] and membrane filtration [13]. Among them, the adsorption method could be a practical and economic method compared to other techniques because of its comparatively low cost, high efficiency, simplicity of operation and lower secondary pollution [14]. Multiple sorbents have been widely investigated to capture mercury from wastewater, including zeolites [15], activated carbons [16], metal oxidize [17] and nanocellulose [18]. However, such materials usually face challenges with relatively low adsorption capacities, low surface area and moderate affinity for mercury [19]. The main mechanism of them were physisorption, which results in low adsorption capacity due to the weak binding ability. Therefore, exploring a stable, large surface area and effective adsorbent for removal of mercury ions is of considerable importance.

Metal organic frameworks (MOFs) are composed of organic ligands and metal ions or clusters with infinite network, which are new type of microporous and mesoporous materials. MOFs have advantages of high porosity, diversity in structure, large specific surface area, relatively easy modification, chemistry and thermal stability, etc [20]. The network topology, shape and pore size of the material can be controlled by selecting different metal ions and organic ligands to achieve specific applications. Because of the advantages proposed above, MOFs are widely used in gas storage [21], adsorption [22], separation [23,24], catalysis [25] and fluorescence sensing [26]. In recent years, the research on the removal and adsorption of heavy metal pollutants from aqueous environment by MOFs is attracting attentions [27–30]. For example, an ethylenediamine-functionalized MIL-101-Cr was used

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to adsorb Pb^{2+} in lake and river water samples [31], the results revealed that the sorbent could reduce the lead concentrations to as low as 0.3–0.5 mg L^{-1} from 10 mg L^{-1}. So far, most of the researches are mainly about removal of heavy metal pollutants at comparable higher mg L^{-1} concentrations, but effective removal of heavy metal pollutions at μg L^{-1} levels is still a challenge [32]. The absorption performance of trace Hg^{2+} was detected by using unmodified MOF-74-Zn material and the removal efficiency of 57.08%, 54.48% and 72.26% were obtained at 45°C when its concentrations were at 10 μg L^{-1}, 20 μg L^{-1} and 50 μg L^{-1}, respectively [33]. However, it is still a big challenge to reduce the residual Hg^{2+} to below 1 μg L^{-1} in solution. This is due to the lack of strong binding capacity among metal ions and action sites which hinders the capture of metal ions.

(Dresden University of Technology) DUT-67 (Zr) was a water and acidic stable metal-organic framework with the composition of $[Zr_6O_6(OH)_2(tdc)_4(CH_3COO)_2]$ [34], which had large specific surface area，the ligand of thiophere aromatic had a S element and could be a potential candidate for dealing with heavy metals in water. In this work, DUT-67 (Zr) was synthesized and used as an adsorbent to remove trace mercury and methylmercury ions in water. The factors that affected absorption performance including contact time, pH and temperature were studied and the influence of humic acid (HA) was also investigated. Finally, we applied it to remove the trace mercury and methylmercury ions in the water samples and achieved satisfactory results.

2. Experimental

2.1 *Chemicals and materials*

In this experiment, the solvents and reagents without further purification were commercially available. Zirconium chloride was purchased from Macklin Biochemical Co., Ltd. (Shanghai, China). 2, 5-thiophenedicarboxylic acid (H_2tdc) was from J&K Scientific Ltd. (Beijing, China). N-methyl pyrrolidone (NMP), acetic acid and N, N-dimethylformamide (DMF) were purchased from Fuchen Chemical Reagents Factory (Tianjin, China). Ethanol was purchased from Beijing Chemical Works (Beijing, China). KOH (GR Grade) and NaOH (purity, ≥ 96%) were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). KBH_4 (purity, ≥ 98.5%) was obtained from Tianjin Institute of Fine Chemicals (Tianjin, China). 65% HNO_3 was purchased from Merck KGaA (Darmstadt, Germany). Stock standard solution of mercury (1000 mg L^{-1}) and methylmercury (69.5 mg L^{-1}) were obtained from Putian Tongchuang Biotechnology Co., Ltd. (Beijing, China). Milli-Q Advantage A10 system (Millipore, Molsheim, France) was applied to make ultrapure water.

2.2. *Instruments*

The Bruker D8-Focus Bragg-Brentano X-ray powder diffractometer was used to measure the X-ray diffraction (XRD) pattern of DUT-67 (Zr), which is equipped with a Cu sealed tube (λ = 1.54178). Scanning electron microscope (SEM) image was measured at 15.0 KV on a Shimadzu SS-550 scanning electron microscope. The TGA-50 (SHIMADZU) thermogravimetric analyzer was used to obtain Thermal gravimetric analysis (TGA) image of DUT-67 (Zr) with a heating rate of 10°C min^{-1} under a N_2 atmosphere. Under N_2 absorption at 77 K, the BET of DUT-67 (Zr) was obtained on a Micromeritics ASAP2020 surface area. The concentration of mercury was detected on an AFS-8130 atomic fluorescence spectrometer equipped with a flow injection system.

2.3. *Preparation of DUT-67 (Zr) and characterization*

The DUT-67 (Zr) was synthesized according to the reported method [34]. A solid mixture of H_2tdc (220 mg, 1.34 mmol) and Zirconium chloride (460 mg, 2 mmol) were dissolved in DMF (25 mL) and NMP (25 ml) by sonication for 10 min. After that acetic acid (14 mL, 234 mmol) was added to the solution and sonicated for 10 min. The resulting solution was then transferred into a Teflon lining stainless steel reaction kettle and heated up to 120°C for 48 h. The resulted powder was separated by centrifugation and washed once with DMF and then ethanol for the second time. Afterwards, it was dried at 80°C for 2 h. The XRD, TGA, SEM and N_2 adsorption-desorption experiments were used to analyze the synthesized of DUT-67 (Zr)

2.4. *Removal and determination of Hg^{2+} and CH_3Hg^+*

Considering of the concentration of mercury ions in water environment is usually around μg L^{-1} of magnitudes, we chose 20 ug L^{-1} as the experimental concentration. The effects of varying pH and temperature were studied at a pH range of 2–7 and temperature range of 15°C–55°C, respectively, we keep the sample 10 mg of DUT-67 (Zr) was added to 10 mL of 20 ug L^{-1} Hg^{2+} and CH_3Hg^+ solution. HNO_3 and NaOH were to adjust the pH of the solution. In order to study the kinetic rules of the absorption, approximately 10 mg of DUT-67 (Zr) was immersed in 50 mL of 50 ug L^{-1} Hg^{2+} and CH_3Hg^+ solution with continuous stirring. The concentrations of Hg^{2+} and CH_3Hg^+ in 2 mL supernatant were measured by AFS when it was removed from the solutions at every set time. To determine the effect of HA in the adsorption process, a batch adsorption experiment of varying concentrations of HA from 0 to 2 mg L^{-1} were also

studied. Finally, the adsorption of Hg^{2+} and CH_3Hg^+ by DUT-67 (Zr) in real water samples were evaluated.

The DUT-67 (Zr) was separated from the solution by filtration, the solution was diluted and concentrated HNO_3 was added to the volume of 10 mL and HNO_3 concentration was about 2% (v/v) .Then the concentrations of Hg^{2+} and CH_3Hg^+ in the solution were measured by AFS. The mobile phase were A: 2% KBH_4 (m/v) in 0.5% KOH (m/v) and B: 2% HNO_3 (v/v). The sample, phase A and phase B were mixed firstly and then went through the atomizer. The Hg^{2+} and CH_3Hg^+ was analyzed on-line reducing before cold vapor generation. Table 1 lists the specific experimental conditions about the atomic fluorescence spectrometer (CV-AFS). Each sample in this work were detected three times and took the average.

The removal efficiency (R) of the mercury and the amount of mercury adsorbed by the unit mass adsorbent were calculated by Equations (1) and (2):

Table 1. CV-AFS conditions for mercury determination.

Parameters	Optimized values
Hollow-Cathode Lamp	Mercury HCL 253.7 nm
Lamp current	30 mA
PMT voltage	−270 V
Argon flow rate	200 mL/min
Atomization temperature	Room temperature
KBH_4 concentration	2% (m/v) in 0.5% KOH (m/v)
HNO_3 concentration	2% (v/v) in water
Sampling time	10 s
Injection time	25 s
Signal collection time	5 s

$$R(\%) = \frac{c_0 - c_e}{c_0} \times 100\% \quad (1)$$

$$q = \frac{c_0 - c_e}{m} \times V \quad (2)$$

In the above formulas, the initial and equilibrated concentrations of mercury are expressed in c_o (mg L^{-1}) and c_e (mg L^{-1}), respectively. m (g) represents the quality of the absorbent. q (mg g^{-1}) is the amount adsorbed per gram of adsorbent, and the initial volume of the mercury solution is represented by V (L).

3. Results and discussion

3.1. *Characterization of DUT-67 (Zr)*

The characteristic XRD pattern of the as-synthesized DUT-67 (Zr) was shown in Figure 1(a). The measured and simulated of diffraction peaks for DUT-67 (Zr) were in good agreement. Thermogravimetric analysis of DUT-67 were shown in Figure 1(b). The first step in the curve shows the loss of mass (28%) was in the range of temperature from 34°C to 100°C，which was associated with the removal of free guest solvent and water molecules in pores. The framework was stable up to 350°C, beyond which the structure would be decomposed. The scanning electron microscope (SEM) image of DUT-67 (Zr) (Figure 1(c)) indicates that it consisted of globular crystallites with an average particle size of about 2.5 μm. The nitrogen sorption-desorption isotherms of the as-synthesized

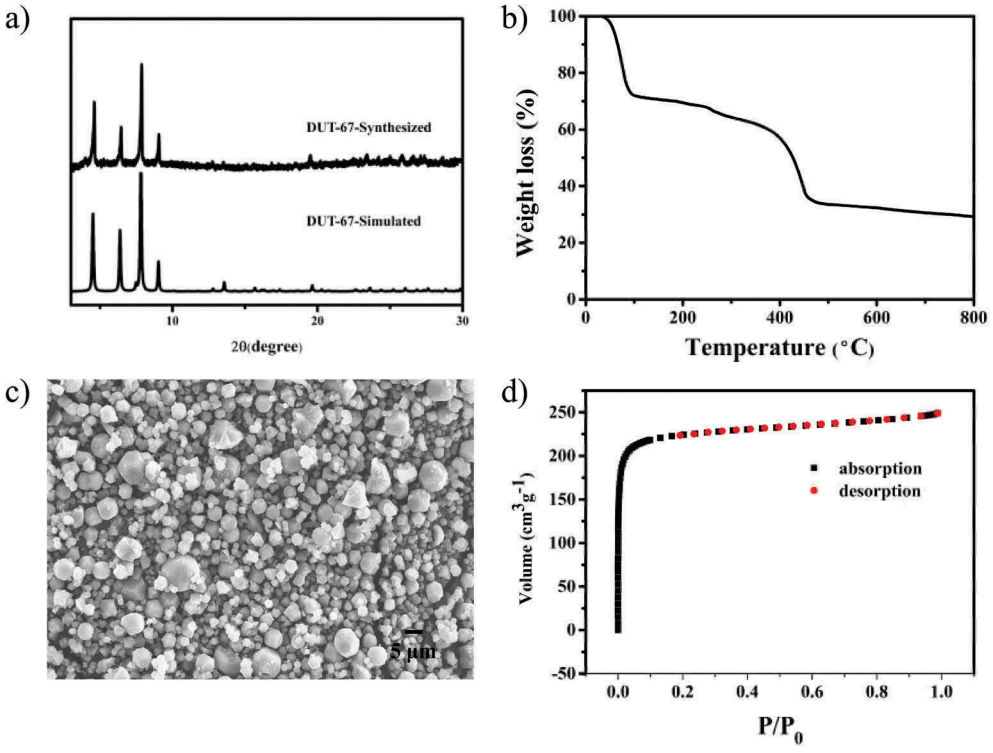

Figure 1. (a) XRD of the synthesized DUT-67 (Zr), and the simulated XRD curve. (b) TGA image of the synthesized DUT-67 (Zr). (c) SEM image of the synthesized DUT-67 (Zr). (d) nitrogen sorption-desorption isotherms image of the synthesized DUT-67 (Zr).

sample were measured as well (see Figure 1(d)). 781.8 m^2 g^{-1} and 0.3412 cm^3 g^{-1} (P/P_0 = 0.2) were the total pore volume and surface area of the adsorption, respectively. The average diameter of the pore was 1.766 nm, which indicated that the synthesized DUT-67 (Zr) was one kind of micro-pore material.

3.2. *Effect of pH on adsorption*

The effect of pH on the adsorption of DUT-67 (Zr) is of great importance due to the different forms of Hg^{2+} and CH_3Hg^+ at different pH. When the pH of the aqueous solution is lower than 3, mercury ions exist as Hg^{2+}. However, when the solution pH higher than 6, $Hg(OH)_2$ is its dominant form. When pH between 3 and 6, three kinds of forms co-exist, including Hg^{2+}, $Hg(OH)_2$, $Hg(OH)^+$ [35]. For methylmercury, the main form in the acid condition is CH_3Hg^+. With the increase of pH, the CH_3Hg^+, $(CH_3Hg)_2OH^+$ and CH_3HgOH may co-exist in the solution. However, under alkaline conditions (pH> 8), CH_3HgOH is the main form of existence [36]. To select the best pH of adsorption, the adsorption behavior of Hg^{2+} and CH_3Hg^+ on DUT-67 (Zr) were investigated at the pH range of 2–7. The results were shown in Figure 2. The results showed that there was a relatively lower removal efficiency of Hg^{2+} at the low pH condition, and as the pH increasing, the adsorption efficiency of Hg^{2+} was significantly increased and reached the maximum value when pH = 6. This results was mainly caused by the protonation of the active sites of DUT-67 (Zr) under the lower pH. The protonation of active sites of DUT-67 (Zr) decreased with the pH increases and the active sites became more beneficial for sorption of Hg^{2+} to DUT-67 (Zr). When the pH > 6, the adsorption efficiency of Hg^{2+} decreased due to the hydrolysis of metal ion and it competed the metal ion adsorption on DUT-67 (Zr). However, the change of pH value did not have obvious effect on the adsorption of CH_3Hg^+. Thus, the pH 6 was chosen in the subsequent adsorption experiments.

The aperture size of DUT-67 (Zr) was about 14.2 Å and 11.7Å [34], which is large enough for Hg^{2+} (2.2 Å) [37], $Hg(OH)^+$ and $Hg(OH)_2$ (8.22 Å) [38]. Meanwhile, the size of CH_3Hg^+ was about 4 Å which can also be passed through the hole [39]. According to the structural features, the ligand of S-heterocyclic aromatic compound coordinate with mercury species, and there could be slight π-complexation between thiophene ring of DUT-67 (Zr) and Hg^{2+}.

3.3. *Effect of temperature and thermodynamic parameters*

The adsorption of Hg^{2+} and CH_3Hg^+ by DUT-67 (Zr) were observed by varying the adsorption temperature from 15°C to 55°C (see Figure 3). With the increase of the temperature from 15°C to 55°C, the removal efficiency of Hg^{2+} and CH_3Hg^+ increased from 47% to 65% and from 42% to 55%, respectively. The increase of removal efficiency with temperature increase implies that the adsorption could be an endothermic process, which meant there may be chemical adsorption exist, such as the ligand of S-heterocyclic aromatic compound coordinate with mercury species and the π-complexation between thiophene ring of DUT-67 (Zr) and Hg^{2+}. Accordingly, the value of 55°C was selected as the optimum temperature in the subsequent adsorption experiments.

Furthermore, the Gibbs free energy of adsorption (ΔG, kJ· mol^{-1}), the change of entropy (ΔS, J· mol^{-1}· K^{-1}) and the change of enthalpy (ΔH, kJ· mol^{-1}) as the three basic thermodynamic parameters were calculated by using the following Equation (3), (4) and (5).

$$\Delta G = \Delta H - T\Delta S \tag{3}$$

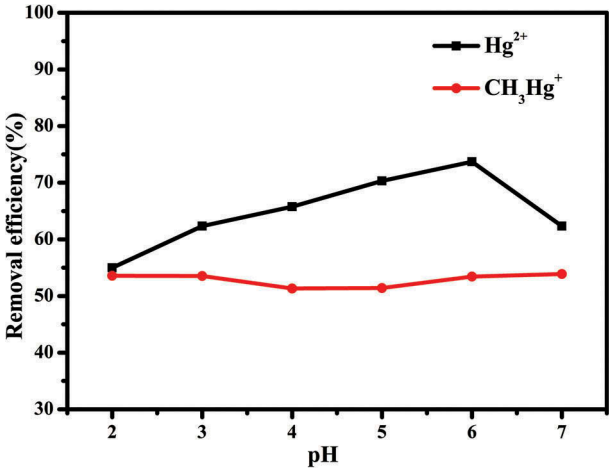

Figure 2. The removal efficiency of DUT-67 (Zr) for Hg^{2+} and CH_3Hg^+ at different pH. c_0 = 20 ppb,V = 10 mL, m = 10 mg, t = 2 h, T = 25°C.

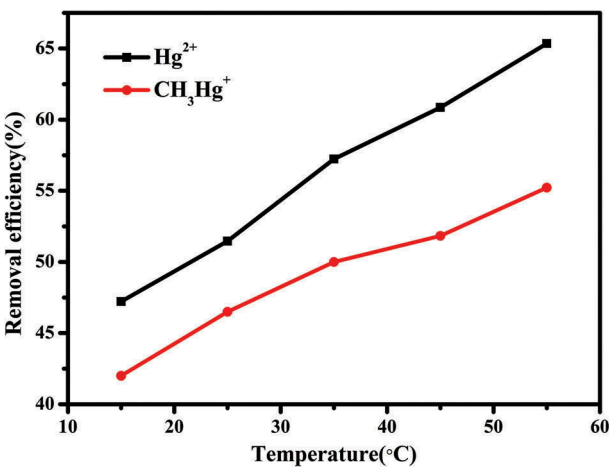

Figure 3. The effects of different temperature on the removal efficiency of DUT-67 (Zr) for Hg^{2+} and CH_3Hg^+. c_0 = 20 ppb, V = 10 mL, m = 10 mg, t = 2 h, pH = 6.

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (4)$$

$$K_d = \frac{V}{m} \times \frac{c_0 - c_e}{c_e} \quad (5)$$

The changes of Gibbs free energy, enthalpy and entropy are expressed in ΔG (kJ mol^{-1}), ΔH (kJ mol^{-1}) and ΔS (J $(mol\ K)^{-1}$), respectively. R (8.314 J $(mol\ K)^{-1}$) represents the universal gas constant. The distribution coefficient of adsorption is K_d. T (K) is the Kelvin temperature. According to the slope and intercept of the plot of $\ln K_d$ against 1/T, the results of ΔH and ΔS were obtained respectively. The values of ΔS, ΔH, and ΔG were shown in Table 2.

The adsorption process was endothermic with the positive value of ΔH. The negative value of the ΔG for these adsorption curves suggested that the spontaneous process of the adsorption reaction. The positive value of ΔS confirmed that during the adsorption process, the degrees of freedom and randomness on the DUT-67 (Zr)-solution interface were enhanced.

3.4. *Adsorption kinetics*

The adsorption kinetics was investigated to obtain the adsorption rate at the optimized pH (= 6) and temperature (55°C) (Figure 4). The result revealed that the adsorption rate rapidly increased during the first 20 minutes and then increased slowly. The adsorptive equilibrium was obtained within 1 h.

The pseudo-first-order and pseudo-second-order model was used to evaluate the effect of the contact time, which was shown as Equation (6) and (7), respectively.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (6)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (7)$$

The adsorption capacity are defined as q_e (mg g^{-1}) and q_t (mg g^{-1}) at equilibrium and time t, respectively. k_1 (min^{-1}) and k_2 (g $(mg\ min)^{-1}$) are the rate constant of the pseudo-first-order kinetic model and pseudo-second-order kinetic model.

Table 3 showed several parameters and the regression coefficient (R^2) that were obtained from the kinetic models. As observed in Figure 5 and Table 3, the experimental data were very consistent with the pseudo-second-order kinetic model, and the theoretical values of qe (0.0461 mg g^{-1} and 0.0376 mg g^{-1} for Hg^{2+} and CH_3Hg^+, respectively) obtained from pseudo-second-order kinetic model was very close to the experimental result (0.0451 mg g^{-1} and 0.0374 mg g^{-1}). It was believed that mechanism of physisorption and chemisorption were involved in the current Hg^{2+} and CH_3Hg^+ adsorption process. According to the structural features, the ligand of S-heterocyclic aromatic compound coordinate with mercury species [40], and act as strong sites for its chemisorption. Meanwhile, there were slight π-complexation between thiophere ring of DUT-67(Zr) and Hg^{2+}.

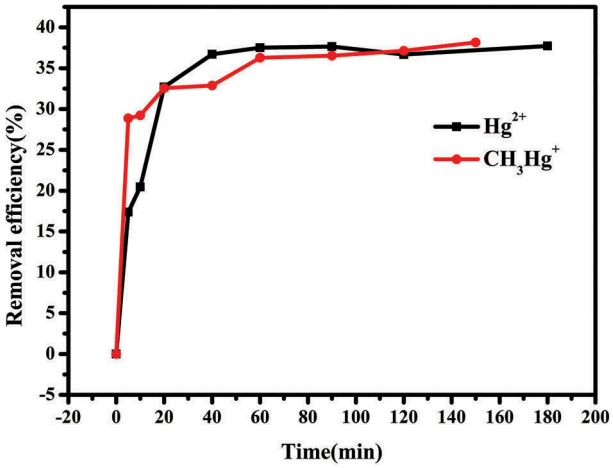

Figure 4. The effects of different contact time on the removal efficiency of DUT-67 (Zr) for Hg^{2+} and CH_3Hg^+. c_0 = 50 ppb, V = 10 mL, m = 10 mg, pH = 6, T = 25°C.

Table 3. The parameters of the Hg^{2+} and CH_3Hg^+ adsorption for the kinetic model.

Adsorbate	Kinetics model	Parameter	Quantitative value
Hg^{2+}		q_e(exp) (mg g^{-1})	0.0451
	Pseudo-first-order	q_e(cal) (mg g^{-1})	0.0169
		k_1(min^{-1})	0.0414
		R^2	0.5627
	Pseudo-second-order	q_e(cal) (mg g^{-1})	0.0461
		k_2(g mg^{-1} min^{-1})	5.6916
		R^2	0.9977
CH_3Hg^+		q_e(exp) (mg g^{-1})	0.0374
	Pseudo-first-order	q_e(cal) (mg g^{-1})	0.0135
		k_1(min^{-1})	0.0244
		R^2	0.7939
	Pseudo-second-order	q_e(cal) (mg g^{-1})	0.0376
		k_2(g mg^{-1} min^{-1})	9.0764
		R^2	0.9984

Table 2. The thermodynamics data of Hg^{2+} and CH_3Hg^+ adsorption onto DUT-67 (Zr).

Adsorbate	ΔH° (kJ mol^{-1})	ΔS° (J mol^{-1} K^{-1})	ΔG° (kJ mol^{-1})				
			288.15	298.15	308.15	318.15	328.15
Hg^{2+}	14.73	101.76	−14.59	−15.61	−16.63	−17.64	−18.66
CH_3Hg^+	10.18	90.23	−15.82	−16.72	−17.62	−18.53	−19.43

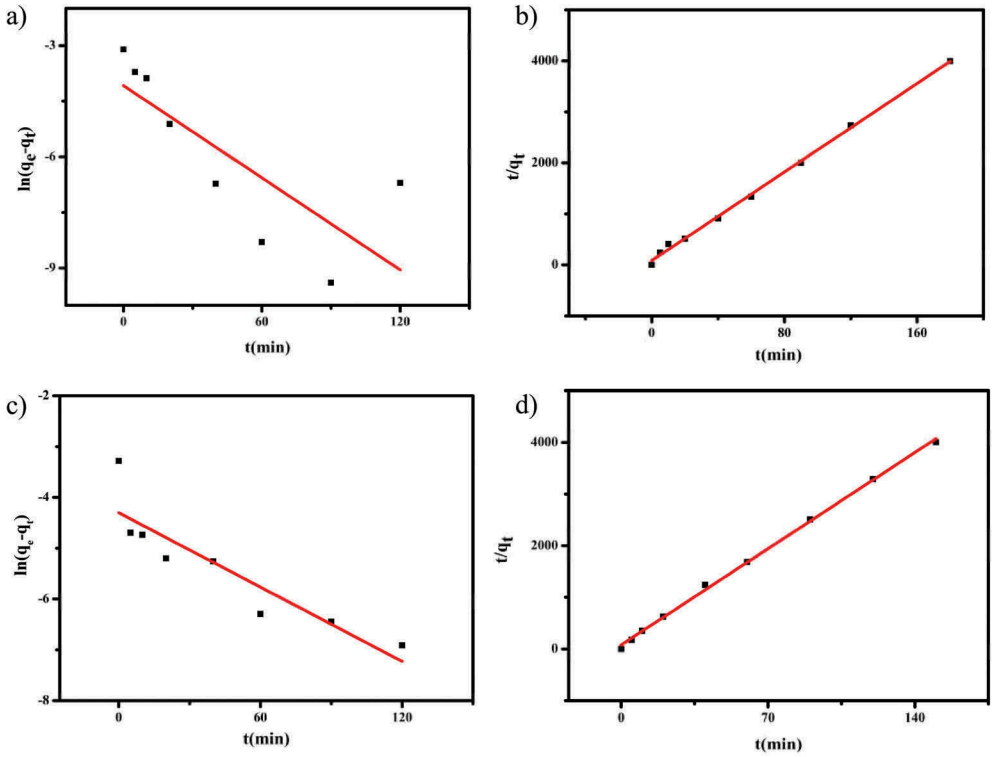

Figure 5. (a) Pseudo-first-order adsorption kinetics of Hg^{2+} (b) Pseudo-second-order adsorption kinetics of Hg^{2+} (c) Pseudo-first-order adsorption kinetics of CH_3Hg^+ (d) Pseudo-first-order adsorption kinetics of CH_3Hg^+.

3.5. *Effect of humic acid on the adsorption of Hg^{2+} and CH_3Hg^+*

Natural organic matter is a kind of complex material, widely exists in natural and artificial water environment, and plays an important role in the chemical reactions occurring in water environment. A number of studies proved its intramolecular mainly containing carbonyl, carboxyl, hydroxyl, phenolic hydroxyl and other active functional groups, can complex with many organic and inorganic compounds [41]. There are two binding sites with mercury in the natural organic matter, the reduced sulfur is strongly bound to mercury, while carbonyl and phenolic are weakly bound to mercury [42]. It is an important substance that affects DUT-67 (Zr) adsorption of heavy metals in the environment water. It can be seen in Figure 6, as the concentration of HA increased, the adsorption efficiency of Hg^{2+} did not changed significantly which could be attributed to the strong attraction of DUT-67 (Zr) towards Hg^{2+} than HA. However, the removal efficiency of CH_3Hg^+ decreased with the increase of HA concentration. The reason may be there are physisorption and chemisorption between DUT-67 (Zr) and Hg^{2+}, but only physisortion adsorption between CH_3Hg^+ and DUT-67 (Zr), and the reduced sulfur and carboxyl sites in HA could bind with CH_3Hg^+ [43,44]. We tested the infrared spectrum of the DUT-67 (Zr) before and after the adsorption of methyl mercury, but there was no significant change. So, HA in water could reduce the adsorption efficiency of CH_3Hg^+.

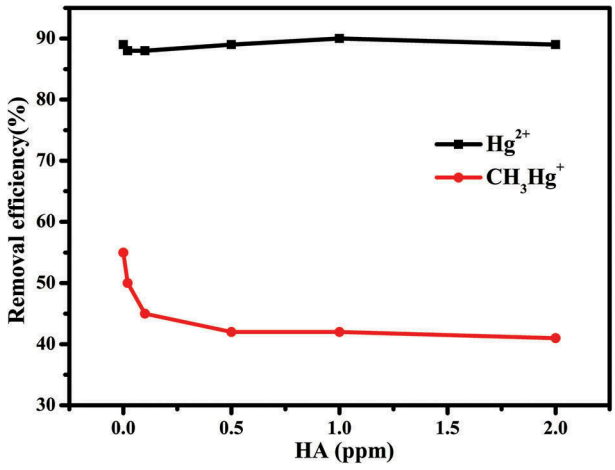

Figure 6. The effects of HA on the removal efficiency of DUT-67 (Zr) for Hg^{2+} and CH_3Hg^+. c_0 = 20 ppb, V = 10 mL, m = 10 mg, pH = 6, T = 25°C.

3.6. *Removal of Hg^{2+} and CH_3Hg^+ with DUT-67 (Zr) in real water samples*

The above method was applied to remove the Hg^{2+} and CH_3Hg^+ in natural water. The results were listed in Table 4. It showed the test water samples contained certain amount of mercury (0.67 μg L^{-1}, 0.51 μg L^{-1} for river water and lake water, respectively). The removal efficient of Hg^{2+} was more than 90% for all concentrations in natural water, and CH_3Hg^+ was 30%-76%. When the concentration of Hg^{2+} was

Table 4. Adsorption of Hg^{2+} and CH_3Hg^+ in real water.

Sample	Real sample (total mercury μg/L)	Adsorbate	Added (μg/L)	Found (μg/L)	Residual (μg/L)	Removal efficient (%)
River water	0.67	Hg^{2+}	10	8.8	0.4	95.45
			20	17.96	0.73	95.93
			50	53.78	5.24	90.26
		CH_3Hg^+	10	11.07	3.31	70.10
			20	22.38	11.09	50.45
			50	49.20	34.20	30.49
Lake water	0.51	Hg^{2+}	10	10.59	0.84	92.07
			20	21.73	0.98	95.49
			50	60.58	4.81	92.06
		CH_3Hg^+	10	9.07	2.12	76.63
			20	18.28	9.82	46.28
			50	48.61	22.87	52.95

lower than 20 μg L^{-1}, the remaining Hg^{2+} levels could reach the standard of WHO (1 μg L^{-1}).

4. Conclusions

This study systematically evaluated the removal of Hg^{2+} and CH_3Hg^+ ions using the synthesized DUT-67 (Zr) from water. The optimum pH value of 6 and temperature (55°C) were selected for Hg^{2+} and CH_3Hg^+ with the removal efficient of 90% and 55% at 20 μg L^{-1}, respectively. Furthermore, the equilibrium data of Hg^{2+} and CH_3Hg^+ agreed with pseudo-second order kinetic model. DUT-67 (Zr) was an effective adsorbent for trace Hg^{2+} and CH_3Hg^+ in natural water, the removal efficiency was about 90% when the concentration of Hg^{2+} was lower than 20 μg L^{-1}, and the residual of mercury ions could reach the standard of 1 μg L^{-1} of WHO. There are physisorption, chemisorption between DUT-67 (Zr) and Hg^{2+}, the S element in thiophene has a relatively weak adsorption capacity for mercury, and there could be slight π-complexation between thiophere ring of DUT-67 (Zr) and Hg^{2+}, while there only was physical adsorption between DUT-67 (Zr) and CH_3Hg^+.

Furthermore, in order to enhance the adsorption capacity for low concentration pollutants, it is feasible scheme to modify the group with strong ability to combine with the target pollutants. For example, thiol-functionalizend material was used to remove mercury [45]. At the same time, the anti-interference ability of MOFs should be improved because of the complexity of environmental water. Meanwhile, we need to consider a quick and simple method to separate the adsorbents from environmental water.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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