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Adsorption behavior and mechanism of Hg(II) on highly stable Zn-based metal organic frameworks

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Abstract: A novel adsorbent (MTZ-MOFs) was synthesized by a one-step reaction of zinc nitrate hexahydrate and 1-(2-dimethylaminoethyl)-1H-5-mercaptotetrazole to remove mercury from waste water. The results showed that MTZ-MOFs had excellent selectivity and repeatability for Hg(II), the optimum pH was 3.0, the maximum adsorption capacity was 872.8 mg/g, and the process was a spontaneous exothermic reaction. The adsorption behavior was chemisorption, which conformed to the pseudo-second-order kinetic and Freundlich isothermal model. Moreover, the adsorption mechanism showed that the adsorption process mainly depended on ion exchange and chelation, and the synergistic action of S and N atoms played a key role. So, MTZ-MOFs were an efficient adsorbent for mercury ion removal.

Key words: metal organic frameworks (MOFs); Hg(II); adsorption; selectivity; mechanism

1 Introduction

In recent decades, intensive human activities have released a large amount of toxic mercury (Hg) into the environment, posing a serious threat to the global environment and ecosystem health. Anthropogenic Hg contaminants are mainly derived from emissions related to electronics, medicine, chemicals, and agriculture activity [1]. The toxicity of mercury pollutants varies greatly among their presented chemical forms. In general, organic mercury is more toxic than inorganic mercury [2]. Inorganic mercury is harmful to the human immune system and kidney organs. Organic mercury causes damage to the brain and cardiovascular system through accumulation in the body [3]. Mercury is highly toxic, non-biodegradable and non-metabolizable in aqueous solution [4]. Therefore, we need to effectively remove mercury ions from water to ensure water quality and safety.

Currently, many technologies are used to remove mercury contamination, such as ion exchange, chemical precipitation, liquid extraction, reverse osmosis and adsorption [5,6]. Among these methods, adsorption is the best choice for mercury removal because of its simplicity, low cost and without secondary pollution [7]. Activated carbon, zeolite and resin are commonly used as adsorbents, but their selectivity and reproducibility are poor. Also,

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they cannot deal with complex environmental problems. Therefore, exploring and developing a new adsorbent with excellent comprehensive performance is necessary.

Metal organic frameworks (MOFs) are porous crystalline materials composed of metal ion clusters and organic ligands [8]. Because of their flexible chemical composition and physical stability, they have great application potential in catalysis, separation, etc [8]. Recently, MOFs have been widely applied in the field of wastewater treatment. ABU TARBOUSH et al [9] synthesized Zn-MOF-74 by precipitation method to remove As(V)with a maximum adsorption amount of 99 mg/g. FU et al [10] reported that the mercury ions adsorption quantity of UIO-66 was 59.3 mg/g. These MOFs have some shortcomings, such as low stability or low adsorption capacity, so many scholars have started to modify or functionalize MOFs to develop new MOFs [11]. KE et al [8] found that functionalized Cu-based (3D) MOFs exhibited good stability and selectivity with an adsorption capacity as high as 714.29 mg/g. Therefore, to achieve the purpose of stable, efficient, and selective removal of Hg(II), relevant studies were carried out in this experiment.

Based on the theory of hard soft acid bases (HSAB) [12], the sulfur-containing groups have strong binding force to mercury ions and can effectively adsorb mercury ions from wastewater. In the present study, MTZ-MOFs were directly prepared by a hydrothermal method using zinc nitrate hexahydrate and 1-(2-dimethylaminoethyl)-1H-5-mercaptotetrazole. The effects of pH, time, and initial concentration on the adsorption of Hg(II) were investigated. The samples were characterized by BET, XRD, XPS, FTIR and FESEM. In addition, the adsorption mechanism was studied by adsorption kinetics, isotherms and thermodynamics, and the binding energy of MTZ-MOFs to Hg(II) was also calculated by density functional theory (DFT).

2 Experimental

2.1 Materials

Zinc nitrate hexahydrate was purchased from Tianjin Beilian Fine Chemicals Development Co., Ltd. 1-(2-dimethylaminoethyl)-1H-5-mercapto-tetrazolium (MTZ, 98%) was obtained from Aladdin Co., Ltd. N, N-dimethylformamide (DMF) and ethanol absolute were purchased from Sinopharm Group Chemical Reagent Co., Ltd. Mercury solution (1000 μ g/mL) was purchased from the National Nonferrous Metals and Electronic Materials Analysis and Testing Center. The wastewater was a laboratory simulated solution.

2.2 Preparation of adsorbent

First, 2 g of zinc nitrate hexahydrate, 1 g of 1-(2-dimethylaminoethyl)-1H-5-mercaptotetrazolium and 50 mL of DMF were added to a flask. After the solid was completely dissolved, the solution reacted at 393 K for 48 h. The product was then washed three times with DMF and deionized water, respectively. Finally, the product was dried in a vacuum drying oven at 353 K for 24 h and named as MTZ-MOFs. The preparation diagram is shown in Scheme 1.



Scheme 1 Synthesis pathway of MTZ-MOFs

2.3 Batch experiment

The influences of pH, oscillation speed, reaction time, initial concentration and temperature on Hg(II) adsorption, as well as the selectivity and repeatability of MTZ-MOFs, were investigated by batch experiments. All experiments (unless otherwise specified) were carried out at room temperature for 24 h.

The optimum pH value was determined by adding 10 mg of adsorbent to 15 mL of solution with an initial Hg(II) concentration of 100 mg/L at various pH (1.0-7.0). 10 mg of adsorbent and 10 mL of mercury solution (100 mg/L, pH=3.0) reacted at 100-300 r/min for 4 h to evaluate the optimum oscillation rate. Adsorption kinetics was performed with 10 mg of adsorbent and 10 mL of mercury solution (100 mg/L, pH=3.0) for 10-720 min. Adsorption isotherms were obtained with 10 mg of adsorbent and 20 mL of mercury solution (100–700 mg/L, pH=3.0). 10 mg of adsorbent and 15 mL of mercury solution (150 mg/L, pH=3.0) were used to conduct

thermodynamic studies at 298, 308 and 318 K. Selective experiments were performed with 10 mg of adsorbent and 15 mL of simulated wastewater containing different metal ions, and repeatability experiments were performed with 40 mg of adsorbent and 40 mL of mercury solution (100 mg/L, pH=3.0). The related expressions were expressed as follows:

$$Q_{\rm e} = \frac{(C_0 - C_{\rm e})V}{m} \tag{1}$$

$$\eta = \frac{(C_0 - C_e)}{C_0} \times 100\%$$
 (2)

where Q_e (mg/g) is the saturated adsorption amount; C_0 (mg/L) and C_e (mg/L) are the initial and residual Hg(II) concentration, respectively; η (%) is the adsorption rate; V (mL) is the solution volume; m(mg) is the mass of MTZ-MOFs.

2.4 Instruments

Fourier transform infrared spectroscopy (FTIR) was performed by Thermo Nicolet 6700. X-ray photoelectron spectroscopy (XPS) was performed by EscaLab Xi+. The specific surface area was determined via BET (JW-BK112, Beijing JWGB Sci & Tech Co., Ltd., China). The ion concentration was determined by ICP-OES (720 ES, Agilent, USA). The morphologic characteristics of MTZ-MOFs were measured via field emission scanning electron microscopy (FESEM, Nova 400 NanoSEM, USA). X-ray diffraction (XRD) experiment was performed by Empyrean 2 (PANalytical, Netherlands).

3 Results and discussion

3.1 Morphology and structure

Figure 1(a) shows the FTIR results of MTZ-MOFs and MTZ-MOFs-Hg. For MTZ-MOFs, the characteristic peak of — OH appeared at 3415 cm^{-1} [13], while the peak at 616 cm^{-1} could infer the presence of C—S [14]. The Zn—N [15] bond formed by the combination of zinc group and 1-(2-dimethylaminoethyl)-1H-5-mercaptotetrazole could make the peak appear at 802 cm⁻¹. The peaks of N—N and C—N were at 1117 and 1389 cm⁻¹, respectively [1,16]. The peak caused by C==N appeared at 1618 cm⁻¹ [17]. The vibration peaks of some bonds were changed after absorption, the peaks of Zn—N and N—N moved to 836 and

1149 cm⁻¹, respectively. Other vibration peaks barely changed.

Figure 1(b) shows the XRD results of MTZ-MOFs before and after adsorption. The high peak intensity indicated that the crystal shape of MTZ-MOFs was good. In Fig. 2(a), the morphology of MTZ-MOFs was dense, the distribution of adsorbent was relatively uniform, and there was no large agglomeration phenomenon. Meanwhile, the elements shown in the EDS spectrum (Fig. 2(b)) were the same as those made up MTZ-MOFs, including C, N, O, S and Zn. According to the above results, it could be speculated that the synthesis of MTZ-MOFs was successfully. In addition, the N2-adsorptiondesorption results indicated that the specific surface area of MTZ-MOFs was 32.78 m²/g, pore volume (V) was 0.061 cm^3/g , and average pore diameter (D) was 7.47 nm (Figs. 3(a, b)).



Fig. 1 FTIR results (a) and XRD patterns (b) of MTZ-MOFs before and after adsorption

3.2 Influence of pH on adsorption

pH is a critical factor in adsorption experiments [18]. A proper pH could facilitate the reaction and reduce the interference of the matrix. The influence of pH on the Hg(II) adsorption by MTZ-MOFs is presented in Fig. 4(a). When the pH was 1.0–2.0, the adsorption effect of MTZ-MOFs was worse than that at other pH values. The reason is that at low pH, MTZ-MOFs were protonated, and the chelation between mercury ions and MTZ-MOFs was inhibited. When the pH was higher than 5.0, the adsorption effect decreased due to the generation of mercury hydroxide, reducing the adsorption capacity of MTZ-MOFs. Moreover, the hydrolysis reactions of mercury ions could

occur to generate hydroxides that could not be absorbed by MTZ-MOFs, which further interfered with the removal of mercury ions. Thus, the optimum pH was 3.0, and the corresponding Hg(II) removal rate was approximately 99.8%. Impressively, the removal rate of mercury ions by MTZ-MOFs exceeded 99.7% at pH 1.0–7.0, which might be mainly due to the potent combination of sulfhydryl groups, nitrogen-containing groups and Hg(II). In summary, MTZ-MOFs have a good ability to remove Hg(II) in acidic solution, and have



Fig. 2 FESEM image (a) and EDS result (b) of MTZ-MOFs



Fig. 3 N₂ absorption-desorption (a) and pore diameter (b) of MTZ-MOFs



Fig. 4 Relationship between pH (a), oscillation speed (b) and removal rate

great development value in the future. The effect of the oscillation speed on the mercury removal rate was also explored and is presented in Fig. 4(b). The removal rate gradually tended to balance with the increase of the oscillation speed, indicating that the adsorption reaction was promoted by increasing the oscillation speed. The optimal oscillation speed was 200 r/min.

3.3 Adsorption kinetics

In general, the reaction time determines the degree of reaction. Figure 5(a) shows the relationship between the adsorption amount and time. It could be seen that the adsorption amount gradually increased, and adsorption equilibrium reached within 10 min. Astonishingly, the adsorption rate was more than 99% at 10 min, which was enough to demonstrate the strong ability of MTZ-MOFs to adsorb Hg(II). In the initial stage of adsorption, due to the existence of a large number of active groups on the surface of MTZ-MOFs, it was easy to combine with Hg(II), and the adsorption amount showed an upward trend. However, as the adsorption reached saturation, all the adsorption sites were occupied and the adsorption amount would no longer be increased.

The adsorption mechanism was investigated by three kinetic models (pseudo-first order (PFO), pseudo-second order (PSO) and intra-particle diffusion) [19,20]. PFO and PSO kinetic models have been widely applied in the study of adsorption rate. By comparing the value of R^2 , a suitable model for the adsorption process can be determined, and the adsorption mechanism can also be understood. The fitting results and experimental data are displayed in Table 1 and Fig. 5, respectively. As shown in Table 1, the fitting results of PFO (Fig. 5(b)) and PSO (Fig. 5(c)) were 0.925 and 0.984, respectively, suggesting that the adsorption process of MTZ-MOFs followed the PSO model, which indicated that it was chemisorption. In addition, the theoretical adsorption amount (99.93 mg/g) calculated by the PSO model was close to the experimental result (99.94 mg/g), which also confirmed the above conclusion.



Fig. 5 Relationship between reaction time and adsorption amount (a), PFO model for MTZ-MOFs (b), PSO model for MTZ-MOFs (c), and intra-particle diffusion model for MTZ-MOFs (d)

Kinetic model	Parameter	Value
	$Q_{ m e}/(m mg\cdot g^{-1})$	99.91
PFO	K_1/\min^{-1}	0.613
	R^2	0.925
	$Q_{ m e}/(m mg\cdot g^{-1})$	99.93
PSO	$K_2/(g \cdot mg^{-1} \cdot min^{-1})$	0.423
	R^2	0.984
Intra-particle	$K/(g \cdot mg^{-1} \cdot min^{-1/2})$	0.008
diffusion-total	R^2	0.488
Intra-particle	$K_3/(g \cdot mg^{-1} \cdot min^{-1/2})$	0.028
diffusion-I	R^2	0.887
Intra-particle diffusion-II	$K_4/(g \cdot mg^{-1} \cdot min^{-1/2})$	0.019
	R^2	0.998

Table 1 Kinetic model parameters

The adsorption process by intra-particle diffusion usually involves several steps. As displayed in Table 1, the fitting results R^2 of the two steps were 0.887 and 0.998, respectively. However, the value of the overall intra-particle diffusion model was only 0.488. As shown in Fig. 5(d), the first stage was the external mass transfer process, which was very rapid due to the abundant active sites on the surface of MTZ-MOFs. In the second stage, as all the adsorption sites were occupied, the adsorption reached saturation, which was the internal diffusion process of Hg(II) and was the rate-limiting step of the adsorption process.

3.4 Adsorption isotherm

The relationship between adsorption capacity and concentration was studied in this work, and the corresponding results are presented in Fig. 6(a). The adsorption amount of MTZ-MOFs gradually increased and reached equilibrium after 600 mg/L, and the adsorption amount was 872.8 mg/g. Table 2 shows the comparison of adsorption amount of various adsorbents, from which it could be seen that MTZ-MOFs have excellent mercury absorption performance.

In this work, five adsorption models such as Langmuir, Freundlich, Temkin, Hill and D-R (Fig. 6(b)), were implemented to explore the adsorption mechanism of MTZ-MOFs. The Langmuir model assumes that the surface of the adsorbent is uniform and the reaction process is single-layer adsorption [28]. The Freundlich model



Fig. 6 Relationship between initial concentration and adsorption amount (a) and adsorption isothermal fitting of MTZ-MOFs (b)

Adsorbent	pН	Adsorption amount/($mg \cdot g^{-1}$)	Source
Monolith ZnS-ZIF-8	5	925.9	[21]
Zr-DMBD	6	171.5	[22]
GO/2-PTSC	5	555	[23]
Amine-modified AC	6	119	[24]
SWCNT-SH	5	131.0	[25]
TC-EDA-CS	4	217.1	[26]
Zr-DTDPA	4	960	[27]
CCHLs-DMTD	3	707	[1]
MTZ-MOFs	3	872.8	This study

Table 2 Adsorption amount of adsorbent

mainly describes the multilayer adsorption on the heterogeneous surface of the adsorbent [29]. The Hill model is another form of Langmuir [30]. The Temkin model mainly describes the change of adsorption heat when the adsorbent interacts with ions [31]. The D-R model explains the adsorption characteristics of the adsorbent and the free energy generated during the adsorption process [32].

The fitting results and the corresponding

parameters are shown in Fig. 6(b) and Table 3, respectively. $R_{\text{Freundlich}}^2(0.992) > R_{\text{Temkin}}^2(0.962) > R_{\text{Hill}}^2(0.912) > R_{\text{Langmuir}}^2(0.803) > R_{\text{D-R}}^2(0.735)$, suggesting that the Freundlich model could be applied to describing the adsorption behavior of MTZ-MOFs, which was based on the multilayer adsorption on the heterogeneous surfaces. The D-R model was applied to further studying the adsorption mechanism of MTZ-MOFs. The calculation formula was as follows [10]:

$$E = \frac{1}{\sqrt{2\beta}} \tag{3}$$

The calculated value of E was 25.25 kJ/mol. Based on Table 4, the adsorption mechanism of MTZ-MOFs could be determined as chemical adsorption.

Table 3 Adsorption isothermal parameters

Isotherm model	Parameter	Value
	$q_{ m m}/(m mg\cdot g^{-1})$	803.2
Langmuir	$K_{\rm L}/({\rm L}\cdot{\rm mg}^{-1})$	0.3125
	R^2	0.803
	$K_{\rm F}/({ m mg}^{1-1/n}\cdot{ m g}^{-1}\cdot{ m L}^{-1/n})$	334.9
Freundlich	п	5.63
	R^2	0.992
Temkin	$B_{\mathrm{T}}/(\mathrm{J}\cdot\mathrm{mol}^{-1})$	28.92
	$K_{\mathrm{T}}/(\mathrm{L}\!\cdot\!\mathrm{g}^{-1})$	74.49
	$R/(J \cdot mol^{-1} \cdot K^{-1})$	8.314
	T/K	298
	R^2	0.962
Hill	$q_{ m m}/(m mg\cdot g^{-1})$	872.8
	C	2.466
	M	0.492 1
	R^2	0.916
D-R	$q_{ m m}/(m mg\cdot g^{-1})$	776.6
	$R/(J \cdot mol^{-1} \cdot K^{-1})$	8.314
	T/\mathbf{K}	298
	β	6.81×10^{-4}
	R^2	0.735

Table 4 E values for different adsorption types

$E/(kJ \cdot mol^{-1})$	Adsorption type	
1-8	Physical adsorption	
8-16	Electrostatic interaction	
>16	Chemical adsorption	

3.5 Thermodynamics

By comparing the adsorption capacities at different temperatures, it is possible to assess whether the reaction process is endothermic or exothermic. Thermodynamic parameters could be calculated from the experimental data [15] and the results are presented in Table 5. The Q_e-T (a) and $\ln K-1/T$ (b) graphs are shown in Fig. 7. It was obvious that the adsorption capacity gradually decreased with the increase of temperature, and the Gibbs free energy and enthalpy changes during the reaction process were both negative, indicating that the reaction was a spontaneous and exothermic reaction.

Table 5 Thermodynamic parameters

Τ/	Qe/	V	$\Delta G/$	$\Delta S/$	$\Delta H/$
Κ	$(mg \cdot g^{-1})$		$(kJ \cdot mol^{-1})$	$(J \cdot mol^{-1} \cdot K^{-1})$	$(kJ \cdot mol^{-1})$
298	224.84	2043955	-36.0	81	-24.97
308	224.33	498500	-33.6	81	-24.97
318	224.10	373500	-33.9	81	-24.97



Fig. 7 Relationship between Q_e and T (a), and between $\ln K$ and 1/T (b)

3.6 Selectivity

In fact, there are other metal ions in wastewater in addition to mercury ions. Under such complex conditions, it is worth exploring whether MTZ-MOFs could still efficiently adsorb mercury ions. Therefore, simulated laboratory wastewater was used to explore the selectivity of MTZ-MOFs. The simulated wastewater was composed of metal ion solutions with various concentrations. The selectivity of MTZ-MOFs could be determined by analyzing the changes in ion concentration during the reaction. The data are shown in Fig. 8, and it can be seen that the mercury ion concentration decreased from 99.98 to 0.083 mg/L, which indicated that the adsorbent had a stronger affinity for Hg(II) compared with other ions. In addition, the affinity between the adsorbent and metal ions was usually reflected by the distribution coefficient (K_c) . The larger the K_c value was, the more likely the adsorption reaction was to occur. The expression was as follows [33]:

$$K_{\rm c} = Q_{\rm e}/C_{\rm e} \tag{4}$$

In Table 6, the K_c of Hg(II) was much greater than other ions, which indicated that MTZ-MOFs were more likely to combine with mercury ions. Therefore, it could be considered that MTZ-MOFs



Fig. 8 Selectivity of MTZ-MOFs

Table 6 Related parameters of ions

Ion	$Q_{ m e}/(m mg\cdot g^{-1})$	$C_{\rm e}/({\rm mg}\cdot {\rm L}^{-1})$	$K_{\rm c}/({\rm L}\cdot{\rm g}^{-1})$
Hg	99.89	0.083	1203.578
Mg	0.22	25.36	0.008675
Mn	1.81	29.34	0.061691
Cr	5.52	34.6	0.159538
Al	4.17	21.58	0.193234

could selectively remove mercury ions from wastewater.

3.7 Reproducibility

Sustainability is an important orientation of technological development, so whether the material is repeatable is the key to its long-term development. To explore the repeatability of MTZ-MOFs, related studies were conducted. Since thiourea could efficiently elute metal ions without destroying the adsorbent structure, it was used as a desorption agent in this experiment. The results of five cycles are shown in Fig. 9, and we found that the removal rate of MTZ-MOFs was as high as 99.8% during the first adsorption, and after 5 cycles, the removal rate could still reach more than 99%, which is enough to prove that MTZ-MOFs have good repeatability.



Fig. 9 Reproducibility of MTZ-MOFs

3.8 Adsorption mechanism

The conclusion of the previous analysis adsorption indicated that the process of MTZ-MOFs was chemisorption. This might be because the functional groups of the adsorbent reacted with mercury ions. To verify this hypothesis, MTZ-MOFs-Hg was characterized by FESEM, EDS, FTIR, and XPS. The FESEM image and EDS result of MTZ-MOFs-Hg are shown in Figs. 10(a) and (b), respectively, indicating that Hg(II) reacted with MTZ-MOFs. The morphological characteristics of the adsorbents hardly changed after adsorption, suggesting that the stability of MTZ-MOFs was reliable to a certain extent. The FTIR spectra (Fig. 1(a)) showed that the peak locations of C-N, N-N and C-S were shifted, which might be because of the reaction of the active

sites on MTZ-MOFs with mercury ions. In Fig. 11(a), the Hg 4f peak appeared, indicating that MTZ-MOFs successfully combined with Hg(II). In Figs. 11(b) and (c), for MTZ-MOFs, the four

characteristic peaks were C—N (285.1 eV), C—N (287.7 eV), C—S (286.3 eV) and C—C (283.8 eV), respectively [34,35]. After absorbing mercury ions, the bond energies of C—N and C—C shifted to



Fig. 10 FESEM image (a) and EDS result (b) of MTZ-MOFs-Hg



Fig. 11 XPS spectra of survey peak (a), C 1s (b), S 2p (c), Zn 2p (d) and Hg 4f (e) of MTZ-MOFs before and after adsorption

289.2 and 284.4 eV, respectively. These binding energy changes might be due to the ion exchange between MTZ-MOFs and Hg(II). S 2p_{1/2} (160.89 eV) and S 2p_{3/2} (162.11 eV) increased from the original energy values to 161.92 and 163.21 eV, respectively. Besides, 168.31 and 169.27 eV were the binding energies of sulfide [3,36]. This change might be caused by the formation of the S-Hg bond. The XPS energy spectrum of Zn 2p is shown in Fig. 11(d). There were two peaks of MTZ-MOFs before adsorption, 1020.8 and 1043.9 eV, belonging to $Zn 2p_{3/2}$ and $Zn 2p_{1/2}$ [37], and the $Zn 2p_{3/2}$ and Zn 2p_{1/2} peaks of MTZ-MOFs-Hg were 1022.4 and 1045.5 eV, respectively. Figure 11(e) shows the energy spectrum of Hg 4f. The two peaks were Hg $4f_{7/2}$ and Hg $4f_{5/2}$, and their energy values correspond to 100.6 and 104.7 eV, respectively [37]. By XPS analysis of MTZ-MOFs and MTZ-MOFs-Hg, it was found that the binding energies of most bond types changed after MTZ-MOFs reacted with mercury ions, indicating that nitrogenous and sulfur-containing functional groups reacted with mercury ions during the adsorption process. These results were also consistent with the description of hard and soft acid-base theory (HSAB). As a soft acid, mercury ions easily combine with soft bases such as nitrogen-containing and sulfur-containing functional groups to form stable compounds. Considering that the crystal structure of MTZ-MOFs was still good after adsorption, it might be caused by the formation of a stable complex between the active nitrogen-containing sites on MTZ-MOFs and Hg(II). The reaction mechanism is presented in Scheme 2.



Scheme 2 Reaction mechanism of MTZ-MOFs

3.9 DFT calculation and frontier molecular orbitals

DFT calculations are used to further study the internal mechanism of the adsorption process,

which provide a more powerful theoretical basis for the experimental analysis. The possible stable geometries were evaluated using the Vienna ab Initio simulation package of DFT. The geometric structure calculations are performed by Materials Studio 7.0. The approximate exchange correlation potential is determined by generalized gradient correction (GGA) and Perdew-Burke-Ernzerhof (PBE) [38]. A computational model for Hg(II) was performed with mercury nitrate [25]. Moreover, the HOMO-LUMO theory was also applied this experiment (the HOMO was the in highest occupied molecular orbital, and LUMO was the lowest occupied molecular orbital). The following expressions were used for theoretical calculation [39]:

$$\Delta E = E_{\rm LUMO} - E_{\rm HOMO} \tag{5}$$

$$\eta = \frac{E_{\rm LUMO} - E_{\rm HOMO}}{2} \tag{6}$$

$$\mu = \frac{E_{\text{LUMO}} + E_{\text{HOMO}}}{2} \tag{7}$$

$$\omega = \frac{\mu^2}{2\eta} \tag{8}$$

where E_{HOMO} and E_{LUMO} indicate the ability to donate and accept electrons, respectively; ΔE is the energy gap between the LUMO and HOMO; η is chemical hardness, which describes how much the electron cloud of substance is distorted in an electric field; μ is electronegativity, which is the tendency of molecules to attract electrons; ω is the electrophilicity, which represents the capability of a substance to accept electrons.

Figure 12 shows the HOMO and LUMO diagrams of monomer and Hg-monomer. For monomer, the values of the reactivity indices *n*=1.94 eV, $\mu = -3.51 \text{ eV},$ ω =3.19 eV and $\Delta E_{\text{LUMO-HOMO}}$ =3.86 eV could be obtained according to the formula. In fact, the smaller the absolute values of μ and ω are, the stronger the nucleophilicity of the monomer is [38]. The ω value of this monomer was smaller than that of cellulose reported by ZHENG et al [38], indicating that MTZ-MOFs could effectively bind to mercury ions. This characteristic was favorable for MTZ-MOFs to adsorb a large amount of Hg(II). In addition, a small η value indicates that the monomer is a soft molecule, which is more likely to bind mercury ions according to the Pearson's theory (HSAB) [40]. For



Fig. 12 HOMO and LUMO diagrams of monomer, Hg—N1 and Hg—N2/S (a–f), monomer (g), and energy gap (h) (White is H, blue is N, grey is C, and yellow is S)

the Hg-monomer complex, when mercury ions bound to the N1 site of the adsorbent, E_{HOMO} = -5.31 eV, E_{LUMO} =-1.63 eV, and the energy gap was ΔE_1 =3.68 eV. When the mercury ions bound to the N2 and S sites of the adsorbent at the same time, E_{HOMO} =-5.00 eV, E_{LUMO} =-1.77 eV, and the energy gap was ΔE_2 =3.23 eV. The energy gap diagram is shown in Fig. 12(h), since ΔE_2 was less than ΔE_1 , suggesting that Hg-N1 was more stable when Hg(II) was combined with N1. In addition, according to the HOMO-LUMO diagrams of the complex, LUMOs were distributed on the sulfur atoms and aromatic rings, and HOMOs were on Hg(II), indicating that electron cloud density was transferred from the sulfur atoms and aromatic rings to mercury ions. Thus, it is necessary to further investigate what binding mode led to efficient adsorption, and to calculate the binding energy of the adsorbent. The adsorption energy (E_A) and the

energy conversion formula were shown as [41]

$$E_{\rm A} = E_{\rm F} - (E_{\rm Hg} + E_{\rm M}) \tag{9}$$

where $E_{\rm M}$ and $E_{\rm Hg}$ represent the energy of the substrate and Hg(II), respectively, and $E_{\rm F}$ represents the total energy.

The optimized adsorbent geometric models are presented in Fig. 13. In model (a), the bond distance of Hg—N1 was 5.168 Å, and the calculated binding energy was -11.09 eV. In model (b), mercury ions combined with sulfur and nitrogen atoms to form Hg—N2 and Hg—S, with a Hg—N2 bond distance of 3.532 Å, and a total binding energy of -11.16 eV. What appeared in model (c) was that the mercury ions bound to two nitrogen atoms via bidentate coordination (Hg—2N3) with a binding energy of -11.08 eV, and the bond distances of Hg—2N3 were 3.723 Å and 3.902 Å. It was found that the binding energy generated by the model (b) was



Fig. 13 Binding energies and bond distances of MTZ-MOFs and Hg(II) at different sites

more negative than that by other models, but there was little difference in the binding energy of each model. In addition, the Hg—N2 bond formed by Hg(II) and N2 atoms had the shortest bond distance in the Hg—N bond type, indicating that Hg(II) was more likely to bind N2 sites. The above analysis was summarized as follows: the binding of MTZ-MOFs and Hg(II) mainly depended on the joint action of N and S atoms, the N—Hg bond in the product was more stable, and the N atom on the aromatic ring had the best adsorption effect on Hg(II).

4 Conclusions

(1) A novel adsorbent was successfully synthesized, and the MTZ-MOFs were analyzed by BET, XRD, XPS, FT-IR and FESEM.

(2) The batch experiment results showed that the optimum pH of MTZ-MOFs was 3.0, the maximum adsorption capacity was 872.8 mg/g, and the adsorption behavior was chemisorption, which conformed to the pseudo-second-order kinetic model and Freundlich isothermal model. In addition, MTZ-MOFs had good selectivity and repeatability for mercury ions, and the removal rate of mercury ions was above 99% in five repeated experiments.

(3) The adsorption mechanism was investigated by XPS, DFT and frontier molecular orbital theory. The results indicated that the adsorption process mainly depended on ion exchange and chelation, and the synergistic action of N and S atoms played a major role. The formed product containing N—Hg bonds was more stable.

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高稳定性锌基金属有机骨架对 Hg(II)的吸附行为及机理

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摘 要:以六合水硝酸锌和 1-(2-二甲氨基乙基)-1H-5-巯基四唑为原料,通过一步反应合成一种新型吸附剂 (MTZ-MOFs),用以去除废水中的汞。结果表明,MTZ-MOFs 对 Hg(II)具有优异的选择性和重复性,其最佳 pH 为 3.0,最大吸附量为 872.8 mg/g,且反应过程为自发放热过程。吸附行为为化学吸附,符合准二级动力学模型和 Freundlich 等温模型。此外,吸附机理研究表明,吸附过程主要依靠离子交换和螯合作用,其中 S 和 N 原子的协同作用起关键作用。MTZ-MOFs 是一种高效去除汞离子的吸附剂。

关键词: 金属有机骨架(MOFs); Hg(II); 吸附; 选择性; 机制

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