A Novel Coordination Polymer as Adsorbent Used to Remove Hg(II) and Pb(II) from Water with Different Adsorption Mechanisms

Rui-Dong Wang, Mei He, Zhihao Li, Zongling Niu, Rong-Rong Zhu, Wen-Qian Zhang, Suoshu Zhang, Lin Du, and Qi-Hua Zhao*

ABSTRACT: Under the hydrothermal condition, a new type of two-dimensional coordination polymer ([Cd(D-Cam)(3-bpdb)]n, Cd-CP) has been constructed. It is composed of D-(+)-Camphoric-Cd(II) (D-cam-Cd(II)) one-dimensional chain and bridging 1,4-bis(3-pyridyl)-2,3-diaza-1,3-butadiene (3-bpdb) ligands. Cd-CP has a good removal effect for Hg(II) and Pb(II), and the maximum adsorption capacity is 545 and 450 mg/g, respectively. Interestingly, thermodynamic studies have shown that the adsorption processes of Hg(II) and Pb(II) on Cd-CP use completely different thermodynamic mechanisms, in which the adsorption of Hg(II) is due to a strong electrostatic interaction with Cd-CP, while that of Pb(II) is through a weak coordination with Cd-CP. Moreover, Cd-CP has a higher affinity for Hg(II), and when Hg(II) and Pb(II) coexist, Cd-CP preferentially adsorbs Hg(II).

INTRODUCTION

In recent years, the concentrations of heavy metal ions in water have increased at an unimaginable rate because of the continuous development of industry.1–3 These excessive heavy metal ions in water have seriously threatened human health and the safety of the ecosystem.4–6 Among various heavy metal ions, Hg(II) and Pb(II) are not only highly toxic but also the most common heavy metal ions’ pollutants in the water environment.7,8 Therefore, the removal of Hg(II) and Pb(II) pollution from water is currently the most urgent thing.1,9,10 Moreover, wastewater is a complex system with a large number of ions, so it is very meaningful to design and synthesize novel stable and selective adsorbents.11,12

Coordination polymers (CPs), which are inorganic–organic hybrid materials prepared from metal ions and organic ligands, have emerged as excellent materials because of their availability in various applications.12–14 By selecting ligands with functional groups or postsynthetic modification, it is possible to design and synthesize CPs with specific structures and properties.15,16 With the continuous development of CPs, scientists have obtained a variety of CPs for the removal of heavy metal ions in water through presynthesis design or postsynthesis modification.17,18 The Morsali group chose H₂BDC and nitrogen-containing bridging ligand N₁,N₂-bis(pyridin-4-ylmethylene) ethane-1,2-diamine to construct a CP (TMU-40) that can efficiently remove Hg(II) (qₑ = 269 mg/g), and the O-TMU-40 by postsynthesis modification can remove Pb(II) (qₑ = 215 mg/g).19

In this article, a new type 2D Cd-CP has been constructed using the D-(+) Camphoric (D-H₂Cam) and nitrogen-containing bridging ligand 1,4-bis(3-pyridyl)-2,3-diaza-1,3-butadiene (3-bpdb), which can effectively remove Hg(II) and Pb(II) in water. We have studied the effects of pH, treatment time, temperature, and other conditions on the adsorption. It is worth noting that Cd-CP adsorption processes of Hg(II) and Pb(II) have completely different thermodynamics, which has not been reported to our knowledge. The different thermodynamic processes also caused the difference in the adsorption behavior of Cd-CP for Hg(II) and Pb(II).
with 75% yield based on 3-bpdb. The calculated elemental analysis values (%) for CdC$_{22}$H$_{24}$N$_{4}$O$_{4}$ were C, 50.77%; H, 4.62%; N, 10.77% (measured: C, 50.25%; H, 4.73%; N, 10.54%).

Crystal Structures of Cd-CP. X-ray diffraction indicates that Cd-CP crystallizes in the $P2_1/c$ space group of monoclinic system. The asymmetric unit consists of a Cd(II), a deprotonated D-H$_2$Cam ligand and two different half of 3-bpdb ligands. Cd(II) ion is six-coordinated with four O atoms (O1, O3, O2i, O4i) from two different D-Cam ligands and two N atoms (N3, N4) from two different 3-bpdb ligands (Figure 1a). From the $a$ axis, Cd(II) is linked by D-Cam ligands in chelated coordination mode to form a 1D [Cd(D-Cam)]$_n$ chain (Figure 1b). In the $ab$ plane, the 2D structure is formed by bridging adjacent 1D chains of [Cd(D-Cam)]$_n$ through 3-bpdb ligands (Figure 1c). The chiral D-H$_2$Cam molecule has a phenomenon similar to racemization in the coordination policy, and thus, Cd-CP is achiral (Figure 1d). Except for the C atoms (C$^{13}$, C$^{14}$, C$^{158}$, C$^{148}$) on the two carboxylic acids, the C atoms from the D-H$_2$Cam molecule are disordered, and the space occupation rate of all disordered C atoms are 50%.

Characteristic of Cd-CP. The powder profile of the synthesized Cd-CP is consistent with the fitted data, demonstrating its high purity (Figure S2). Cd-CP has excellent thermal stability and remains stable up to 316 °C, and its structure begins to collapse when the temperature exceeds 316 °C (Figure S4).

Effect of pH. The pH of the solution will affect the form of heavy metal ions and thus the adsorption performance of the adsorbent.$^{20}$ The experiment to determine the influence of pH is carried out in the range of 2–7. First, the stability of Cd-CP is studied. After immersing Cd-CP in a solution with different pH value for 3 days, the concentration of Cd$^{2+}$ ions in the solution does not increase, indicating that Cd-CP has good stability.$^{10,21}$

As shown in Figure 2, when the pH range is 2–4, as the pH value increases, and the adsorption capacity of Cd-CP on Hg(II) and Pb(II) also increases rapidly. After that, with the increase of pH, the adsorption capacity of Cd-CP remains stable (pH = 4–7). Considering that the industrial wastewater after simple treatment is weakly acidic or weakly alkaline, the subsequent series of experiments are carried out in ultrapure aqueous solutions without adjusting pH.$^5$

Figure 1. (a) Coordination environment of the Cd(II) ions in Cd-CP. (b) The 1D [Cd(D-Cam)]$_n$ chains. (c) 2D structure of Cd-CP. (d) Coordination environment of disordered D-Cam ligands and Cd(II) ions, considering only C or C$'$. Symmetry codes: (i) $x+1$, $y$, $z$; (ii) $-x$, $-y$, $-z+1$; (iii) $-x+2$, $-y+1$, $-z+1$; (iv) $x-1$, $y$, $z$. Ellipsoid probability: 50%. In order to make the structure clear, all H and C$'$ atoms are omitted.

Figure 2. Effect of pH on the adsorption performance and removal rate of Cd-CP on Hg(II) (a) and Pb(II) (b) (298 K, 24 h).
Adsorption Kinetics. The changes in the amount of adsorption of Hg(II) and Pb(II) over time are studied.\textsuperscript{22} The experimental results show that Pb(II) has a faster adsorption efficiency than Hg(II)\textsuperscript{23} (Figure 3). Hg(II) needs 60 h to reach the adsorption equilibrium (545 mg/g), while Pb(II) only takes 16 h (450 mg/g). In order to better evaluate the adsorption efficiency of Cd-CP on Hg(II) and Pb(II),\textsuperscript{23–25} the pseudo-first-order model and the pseudo-second-order model are used to fit the adsorption kinetic data.\textsuperscript{26,27} The pseudo-second-order kinetic model is more in line with the actual adsorption data.\textsuperscript{28} The data are listed in Table 1. In order to save energy and obtain the highest adsorption efficiency, the subsequent series of adsorption experiments are maintained at 24 h.\textsuperscript{29}

It can be seen from Table 2 that the adsorption capacity of Cd-CP is comparable to or even better than other CPs. It is worth noting that Cd-CP has a relatively high adsorption capacity for both Hg(II) and Pb(II), which is relatively rare. Although the adsorption capacity of Cd-CP is still lower than that of the derivatives of CPs (Fe\textsubscript{3}O\textsubscript{4}@TMU-32), it shows that we can obtain adsorbents with better adsorption properties by modifying Cd-CP.

Effect of Initial Concentration. In order to explore the actual maximum adsorption capacity, adsorption experiments of Hg(II) and Pb(II) are carried out at different concentrations\textsuperscript{15–300 mg/L}. As shown in Figure 4a,b, with the increasing concentration of ions, the adsorption capacity of Hg(II) and Pb(II) gradually increases to the maximum.\textsuperscript{33} The maximum adsorption capacity of Hg(II) is 407 mg/g, and the maximum adsorption capacity of Pb(II) is 420 mg/g. Langmuir and Freundlich models are used to analyze the adsorption isotherms of Hg(II) and Pb(II) on Cd-CP.\textsuperscript{34}

Comparing the \( R^2 \) of the Langmuir and Freundlich models and the calculated theoretical maximum adsorption value, the Langmuir model is more suitable for fitting the adsorption isotherm than the Freundlich model\textsuperscript{29} (Table 3). It shows that the adsorption of Hg(II) and Pb(II) by Cd-CP could be considered as a single-layer adsorption process that conforms to the Langmuir model.\textsuperscript{35} The theoretical maximum adsorption capacity values of Hg(II) and Pb(II) calculated by the Langmuir model are 448 and 436 mg/g, respectively, which are relatively close to the experimental results.\textsuperscript{36}

An interesting result is obtained by thermodynamic research (Figure 4c,d). The results show that the adsorption of Hg(II) of Cd-CP (\( \Delta H_{\text{Hg}} > 0 \)) is an endothermic process, but that of Pb(II) (\( \Delta H_{\text{Pb}} < 0 \)) is an exothermic process\textsuperscript{37} (Table S3). What is more surprising is that the adsorption of Pb(II) (\( \Delta G_{\text{Pb}} > 0 \)) by Cd-CP is a rare nonspontaneous process, while that of Hg(II) (\( \Delta G_{\text{Hg}} < 0 \)) is a common spontaneous process.\textsuperscript{1,38} The positive \( \Delta S_{\text{Hg}} \) value indicates the random increase of the solid–liquid interface and the adsorption affinity of Cd-CP toward Hg(II)\textsuperscript{1}. It is worth noting that the adsorption capacity of Cd-CP for both Hg(II) and Pb(II) increase with the increase of temperature, which indicates that temperature is one of driving force for Cd-CP to adsorb Pb(II). Such different thermodynamic data indicate that the adsorption of Hg(II) and Pb(II) is likely to be different adsorption mechanisms.

Adsortion Selectivity. We studied the removal efficiency of Cd-CP for different metal ions, and the study showed that Cd-CP has a good removal rate for both Hg(II) than Pb(II) (Figure 5a). Moreover, the preferential selectivity of Cd-CP to Hg(II) and Pb(II) and the change of the adsorption capacity of Cd-CP to Hg(II) and Pb(II) in the presence of other ions are studied.
Amazingly, in water system where multiple ions coexist (\(M^{n+} = 300 \text{ mg/L}, \ Cl^- > 100 \text{ mg/L} \) and \(\text{NO}_3^- > 100 \text{ mg/L}\)), Cd-CP basically does not adsorb Pb(II), but the adsorption capacity for Hg(II) is still as high as 400 mg/g. This may be that Cd-CP has much greater affinity for Hg(II) than Pb(II)\(^1\).

(Figure 5b).}
Figure 6. SEM images of Cd-CP (a–c), Hg@Cd-CP (d–f), and Pb@Cd-CP (g–i).

Figure 7. (a) PXRD patterns of Cd-CP, Hg@Cd-CP, and Pb@Cd-CP. (b) FT-IR spectrum of Cd-CP, Hg@Cd-CP and Pb@Cd-CP. (c) XPS survey of the Cd-CP, Hg@Cd-CP, and Pb@Cd-CP. (d) XPS Hg 4f of Hg@Cd-CP and HgCl₂. (e) XPS Pb 4f of Pb@Cd-CP. (f) XPS N 1s of Cd-CP, Hg@Cd-CP, and Pb@Cd-CP.
**DISCUSSION**

Figure 6a–i shows the scanning electron microscope (SEM) images of Cd-CP before and after the adsorption of heavy metal ions. The microstructure of Cd-CP presents a regular block structure, while the morphology of Cd-CP has changed significantly after adsorbing heavy metal ions.39 After the adsorption of Hg(II), the surface of Cd-CP appears to have flake accumulation, which may be caused by the deposition of HgCl2.26 EDS analysis also shows the appearance of Hg(II) and Cl(I), which indicate that Hg(II) may be removed by deposition (Figure S5). After the adsorption of Pb(II), the regular structure of Cd-CP is destroyed, but it is different from the morphology of a flake accumulation after adsorption of Hg(II), which indicates that the adsorption mechanism of Hg(II) and Pb(II) may be different.40

**PXRD, FT-IR, and XPS.** In order to further verify the adsorption mechanism of Cd-CP, we have conducted PXRD, FT-IR, and XPS studies.40 As shown in Figure 7a, the PXRD data of Cd-CP and Hg@Cd-CP are the same, indicating that the structure of Cd-CP has not changed after adsorbing Hg(II).41 However, after the adsorption of Pb(II), the PXRD data of Cd-CP has changed. Pb@Cd-CP has new strong diffraction peaks at 9.4° and 17.7°, while the strong diffraction peaks at 9°, 11.1°, 11.5°, and 16.9° have disappeared. These data confirm the structural transformation of Pb@Cd-CP, indicating that Pb(II) may be removed by coordination.

In Figure 7b, the FT-IR spectrum of Hg@Cd-CP does not change significantly compared with that of Cd-CP, but the FT-IR spectrum of Pb@Cd-CP is significantly different.42 Compared with Cd-CP, some sharp peaks in the FT-IR spectrum of Pb@Cd-CP are obviously weakened or even disappeared.43 The peak at 1630 cm⁻¹ should be attributed to the C=O bond, and the decrease in its intensity is probably caused by the coordination of Pb(II) with the uncoordinated N atom in the 3-bpdb ligand, which limits the stretching and vibration of C=O and lead to the disappearance of some peaks in the range of 640–700 cm⁻¹ and 870–1060 cm⁻¹.44

XP further verified the different adsorption mechanisms of Hg(II) and Pb(II) (Figure 7c–f). Figure 7c shows the XPS spectra of Cd-CP before and after the adsorption of Hg(II) and Pb(II). The absorption spectrum clearly shows Hg 4f, Pb 4d, and Pb 4f peaks, which confirm the successful adsorption of Hg(II) and Pb(II).35,45 Compared with the binding energy of Hg(II) (104.38 and 100.33 eV) of HgCl2, that of Hg(II) (103.47 and 99.48 eV) of Hg@Cd-CP is low, which indicates that there is a strong electrostatic interaction between Hg(II) and Cd-CP (Figure 7d).1,46,47 After adsorption of Pb(II), the binding energy of the lower N 1s peak increases from 397.69 to 397.87 eV (Figure 7f),1,11,48 which indicates that the adsorption mechanism of Cd-CP for Pb(II) is the coordination between Pb(II) and the N on 3-bpdb ligand. XPS proves that Cd-CP has greater affinity for Hg(II) than Pb(II).1 This explains that the adsorption capacity of Pb(II) is greater than that of Pb(II),32,49 and when Hg(II) and Pb(II) exists together in the solution, the adsorption capacity of Cd-CP on Hg(II) is basically not reduced, but Pb(II) is hardly adsorbed.

**Desorption Repeat Experiment.** Desorption is one of the methods to verify the adsorption mechanism.50 When Hg@Cd-CP and Pb@Cd-CP are washed by the d 0.03 M HCl and 0.3 M thiourea solution, the Cd-CP after the adsorption of Pb(II) can be reused, but the Hg(II) adsorbed by Cd-CP cannot be washed away and cannot be reused. Even after being recycled for 5 times, Cd-CP can still maintain about 70% of the adsorption capacity of Pb(II) (Figure S7).

**CONCLUSIONS**

In this article, a new type of 2D Cd-CP has been successfully synthesized. Cd-CP exhibit a good removal effect for both Hg(II) and Pb(II), and the maximum adsorption capacity is 545 mg/g and 450 mg/g, respectively. Unexpectedly, thermodynamic studies have shown that the adsorption of Hg(II) and Pb(II) are completely different thermodynamic process, that the adsorption of Pb(II) by Cd-CP is a rare nonspontaneous process, while the adsorption of Hg(II) by Cd-CP is a common spontaneous process. Further research shows that the adsorption processes of Hg(II) and Pb(II) by Cd-CP use different adsorption mechanisms, and the affinity of Cd-CP to Hg(II) is much greater than that of Pb(II). This work provides an idea for the removal and separation of heavy metal ions in water.

**METHODS**

**Materials and Methods.** All reagents and solvents used in the experiments were commercially available and used without further purification (Innochem, China). The FT-IR absorption spectra for Cd-CP, Hg@Cd-CP and Pb@Cd-CP were collected from KBr pellets using a Thermo Scientific FTIR-Nicolet iS10 spectrometer in the range of 4000–400 cm⁻¹ (Thermo Scientific, U.S.A.). Powder X-ray diffraction (PXRD) was performed in the 2θ range of 5–50° on a Rigaku X-ray diffractometer with Cu Kα radiation (λ = 1.5418 Å) (Rigaku, Japan). Elemental analyses were carried out on a PerkinElmer 2400C elemental analyzer (Elementar, Germany). TGA data were acquired using a Mettler-Toledo simultaneous thermal analyzer from room temperature to 800 °C under an N2 atmosphere at a heating rate of 10 °C min⁻¹ (Netzsch, Germany). XPS was performed using a K-Alpha X-ray photoelectron spectrometer (Thermo Scientific, USA). The morphology and energy-dispersive spectroscopy (EDS) data of Cd-CP, Hg@Cd-CP, and Pb@Cd-CP were obtained using a Nova NanoSEM 450 field-emission scanning electron microscope (SEM) at 10 kV (Thermo Scientific, U.S.A.). The concentration of metal ions was determined with an iCAP6300 ICP-AES (Thermo Scientific, U.S.A.).

**X-ray Crystallography.** The selected single crystal with suitable dimensions was mounted on a glass capillary for X-ray diffraction analyses. Crystallographic data were collected on a Bruker Smart AXS CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) using the o-scan technique (Bruker, Germany). Empirical absorption corrections were applied using the SADABS program. The structure was solved in each case by using the SHELXL package and refined with the full matrix least-squares method based on F² using the SHELX-2014 program.1,53 All nonhydrogen atoms were located in different Fourier syntheses and finally refined with anisotropic thermal parameters. Crystallographic data and the details of data collection and structural refinements of Cd-CP are given in Table S1. The selected bond lengths and angles of Cd-CP are listed in Table S2. CCDC: 2101129 for Cd-CP Adsorption Experimental System. First, 10 mg of Cd-CP and 30 mL of a heavy metal ions’ (HgCl2 and others are nitrate) aqueous solution are placed into a glass sample bottle of 40 mL in a shaker and shaken at 180 rpm for 24 h. Subsequently, the solution is then filtered with a 0.45-μm filter. The adsorbed
filtrate is collected in a 10 mL centrifuge tube and analyzed for concentration of ions by ICP-AES.

The pH value of the solution is adjusted with 1 M HCl and 0.1 M NaOH solutions. The adsorption time of the kinetic research is extended to 72 h, at 298 K. The thermodynamic experiment is carried out in the range of 298–318 K.

■ ASSOCIATED CONTENT

+ Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/10.1021/acsomega.1c06606.

Crystallographic data (ZIP)

Synthesis of 3-bpdb, BET data, PXRD data, TGA, EDS spectrum, thermodynamic parameter, crystal data, and selected bond lengths and angles (PDF)

■ AUTHOR INFORMATION

Corresponding Authors
Qi-Hua Zhao — School of Chemical Science and Technology and Key Laboratory of Medicinal Chemistry for Natural Resource, Ministry of Education, Yunnan Research & Development Center for Natural Products, Yunnan University, Kunming 650091, People’s Republic of China; orcid.org/0000-0001-8165-1793; Email: qzhao@ynu.edu.cn
Lin Du — School of Chemical Science and Technology and Key Laboratory of Medicinal Chemistry for Natural Resource, Ministry of Education, Yunnan Research & Development Center for Natural Products, Yunnan University, Kunming 650091, People’s Republic of China; Email: lindu@ynu.edu.cn

Authors
Rui-Dong Wang — School of Chemical Science and Technology, Yunnan University, Kunming 650091, People’s Republic of China
Mei He — School of Chemical Science and Technology, Yunnan University, Kunming 650091, People’s Republic of China
Zhihao Li — School of Chemical Science and Technology, Yunnan University, Kunming 650091, People’s Republic of China
Zongling Niu — School of Chemical Science and Technology, Yunnan University, Kunming 650091, People’s Republic of China
Rong-Rong Zhu — School of Chemical Science and Technology, Yunnan University, Kunming 650091, People’s Republic of China
Wen-Qian Zhang — College of Pharmaceutical Engineering, Xinyang Agricultural and Forestry University, Henan 464000, People’s Republic of China
Suoshu Zhang — School of Chemical Science and Technology, Yunnan University, Kunming 650091, People’s Republic of China

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.1c06606

Author Contributions
⊥(R.-D.W., M.H.) These authors contributed equally to this work.

Notes
The authors declare no competing financial interest.

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