Thiosemicarbazide-Linked Covalent Organic Framework: Preparation, Properties and Applications

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Abstract

With the unique advantages in structure and property, covalent organic frameworks have been widely employed for separation and enrichment. In this work, the thiosemicarbazide-linked covalent organic framework (TpTc) was prepared by using 1,3,5-triformylphloroglucinol and non-rigid thiosemicarbazide as building blocks for the first time. The as-prepared TpTc COF was fully characterized, presenting an agaric-like structure, large specific surface area ($63.5 \text{ m}^2 \text{ g}^{-1}$), uniform pore size distribution (1.36 nm), inherent porosity and ordered crystallinity. The potential of TpTc as adsorbent for metal ions capture was investigated by static batch adsorption experiment using the one-factor procedure. The maximum adsorption capacities of 73.50, 56.53 and 94.13 mg g^{-1} were obtained for Cu (II), Pb (II) and Cd (II) at natural pH, respectively. The anchoring of three metal ions onto TpTc is a multi-layer sorption involving chemical adsorption, and obeys the Freundlich and pseudo-second-order model. According to XPS analysis, the adsorption mechanism may be attributed to the coordination and electrostatic interaction between metal ions and N, O and S atoms on TpTc COF. This work not only provides a candidate for the application of COFs in metal ions capture, but also a reference for exploring functional design of COFs.

1. Introduction

Covalent organic frameworks (COFs) are a class of rapidly developing crystalline porous materials connected by covalent bonds, which was composed of organic building blocks containing only light elements¹. Owing to their custom-design properties, ordered interconnecting channels and fine-tunable structures at atomic level, COFs have been explored for varied applications including gas storage², sensors³, catalysis⁴, optoelectronics⁵, drug delivery⁶ and sample pretreatment⁷. Generally, the application category of COF depends on its structural design. Most of the COFs reported so far are composed by rigid monomers with directional symmetry, and the topological type and channel shape of COFs depend on the shape, size and symmetry of building blocks⁸. This limitation greatly hinders the in-depth study on functionalized COFs.

Similarly, COFs are considered as ideal platforms for adsorption and separation due to their large specific surface areas and fully exposed active sites⁹. The covalent organic framework modified graphitic carbon nitride ($\text{g-C}_3\text{N}_4@\text{TpBD}$) was used for the solid phase microextraction of polycyclic aromatic hydrocarbons in environmental water samples¹⁰. The amino-functionalized magnetic covalent organic framework nanocomposites ($\text{Fe}_3\text{O}_4@\text{NH}_2\text{-COFs}$) were fabricated and explored for solid phase extraction of perfluoroalkyl acids from water samples¹¹. Three thio-groups decorated covalent triazine frameworks (CTFs) was prepared and used for selective mercury removal¹². An amine-based redox-active covalent organic framework (COF-LZU1) was used for selective reductive removal of silver ions from acidic solutions¹³.

However, the insertion of functional groups with high binding affinity is relatively troublesome in the pre design stage. Due to the restriction of dynamic covalent chemistry¹⁴, there are few or no active groups in

the rigid building blocks except for the end groups used for connections between monomers. In addition, another option for creating functional groups, the post-synthetic modification strategy is obviously insufficient^{15, 16}. The post-synthesis modification strategy not only exhibits low modification rate due to steric hindrance, but also the possibility of blocking channels and reducing crystallinity¹⁷.

To meet the specific requirements of sample pretreatment, the stability of COFs in liquid media under extreme conditions must be considered¹⁸. Fortunately, β -ketoenamine-based COFs constructed by successive reversible Schiff base reaction and irreversible enol-to-keto tautomerism exhibits super stability in strong acids, strong bases, boiling water and common organic solvents, which has attracted extensive interests in the field of sample pretreatment¹⁹.

In this work, thiosemicarbazide-linked covalent organic framework (denoted as TpTc), a novel β -ketoenamine-based and S-containing COF was synthesized for the first time by using the non-rigid asymmetric thiosemicarbazide as the amino building block. Subsequently, the adsorption behavior and possible mechanism of TpTc for Cu (II), Pb (II) and Cd (II) in aqueous solution were studied.

2. Experimental

2.1. Chemicals

The phloroglucinol and trifluoroacetic acid were received from Aladdin Industrial Corporation (Shanghai, China). Thiosemicarbazide (Tc) and 1,4-dioxane were obtained from Anhui Zesheng Technology co.,Ltd (Anqing, China) and Sinopharm Chemical Reagent Co., Ltd (Shanghai, China), respectively. All other chemicals were at least analytically pure and used directly without further purification. The working solutions for metal ions were prepared by dissolving corresponding chlorides ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, PbCl_2 and $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$) in water directly. The ultra-pure water used in all experiments was prepared by an Elga Purelab Option-Q DV25 water purification system (Marlow, UK).

2.2. Preparation of TpTc

First, the 1,3,5-triformylphloroglucinol (Tp) was prepared according to our previous work²⁰. The thiosemicarbazide-linked covalent organic framework (TpTc) was further directly prepared by vacuum solvothermal reaction. The thiosemicarbazide (Tc, 27.3 mg, 0.3 mmol) and 1,3,5-triformylphloroglucinol (42 mg, 0.2 mmol) were dispersed in the mixed solvent (1,4-dioxane 2.3 mL and water 0.7 mL) and then transferred to a 25 mL pyrex tube. After 15 minutes of sonication and three freezing (77 K, liquid N_2 bath)-pump-thaw cycles, the mixture was sealed and heated at 120°C for 3 days. The obtained brownish-black solid was washed successively with water and ethanol, and then vacuumed overnight at 50°C.

2.3. Characterization

The powder X-ray diffraction (PXRD) data was collected on a Bruker D8 Advance diffractometer operating at 40 kV and 40 mA under Cu Ka X-ray radiation and at a scan speed of 4° min^{-1} in the range of $3\text{--}45^\circ$.

The Fourier-transform infrared (FT-IR) spectra were recorded as KBr pellets using a Nicolet iS5 Spectrometer in the 4000 – 400 cm⁻¹ regions. The morphology observations were determined by field emission scanning electron microscope (FE-SEM, Hitachi S-4800) and transmission electron microscope (TEM, FEI Talos L120C). The composition of the samples was characterized by X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi). The Brunauer-Emmett-Teller (BET) specific surface area and pore size distribution were obtained with a Micromeritics ASAP 2460-4MP specific surface area and porosity analyzer. The concentration of metal ions in aqueous solution was confirmed by inductive coupling plasma-atomic emission spectrometer (ICP-AES, Plasma 1000). The pH of aqueous solution was evaluated by a pH meter (Sartorius PB-10).

2.4. Static adsorption experiments of metal ions onto TpTc

The adsorption performance of TpTc for heavy metal ions was evaluated by static batch adsorption experiments. The pH value, initial concentration, temperature of the metal ions solution and contact time were adjusted according to the investigation conditions. After the adsorption is completed, the mixture was filtered through a 0.22 µm membrane filter, and the residual concentration of heavy metal ions in the filtrate was determined by ICP-AES. The adsorption capacity of metal ions on TpTc is calculated by the following equation (Eq. 1).

$$Q_t = \frac{(C_0 - C_t)V}{m} \quad (1)$$

where C_0 (mg/L) and C_t (mg/L) are the initial concentration of metal ions and the equilibrium concentration at time t , respectively, Q_t (mg/g) the adsorption capacity of metal ions on TpTc, V (0.02 L) and m (0.01 g) are the volume of solution and the mass of TpTc.

The kinetic models used for the simulation of experimental data include pseudo-first-order, pseudo-second-order and intraparticle diffusion (Table S1), while the isotherm models include Langmuir, Freundlich, Temkin and D-R (Dubinin-Radushkevich) (Table S2).

3. Results And Discussion

3.1. Preparation and Characterization of TpTc

The synthesis of thiosemicarbazide-linked covalent organic framework (TpTc) was carried out under vacuum solvothermal reaction in a mixed solvent (1,4-dioxane/water). Firstly, the unstable enol-imine form was obtained by reversible Schiff base reaction between aldehyde building block (1,3,5-triformylphloroglucinol, Tp) and non-rigid asymmetric amino building block (thiosemicarbazide, Tc), and then the stable keto-enamine form was obtained by irreversible enol-to-keto tautomerism (Scheme 1). The keto-enamine-based COFs have higher chemical stability than imine-based COF, showing excellent stability in water, acid, alkali and various organic solvents, which is more suitable for the harsh conditions

in separation engineering²¹. The preparation method of TpTc is relatively simple, and the building unit containing amino groups is also easy to obtain.

The images of SEM and TEM showed that the prepared TpTc COFs with agaric-like structure were stuffed with plenty of nanosheets (Fig. 1). The fracture and formation of chemical bonds during the polycondensation were confirmed by FT-IR spectra (Fig. 2a). The absorbance peaks of Tp at 1643 and 2890 cm^{-1} were attributed to the stretching vibrations of C = O and C-H in the aldehyde group, respectively. In the spectrum of Tc, the peaks at 3369 and 3263 cm^{-1} indicate the asymmetric and symmetric stretching vibrations of N-H in the primary amino group, and the peak at 3180 cm^{-1} corresponds to the N-H stretching vibration of secondary amine. In addition, the peaks at 1534 and 1002 cm^{-1} were associated with the asymmetric and symmetric N-C-N stretching vibrations, while the peaks at 1645 and 1620 cm^{-1} were assigned to the bending vibrations of the amino group. The condensation reaction between aldehyde group and amino group was obviously confirmed by the disappearance of corresponding characteristic peaks. For TpTc, the strong absorption peak was observed at 1592 cm^{-1} arisen from the newly formed C = C stretching vibration, which indicates the formation of β -ketoenamine linkages. Compared to the spectrum of Tc, it was observed that the peak of C = S stretching vibration (802 cm^{-1}) is moved towards higher wavenumbers (824 cm^{-1}) in the TpTc, which confirms the retention of C = S moiety.

The crystal structure of the obtained TpTc COF was studied by the power X-ray diffraction (PXRD) to verify the desired structure. The PXRD pattern of TpTc shows two diffraction peaks at 5.0° and 27.4°, corresponding to the reflection from the (100) and (001) crystal planes, respectively (Fig. 2b). Due to the non-rigid building blocks and flexible connection, the crystal quality of the prepared TpTc COF is not as good as that of the rigid ones²². The N₂ adsorption-desorption isotherms measurement was carried out at 77 K to check the porous feature of TpTc (Fig. 2c), and a typical type-IV isotherm was obtained. The resulting BET surface area of TpTc was 63.5 $\text{m}^2 \text{g}^{-1}$ ($0.12 < P/P^0 < 0.25$), and the single point adsorption total pore volume of TpTc was 0.13 $\text{cm}^3 \text{g}^{-1}$ ($P/P^0 = 0.98$). Meanwhile, the micropore size distribution (1.5–5.9 nm) of TpTc measured by Density Functional Theory (DFT) method has a distinguishable peak at pore widths around 1.36 nm.

3.2 Adsorption properties of TpTc toward metal ions

The pH value of the metal ion solution was adjusted using hydrochloric acid (0.1 M) and sodium hydroxide (0.1 M), and hydroxide precipitation was not allowed at the highest pH value. The pH value of solution environment affects both the existence form of metal ions and the protonation state of organic skeleton, which directly limits the type and strength of the interaction between metal ions and the active sites of TpTc. As shown in Fig. 3a, the adsorption capacities of TpTc for Cu (II) and Cd (II) decreased first and then increased with the increase of pH, while Pb (II) gradually increased. The rising stage of the adsorption capacity may be related to the competitive adsorption between cations and the protonation of the organic skeleton. With the increase of pH value, the decrease of the protonation degree of the adsorbent causes the reduction of the repulsive force between the active site and the metal ions. At the

same time, the decrease of the concentration of H_3O^+ leads to the weakening of the competition between H_3O^+ and metal ions.

In addition, the abnormally high adsorption capacities of Cu and Cd around pH 1.0 may be attributed to the formation of negatively charged metal chloride complexes (CuCl_4^{2-} and CdCl_4^{2-}). The pH values of metal ions solution before (initial pH) and after (final pH) adsorption were also recorded in Fig. 3b. The final pH value was almost unchanged at low initial pH (lower than 3), while decreased slightly at high initial pH (higher than 4), which indicated secondary amine coordinated with metal ions along with deprotonation.

The influence of contact time on the adsorption of three metal ions by TpTc and the kinetic fitting results were given in Fig. 4. The adsorption capacities of TpTc for the three metal ions increased rapidly in the initial period, and then slowly increased. The initial rapid adsorption was due to the high concentration gradient and the large number of available adsorption sites. The fitting results and related parameters of kinetic profiles were included within Table S3. Obviously, the adsorption process could be better described by pseudo-second-order model than other tested models because of its higher coefficient of determination (R^2). The initial adsorption rates originated from pseudo-second-order model followed the order of Pb (1.94) > Cd (1.11) > Cu (1.09) ($h_0 = k_2 Q_e^2$, $\text{mg g}^{-1} \text{min}^{-1}$). The pseudo-second-order model suggests that the adsorption capacity is directly proportional to the density of functional groups on the adsorbent surface, and the adsorption of metal ions onto TpTc is based on chemisorption²³, which mainly involves the sharing and exchange of electrons. The diffusion mechanism of metal ions onto TpTc surface was revealed by the intraparticle diffusion model, which described a continuous process including diffusion through boundary layer, intraparticle diffusion and adsorption. Even though the correlation coefficients were relatively low, two independent stages could still be observed. Two correlation lines fitted by kinetic data describe the processes of external diffusion (Part I) and intraparticle diffusion (Part II), respectively. The positive values of all intercepts indicate the existence of boundary layer effect, that is to say, the adsorption rate of metal ions onto TpTc may be controlled by both external diffusion and intraparticle diffusion. For all three metal ions, the diffusion rates $K_{id(I)}$ is greater than $K_{id(II)}$, while $C_{(I)}$ is less than $C_{(II)}$. The higher adsorption rate in the external diffusion stage is mainly due to the existence of a large number of active sites on the adsorbent surface at the initial stage, while the decrease of the rate in the intraparticle diffusion stage is attributed to the spatial hindrance of the functional groups.

The effect of initial concentration on the adsorption of three metal ions by TpTc and the Adsorption isotherm fitting results were shown in Fig. 5. The adsorption capacities increased rapidly with the increase of initial concentration, because high concentration could provide greater driving force to overcome the mass-transfer resistance between metal ions and adsorbents. The maximum adsorption amounts of TpTc for Cu (II), Pb (II) and Cd (II) were 73.50, 56.53 and 94.13 mg/g, respectively. The adsorption isotherms parameters were summarized in Table S4. According to the R^2 values of the tested isotherm models, the Freundlich model fits well with the experimental data. The Freundlich isotherm

suggests that the essence of metal ion removal is a multilayer adsorption taking place on non-uniform surface. The adsorption capacities of metal ions onto TpTc were also investigated as a function of temperature. The obtained results showed that the adsorption amounts gradually increased with the increase of temperature. The corresponding thermodynamic parameters were deduced from Eq. S1-S4 (see Supporting Information for more details) and presented in Table S5. The positive values of the standard enthalpy change (ΔH°) reveal the endothermic characteristic of the adsorption process, which confirm the formation of complexes between metal ions and active sites on TpTc skeleton. The values of the standard Gibbs free energy change (ΔG°) decrease with the increase of temperature, indicating that the adsorption reaction is favorable at high temperature. This behavior is coherent with the endothermic nature of the adsorption process. Furthermore, the positive values of the standard entropy change (ΔS°) indicate the enhancement of disorder and randomness at the solid-liquid interface between metal ions and TpTc.

3.3. Probable mechanism of metal ions adsorption

The XPS spectra of the TpTc adsorbents before and after adsorption (denoted as Cu@TpTc, Pb@TpTc and Cd@TpTc, respectively) were collected and used for further exploring of the complexation between metal ions and TpTc. As shown in Fig. 6a, the survey spectra of Cu@TpTc, Pb@TpTc and Cd@TpTc with the insertion of Cu2p, Pb4f and Cd3d peaks respectively denoted the loading of metal ions onto TpTc. The high-resolution XPS Cu2p spectrum displayed of two peaks assigned to the Cu2p $_{3/2}$ and Cu2p $_{1/2}$ at binding energies of 933.7 eV and 953.5 eV, respectively (Fig. 6b). The binding energies in 963.8, 957.7, 943.8 and 938.8 eV corresponded to the satellite peaks of Cu2p, which were related to the interaction between Cu (II) and functional groups²⁴. The peaks at 138.8 eV and 143.6 eV in the high-resolution XPS Pb4f spectrum were assigned to Pb4f $_{7/2}$ and Pb4f $_{5/2}$, respectively (Fig. 6c). As shown in Fig. 6d, the doublet peak around 405.6 eV and 412.4 eV was observed in the high-resolution XPS Cd3d spectrum, which could be assigned to Cd3d $_{5/2}$ and Cd3d $_{3/2}$.

The significant changes in the respective deconvoluted peaks of C1s, N1s, O1s and S2p after adsorption were depicted in Fig. S2, which suggest the interaction between N, O, S atoms and metal ions. The C1s spectrum of TpTc could be deconvoluted into four peaks, 284.8, 286.5, 288.6 and 290.5 eV corresponding to C-C/C = C, C-N, C = S and C = O (Fig. 7a). The slight shifts of C = O and C = S characteristic peaks to lower binding energy confirmed the change of electron cloud density of C atoms after adsorption. Two peaks were detected in the N1s spectrum of TpTc, C-N-C (400.0 eV) and N-H (403.5 eV) (Fig. 7b). The changes of N-H binding energies after adsorption confirmed the contribution of N atoms to the complexation with metal ions²⁵. The O1s spectrum of TpTc could be deconvoluted into two peaks at binding energies 531.0 eV(C = O) of and 533.1 eV(C-OH) (Fig. 7c). The O1s spectra after adsorption revealed the positive shifts of the C = O peaks, which indicates that the electronic cloud of O atoms moves toward the metal ions. The S2p deconvoluted peaks of TpTc at 162.2, 164.5 and 168.8 eV could be attributed to S-H, C = S and C-SO_x species, respectively (Fig. 7d). The significant shifts of the S-H peaks to higher binding energies after adsorption manifested the formation of -S-metal complexes²⁶. In

summary, the multiple ligands (N, O and S) on TpTc provide rich electron pair binding sites for the formation of metal complexes through coordination and electrostatic interaction.

4. Conclusions

In this work, the thiosemicarbazide-linked covalent organic framework (TpTc) was prepared by a simple solvothermal method for the first time, and a keto-enamine typed COF was obtained by the sequential Schiff base reaction and enol-to-keto tautomerism. The as-prepared agaric-like TpTc exhibited ordered crystal structure, porosity and relatively large specific surface area, which were confirmed by series characterization methods. Based on the abundant active functional groups on organic skeleton, the obtained TpTc was exploited for the separation of Cu (II), Pb (II) and Cd (II) from aqueous solution. The adsorption amounts were significantly affected by the initial pH and ambient temperature. The thermodynamic and kinetic analysis confirmed that the adsorption process of three metal ions onto TpTc could be better described by Freundlich and pseudo-second-order model, indicating endothermic and multilayer chemical adsorption process.

The presence of rich N, O and S atoms on TpTc skeleton provide rich electron pair binding sites for anchoring metal ions via coordination and electrostatic interaction. It also implied that TpTc COF may hold removal ability for other water pollutants. Hence, this study provides a basis for the design and development of functionalized COFs as tunable materials for wastewater treatment and environmental remediation.

Declarations

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Notes

The authors have declared no conflict of interest.

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Figures

Figure 1

SEM (a) and TEM (b) images of TpTc.

Figure 2

(a) FT-IR spectra of Tp, Tc and TpTc, (b) PXRD pattern of TpTc, (c) N₂ adsorption isotherms (77 K) and pore size distribution of TpTc.

Figure 3

(a) The effect of pH on the adsorption of Cu (II), Pb (II) and Cd (II) onto TpTc in single ion system, (b) The pH changes before and after adsorption. ($C_0=100$ mg/L, $V=20$ mL, $m=10$ mg, $T=298$ K, 180 min, 180 rpm)

Figure 4

Adsorption kinetics of Cu (II) (a), Pb (II) (b) and Cd (II) (c) onto TpTc in single ion system ($C_0=100$ mg/L, $V=20$ mL, natural pH, $m=10$ mg, $T=298$ K, 180 rpm).

Figure 5

Adsorption equilibrium isotherms of Cu (II) (a), Pb (II) (b) and Cd (II) (c) onto TpTc in single ion system ($V=20$ mL, natural pH, $m=10$ mg, $T=298$ K, 180 min, 180 rpm).

Figure 6

(a) XPS survey spectra of TpTc, Cu@TpTc, Pb@TpTc and Cd@TpTc, (b) High-resolution XPS Cu2p spectrum of Cu@TpTc, (c) High-resolution XPS Pb4f spectrum of Pb@TpTc, (d) High-resolution XPS Cd3d spectrum of Cd@TpTc.

Figure 7

High-resolution XPS C1s (a), N1s (b), O1s (c) and S2p (d) spectra of TpTc, Cu@TpTc, Pb@TpTc and Cd@TpTc.

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