Electronic Supplementary Material

A novel carboxylic-functional indole-based aerogel for high effective removal of heavy metals from aqueous solution via synergistic effects of face-point and point-point interactions

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Main materials and measurements

4-Hydroxyindole was purchased from J & K Technology Co., Ltd., and was purified by column chromatography on 100-200 mesh silica gel with petroleum ether (PE) : ethyl acetate (EA)=3.5 : 1. Resorcinol, formaldehyde and 5-Benzylxyindole were purchased from J & K Technology Co., Ltd., and used without further purification. Nickel (II) chloride hexahydrate (NiCl₂·6H₂O), copper(II) sulfate pentahydrate (CuSO₄·5H₂O), chromium(III) chloride hexahydrate (CrCl₃·6H₂O) and zinc(II) sulfate hexahydrate (ZnSO₄·6H₂O) were supplied by Aladdin. The rest of the materials and reagents were obtained from different commercial sources and used without further purification.

FT-IR spectrum was recorded on a Nicolet 6700 FTIR spectrometer. Solid-state cross-polarization magic-angle-spinning (CP/MAS) NMR spectra were recorded on a Bruker Avance III 400 NMR spectrometer. ¹H NMR was performed on AVANCE 300 MHz NMR spectrometers in dimethylsulfoxide (DMSO)-d₆. UV-Visable spectroscopies were analyzed on the UV-3150 instrument. Scanning electron microscopy (SEM) was recorded on an S-4800 (Hitachi Ltd) field emission scanning electron microscope. Digital photos were taken using a Cannon 600D camera. N₂ sorption isotherms were measured at −196 °C by using a Autosorb IQ instrument, where the specific surface area (S_{BET}) and pore size distribution was evaluated using the Brunauer–Emmett–Teller (BET) method (P/P₀
= 0.05 – 0.30\textsuperscript{11} and Barrett–Joyner–Halenda (BJH) method\textsuperscript{2} (desorption branches of nitrogen isotherms), respectively. The metal ion concentrations in solutions before and after adsorption were measured using ICP-AES (Jarrel-ASH, ICAP-9000) and ICP-MS (NexION 300X) for much low concentrations. For determining the compositions of the solid samples, ICP-AES (~0.1 M HNO\textsubscript{3} solution was used to dissolve the solids).

**Supercritical drying**

The acetone-filled gel was exchanged for the liquefied CO\textsubscript{2} in the autoclave. After partial exchange of the acetone with CO\textsubscript{2}, part of the acetone was drained, then the autoclave was refilled with CO\textsubscript{2}. The CO\textsubscript{2}-filled gel was dried at 45°C and 7.5 Mpa for 7 days.

**Heavy Metal Uptake Experiments**

The heavy metal uptakes from aqueous solutions with various concentrations were studied using the batch method. 0.02 g CHIFA solid was mixed with 25 mL (V/m = 1250 mL g\textsuperscript{-1}) of each solution, under stirring for 24 h. After the adsorption experiments completed, centrifugation was performed, and the solid samples were dried in air for further characterization. Meanwhile, the metal concentrations in the supernatant solutions and their mother solutions were determined using inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and ICP-MS for much low concentrations. The experiments were repeated three times and the result was
presented as average at room temperature. The pH value of Ni(II), Cu(II), Cr(III) and Zn(II) solutions were adjusted using 0.1 mol L\(^{-1}\) HNO\(_3\) or 0.1 mol L\(^{-1}\) NaOH solution. Fresh prepared solutions were utilized for all experiments.

Equilibrium adsorption isotherm studies for Ni(II), Cu(II), Cr(III) and Zn(II): The concentrations of Ni(II), Cu(II), Cr(III) and Zn(II) ions were in the range of 10–1000 ppm to ensure adsorption equilibration was achieved. An amount of 0.02 g CHIFA added in 25 mL solution was used to have a V/m value of 1250 mL g\(^{-1}\). The contact time was about 24 h.

Adsorption kinetics of Ni(II), Cu(II), Cr(III) and Zn(II): An amount of 0.04 g CHIFA was added into the 50 mL (V/m = 1250 mL g\(^{-1}\)) solution with a concentration of \(\approx\) 10 ppm, undergoing vigorous stirring continuously for 2 min, 5 min, 30 min, 1 h, 2 h, 3 h and 4 h. The contact time was varied to check the adsorption kinetics.

Regeneration study: After the equilibrium study, metal-loaded CHIFA was collected and washed with deionized water and dried to the constant weight. Then the adsorbents (0.1 g) were shaken with 50 ml of HCl (1 mol L\(^{-1}\)) in 250 mL Erlenmeyer flasks at 150 rpm on an orbital shaker at 25°C for 2 h, filtered and soaked again until the concentration of heavy metal ions in the filtrate measured using ICP-MS (NexION 300X) decreased to below 0.01 ppm. After washing with deionized water, the treated CHIFA was ready for the next use.
Data treatment: The distribution coefficient \( (K_d) \) is defined by the equation of
\[
K_d = \frac{V[(C_0 - C_f)/C_f]}{m},
\]
where \( C_0 \) and \( C_f \) are, respectively, the initial and equilibrium concentrations of \( M^{n+} \) (ppm, \( \mu \text{g mL}^{-1} \)) after the contact, \( V \) is the solution volume (mL), and \( m \) is the solid amount (g). The % removal is calculated with the equation of \( 100 \times (C_0 - C_f)/C_0 \). The removal capacity \( (q_m) \) is given by the equation: \( q_m = 10^{-3} \times (C_0 - C_f) \cdot V/m. \)

**Synthesis and characterization of 5-Hydroxyindole-3-acetic acid**

A solution of the 5-Benzylxoyindole (10.0 mmol) in anhydrous ether (50-75 ml) was added dropwise at 5 °C, during 5-20 min, to the Grignard reagent, prepared from magnesium turnings (20.0 mmol) and ethyl iodide (20.0 mmol) in anhydrous ether (10 ml). The solution was boiled under reflux for 45 –min to complete the formation of the indole Grignard reagent. The solution was cooled to 10 °C, and ethyl chloroacetate) (11 mmol) added dropwise, with stirring, during 10 min. The resulting reaction mixture was cooled to 0 °C. and the stirring continued for a further 15 min. The reaction mixture was poured into ice-water and extracted with ether (3 \( \times \) 50 ml). The combined ether extracts were washed with saturated aqueous sodium bicarbonate, dried (\( \text{Na}_2\text{SO}_4 \)), and concentrated to dryness in vacuum. The crude products was recrystallized from benzene - light petroleumm to afford 5-Benzylxoy-3-carbethoxyindole (yield 96%).
A solution of the 5-Benzylxoy-3-carbethoxyindole (0.2 g) in a mixture of 1-propanol (30 ml), ethanol (3 ml), and 2 mol/L aqueous potassium hydroxide (14 ml) was heated at 75 °C for 5 h and at room temperature for 1 d. The solution was then evaporated to small bulk in vacuum, diluted with water, extracted with ether (3 × 20 ml), and the ether extracts discarded. The pH of the aqueous solution was adjusted to 3 with hydrochloric acid and extracted with ether (3 × 30 ml). The combined, dried (Na₂SO₄) ether extracts were evaporated to dryness in vacuum to give the 5-Benzylxoyindoleacetic acid (yield 91%).

A solution of the 5-Benzylxyindole-3-acetic (0.25 g) in methanol (50 ml) containing a palladium-on-charcoal catalyst (5 %; 0.125 g) was shaken in a hydrogen atmosphere at room temperature and under atmospheric pressure for 1 h. The reaction mixture was filtered through Celite 545 (Fisher) and concentrated to dryness in vacuum. The crude products were purified by recrystallization from benzene/ethanol to afford 5-Hydroxyindole-3-acetic acid (yield 81%) (Scheme S1).

Scheme S1. Synthesis of 5-Hydroxyindole-3-acetic acid
Fig. S1. FT-IR of 5-Hydroxyindole-3-acetic acid.

Fig. S2 $^1$H NMR spectrum of 5-Hydroxyindole-3-acetic acid.
Preparation of the RFA, HIFA and CHIFA aerogels

**RFA:** The RFA was prepared by mixing resorcinol with formaldehyde in deionized water in a molar ratio of 1 : 2. The total solid content in the pre-gelsolution was kept at 20%. Sodium carbonate was used as catalyst with the molar ratio of resorcinol : Na$_2$CO$_3$ = 50 : 1. And the above solution was stirred for 20 min, then poured into ampoule bottles, followed by heat treatment at 80 °C for 24 h and was capable of gelling. Before supercritical drying, water in wet gel was replaced by solvent exchange with acetone for three times. After that, the gel was supercritical dried at 45 °C for 7 days and RFA was obtained, finally.

**Fig. S3** $^{13}$C NMR spectrum of 5-Hydroxyindole-3-acetic acid.
**HIFA:** The HIFA was prepared by mixing 5-hydroxyindole with formaldehyde in CH$_3$CN in a molar ratio of 1 : 2. The total solid content in the pre-gelsolution was kept at 20%. Sodium carbonate was used as catalyst with the molar ratio of 5-Hydroxyindole : Na$_2$CO$_3$ = 10 : 1. And the above solution was stirred for 20 min, then poured into ampoule bottles, followed by heat treatment at 60 °C for 60 min and was capable of gelling. Before supercritical drying, CH$_3$CN in wet gel was replaced by solvent exchange with acetone for three times. After that, the gel was supercritical dried at 45 °C for 7 days and HIFA was obtained, finally.

**CHIFA:** The CHIFA was prepared by mixing 5-Hydroxyindole-3-acetic acid with formaldehyde in deionized water in a molar ratio of 1 : 2. The total solid content in the pre-gelsolution was kept at 20%. Sodium carbonate was used as catalyst with the molar ratio of 5-Hydroxyindole-3-acetic acid : Na$_2$CO$_3$ = 1 : 1.2. And the above solution was stirred for 20 min, then poured into ampoule bottles, followed by heat treatment at 80 °C for 24 h and was capable of gelling. Before supercritical drying, water in wet gel was replaced by solvent exchange with acetone for three times. After that, the gel was supercritical dried at 45 °C for 7 days and CHIFA was obtained, finally.
**Scheme S2** Synthesis of RFA

![Scheme S2](image)

**Scheme S3** Synthesis of HIFA

![Scheme S3](image)

**Scheme S4** Synthesis of CHIFA

In order to confirm the successful formation of the resulting CHIFA aerogel, it was characterized at molecular levels by a FTIR spectrometer and $^{13}$C CP/MAS NMR spectrometer. The FTIR spectrum for the porous material is shown in Fig. S4a, in which the broad absorption peak at about 3414 cm$^{-1}$ correspond to O–H and N–H stretching vibrations. The band at 1356 cm$^{-1}$ comes from O-H bending
vibrations. The band at 1715 cm\(^{-1}\) corresponds to C=O stretching vibration, whereas medium to weak absorption bands at 1213 and 1042 cm\(^{-1}\) indicate that methylene ether linkages between indole rings are present but not dominant. The structural information of the prepared CHIFA was also obtained by \(^{13}\)C CP/MAS NMR spectroscopy (Fig. S4b). The peak at about 175 ppm is ascribed to the carbonyl group carbons, and the peak at about 147 ppm is ascribed to the phenolic carbons of substituted 5-Hydroxyindole-3-acetic acid. (Fig. S4b 3 and 12), the broad peaks at 132–109 ppm are ascribed to the indole group carbons (Fig. S4b 5–11). Consistent with the IR spectrum, the smaller peak at 68 ppm is assigned to the small amount of CH\(_2\)-O-CH\(_2\) bridges and the broad peak at about 31 ppm is assigned to the different types of CH\(_2\) bridges, which is perfectly consistent with a previous study about acid-catalyzed resorcinol-formaldehyde aerogels.\(^{[3]}\) In conclusion, the characterization data can confirm that the desired aerogel has been synthesized successfully. Additionally, the RFA and HIFA aerogels were also characterized by a FTIR spectrometer and \(^{13}\)C CP/MAS NMR spectrometer. and the satisfactory results were in good agreement with the proposed structures.
**Fig. S4** The characterizations of CHIFA aerogel, (a): FT-IR spectrum, (b): $^{13}$C CP/MAS NMR spectrum.

**Fig. S5** The characterizations of HIFA aerogel, (a): FT-IR spectrum, (b): $^{13}$C CP/MAS NMR spectrum.

**Fig. S6** FT-IR spectrum of RFA aerogel.
SEM image, nitrogen adsorption – desorption isotherms and the pore size distribution of RFA and HIFA

Fig. S7 (a) SEM image of RFA, (b) Nitrogen adsorption – desorption isotherms and the pore size distribution (inset) of RFA, (c) SEM image of HIFA, (d) Nitrogen adsorption – desorption isotherms and the pore size distribution (inset) of HIFA.

PH effect on the removal of Ni$^{2+}$, Cu$^{2+}$, Cr$^{3+}$ and Zn$^{2+}$ by CHIFA
**Fig. S8** pH effect on the removal of Ni$^{2+}$, Cu$^{2+}$, Cr$^{3+}$ and Zn$^{2+}$ by CHIFA ($C_0 = 100$ mg/L; $m = 0.02$ g, $V = 25$ mL, $V/m = 1250$ mL g$^{-1}$; Contact time: 24 h).

The pH of solution is one of the most important parameters affecting sorption process. Fig. S8 shows the dependences of the adsorption capacity for Ni$^{2+}$, Cu$^{2+}$, Cr$^{3+}$ and Zn$^{2+}$ on the pH value (2.0 – 6.0) over CHIFA in order to eliminate the effect of precipitation at higher pH values. Notably, that the ions adsorption of Ni$^{2+}$, Cu$^{2+}$, Cr$^{3+}$ and Zn$^{2+}$ was increased with the increase of pH value from 2.0 to 6.0. The phenomenon could be explained that at lower pH, the relatively high H$^+$ concentration would strongly compete with metal ions for the adsorption sites, resulting in low adsorption capacity. Meanwhile, the hydroxyl and carboxyl groups of the CHIFA would be protonated to form $-\text{OH}^{2+}$ groups, which lead to electrostatic repulsion between the metal cations and the protonated groups, and prevent the uptake of the metal ions. With the increase of pH, the competition between H$^+$ and other cations could be neglected, and the hydroxyl and carboxyl groups groups would be deprotonated to form $-\text{O}^{−}$ and $-\text{COO}^{−}$ groups and thereby enhancing the electrostatic attraction between the adsorbent sites and metal
cations. In view of the fact that the precipitation of Ni$^{2+}$, Cu$^{2+}$, Cr$^{3+}$ and Zn$^{2+}$ takes place at pH $\geq 7$, pH 6.0 was selected as the optimum pH for the following batch experiments to eliminate the effect of precipitation.

**Kinetics data of Ni$^{2+}$, Cu$^{2+}$, Cr$^{3+}$ and Zn$^{2+}$ using CHIFA**

| C$_0$ [ppm]$^a$ | Time (min) | C$_f$ [ppm] | Removal [%] | K$_d$ [mL g$^{-1}$] |
|----------------|------------|-------------|-------------|---------------------|
| 9.83           | 2          | 0.25        | 97.46       | 4.8 x 10$^4$        |
|                | 5          | 0.132       | 98.66       | 9.2 x 10$^4$        |
|                | 30         | 0.062       | 99.37       | 2.0 x 10$^5$        |
|                | 60         | 0.039       | 99.60       | 3.1 x 10$^5$        |
|                | 120        | 0.018       | 99.82       | 6.8 x 10$^5$        |
|                | 180        | 0.014       | 99.86       | 8.8 x 10$^5$        |
|                | 240        | 0.01        | 99.90       | 1.2 x 10$^6$        |

$^a$m = 0.04 g, V = 50 mL, V/m = 1250 mL g$^{-1}$, pH value: 6.0.
**Table S2.** Kinetics data of Cu$^{2+}$ using CHIFA.

| $C_0$ [ppm]$^{a)}$ | Time (min) | $C_f$ [ppm] | Removal [%] | $K_d$ [mL g$^{-1}$] |
|---------------------|------------|-------------|-------------|------------------|
| 10.67               | 2          | 0.11        | 98.97       | $3.5 \times 10^4$ |
|                     | 5          | 0.059       | 99.45       | $2.2 \times 10^5$ |
|                     | 30         | 0.024       | 99.78       | $5.5 \times 10^5$ |
|                     | 60         | 0.016       | 99.85       | $8.3 \times 10^5$ |
|                     | 120        | 0.009       | 99.92       | $1.5 \times 10^6$ |
|                     | 180        | 0.006       | 99.94       | $2.2 \times 10^6$ |
|                     | 240        | 0.005       | 99.95       | $2.7 \times 10^6$ |

$a^) m = 0.04$ g, $V = 50$ mL, $V/m = 1250$ mL g$^{-1}$, pH value: 6.0.

**Table S3.** Kinetics data of Cr$^{3+}$ using CHIFA.

| $C_0$ [ppm]$^{a)}$ | Time (min) | $C_f$ [ppm] | Removal [%] | $K_d$ [mL g$^{-1}$] |
|---------------------|------------|-------------|-------------|------------------|
| 9.81                | 2          | 0.223       | 97.73       | $5.4 \times 10^4$ |
|                     | 5          | 0.19        | 98.06       | $6.3 \times 10^4$ |
|                     | 30         | 0.162       | 98.35       | $7.4 \times 10^4$ |
|                     | 60         | 0.143       | 98.54       | $8.5 \times 10^4$ |
|                     | 120        | 0.132       | 98.65       | $9.2 \times 10^4$ |
|                     | 180        | 0.125       | 98.73       | $9.7 \times 10^4$ |
|                     | 240        | 0.123       | 98.75       | $9.8 \times 10^4$ |

$a^) m = 0.04$ g, $V = 50$ mL, $V/m = 1250$ mL g$^{-1}$, pH value: 6.0.
### Table S4. Kinetics data of Zn$^{2+}$ using CHIFA.

| C$_0$ [ppm]$^a)$ | Time (min) | C$_f$ [ppm] | Removal [%] | K$_d$ [mL g$^{-1}$] |
|------------------|------------|-------------|-------------|---------------------|
| 10.10            | 2          | 0.244       | 97.58       | $5.0 \times 10^4$   |
|                  | 5          | 0.179       | 98.23       | $6.9 \times 10^4$   |
|                  | 30         | 0.135       | 98.66       | $9.2 \times 10^4$   |
|                  | 60         | 0.117       | 98.84       | $1.1 \times 10^5$   |
|                  | 120        | 0.092       | 99.09       | $1.4 \times 10^5$   |
|                  | 180        | 0.083       | 99.18       | $1.5 \times 10^5$   |
|                  | 240        | 0.071       | 99.30       | $1.8 \times 10^5$   |

$^a)$ m = 0.04 g, V = 50 mL, V/m = 1250 mL g$^{-1}$, pH value: 6.0.

### Table S5. Kinetics parameters (pseudo-second-order-model) for adsorbing metal ions onto 4-HIFA.

| Ions   | $q_{e,exp}$ (mg/g) | $k_2$  | $q_{e,cal}$ (mg/g) | $R^2$ |
|--------|--------------------|--------|---------------------|-------|
| Ni$^{2+}$ | 12.28              | 0.696  | 12.28               | 1     |
| Cu$^{2+}$ | 13.33              | 1.736  | 13.33               | 1     |
| Cr$^{3+}$ | 12.11              | 1.015  | 12.12               | 1     |
| Zn$^{2+}$ | 12.54              | 0.533  | 12.53               | 1     |
Sorption data of CHIFA toward Ni$^{2+}$, Cu$^{2+}$, Cr$^{3+}$ and Zn$^{2+}$

Table S6. Sorption data of CHIFA toward Ni$^{2+}$.

| $C_0$ [ppm]$^a$ | $C_r$ [ppm] | Removal [%] | $q_m$ [mg g$^{-1}$] | $K_d$ [mL g$^{-1}$] |
|----------------|-------------|-------------|-------------------|------------------|
| 9.88           | 0.0014      | 99.99       | 12.3              | $8.8 \times 10^6$ |
| 51.1           | 0.158       | 99.69       | 63.7              | $4.0 \times 10^5$ |
| 99             | 1.97        | 98.01       | 121.3             | $6.2 \times 10^4$ |
| 196            | 25          | 87.24       | 213.8             | $8.6 \times 10^3$ |
| 509            | 279         | 45.19       | 287.5             | $1.0 \times 10^3$ |
| 996            | 758         | 23.90       | 297.5             | $3.9 \times 10^2$ |

$^a$ m = 0.02 g, V = 25 mL, V/m = 1250 mL g$^{-1}$; contact time: 24 h; pH value: 6.0.

Table S7. Sorption data of CHIFA toward Cu$^{2+}$.

| $C_0$ [ppm]$^a$ | $C_r$ [ppm] | Removal [%] | $q_m$ [mg g$^{-1}$] | $K_d$ [mL g$^{-1}$] |
|----------------|-------------|-------------|-------------------|------------------|
| 10.52          | 0.0008      | 99.99       | 13.1              | $1.6 \times 10^7$ |
| 49.6           | 0.046       | 99.91       | 61.9              | $1.3 \times 10^6$ |
| 101            | 0.76        | 99.25       | 125.3             | $1.6 \times 10^5$ |
| 196            | 16          | 91.84       | 225.0             | $1.4 \times 10^4$ |
| 505            | 216         | 57.23       | 361.3             | $1.7 \times 10^3$ |
| 1005           | 699         | 30.45       | 382.5             | $5.5 \times 10^2$ |

$^a$ m = 0.02 g, V = 25 mL, V/m = 1250 mL g$^{-1}$; contact time: 24 h; pH value: 6.0.
### Table S8. Sorption data of CHIFA toward Cr$^{3+}$.

| $C_0$ [ppm]$^a$ | $C_f$ [ppm] | Removal [%] | $q_m$ [mg g$^{-1}$] | $K_d$ [mL g$^{-1}$] |
|-----------------|------------|-------------|---------------------|-------------------|
| 9.62            | 0.067      | 99.30       | 11.9                | $1.8 \times 10^5$ |
| 46.8            | 0.76       | 98.38       | 57.6                | $7.6 \times 10^4$ |
| 98              | 13         | 86.73       | 106.3               | $8.2 \times 10^3$ |
| 203             | 88         | 56.65       | 143.8               | $1.6 \times 10^3$ |
| 489             | 338        | 30.88       | 188.8               | $5.6 \times 10^2$ |
| 981             | 825        | 15.90       | 195.0               | $2.4 \times 10^2$ |

$^a$ m = 0.02 g, V = 25 mL, V/m = 1250 mL g$^{-1}$; contact time: 24 h; pH value: 6.0.

### Table S9. Sorption data of CHIFA toward Zn$^{2+}$.

| $C_0$ [ppm]$^a$ | $C_f$ [ppm] | Removal [%] | $q_m$ [mg g$^{-1}$] | $K_d$ [mL g$^{-1}$] |
|-----------------|------------|-------------|---------------------|-------------------|
| 10.06           | 0.032      | 99.68       | 12.5                | $3.9 \times 10^5$ |
| 53              | 1.4        | 97.36       | 64.5                | $4.6 \times 10^4$ |
| 105             | 11         | 89.52       | 117.5               | $1.1 \times 10^4$ |
| 204             | 68         | 66.67       | 170.0               | $2.5 \times 10^3$ |
| 507             | 343        | 32.35       | 205.0               | $6.0 \times 10^2$ |
| 1009            | 836        | 17.15       | 216.3               | $2.6 \times 10^2$ |

$^a$ m = 0.02 g, V = 25 mL, V/m = 1250 mL g$^{-1}$; contact time: 24 h; pH value: 6.0.
**Table S10.** Adsorption constants of Langmuir models for the adsorption of Ni\(^{2+}\), Cu\(^{2+}\), Cr\(^{3+}\) and Zn\(^{2+}\) ions onto CHIFA.

| Ions   | \(q_m\) (mg/g) | \(b\) (L/mg) | \(R^2\)  |
|--------|----------------|--------------|----------|
| Ni\(^{2+}\) | 298.5          | 0.2343       | 0.9997   |
| Cu\(^{2+}\) | 383.1          | 0.2119       | 0.9994   |
| Cr\(^{3+}\) | 196.9          | 0.0868       | 0.9985   |
| Zn\(^{2+}\) | 217.4          | 0.1054       | 0.9992   |

**Table S11.** Comparison of adsorption capacities of various adsorbents for heavy metal ions.

| target ions | adsorbents                          | \(q_m\) [mg g\(^{-1}\)] | References |
|-------------|-------------------------------------|---------------------------|------------|
| Ni\(^{2+}\) | CHIFA                              | 297.5                     | This work  |
|             | PMCNa hybrid hydrogels             | 224                       | 5          |
|             | Polyvinyl alcohol/corn starch      | 7.3                       | 6          |
|             | hydrogel                           |                           |            |
|             | Fireweed carbon                    | 10.12                     | 7          |
|             | Graphene – chitosan – Mn\(_3\)O\(_4\) | 49.3                     | 8          |
|             | high-pressure steaming hide waste  | 61.92                     | 9          |
|             | (HWSAC)                            |                           |            |
| Cu\(^{2+}\) | CHIFA                              | 382.5                     | This work  |
|             | polypyrrole/MoS\(_4\)\(^{2-}\) (MoS\(_4\) -Ppy) | 111                       | 10         |
|             | SPI/PEI composite                  | 136.2                     | 11         |
| Hydrogels                        | Cr$^{3+}$       | Zn$^{2+}$     |
|---------------------------------|-----------------|---------------|
| EDTA-silica                     | 79              | 216.3         |
| CCS-g-PGMA-c-PEI microspheres   | 229             | 46.8          |
| PEI-cellulose nanofiber         | 90.1            |               |
| CHIFA                           | 195.0           | 121.2         |
| Biomass based hydrogel (SESD–PAA) | 41.7          |               |
| nano chelating resin            |                 |               |
| 2-amino pyridine–functionalized polyacrylonitrile (CPN-AP) | 22 | 15 |
| PMHS-g-PyPz(OEt)2Allyl          |                 |               |

**Adsorption cycle test**

![Image of adsorption cycle test chart](chart.png)
**Fig. S9** Adsorption ($C_0 = 100$ mg/L; $m = 0.02$ g, $V = 25$ mL, $V/m = 1250$ mL g$^{-1}$; Contact time: 24 h, pH = 6) of metal ions on CHIFA after repeated adsorption cycle (treated by 1 mol L$^{-1}$ HCl).

Fig. S9 shows Ni$^{2+}$, Cu$^{2+}$, Cr$^{3+}$ and Zn$^{2+}$ adsorption recycled for 4 times, after 1 cycles reused, metal ions adsorption decreased most, which may due to that part metal ions, that not be desorbed by HCl, occupied part of the adsorption sites. The metal ions adsorption for regeneration 2, 3 and 4 times were relatively close to each other. After 4 cycles reused, the amount of metal ions adsorption for Ni$^{2+}$, Cu$^{2+}$, Cr$^{3+}$ and Zn$^{2+}$ ions was 100, 113, 85 and 102 mg g$^{-1}$, which was 80%, 84.3%, 80.2% and 87.2% of adsorption for the fresh sample, respectively. The excellent recyclablility of the metal ions on CHIFA is very helpful for practical applications, suggesting the long-term use in water purification.

**Adsorption contrast**

![Adsorption contrast](image)
**Fig. S10** (a) Sorption isotherms: (a) Sorption capacity change following initial concentration, (b) Concentration change following contact time of Cu$^{2+}$ adsorption for all three types of aerogels.

**Adsorption mechanism**

![FT-IR spectra](image)

**Fig. S11** (a) FT-IR spectra of CHIFA samples before and after Ni$^{2+}$, Cu$^{2+}$, Cr$^{3+}$ or Zn$^{2+}$ adsorption, (b) UV absorption spectra of 5-Hydroxyindole-3-acetic acid (4-HI-COOH) (100 µM) and its 1:1 complex with Cu$^{2+}$ at pH 7 (1 mM HEPES buffer).

To identify the interaction between CHIFA samples and heavy metal ions during the adsorption process, FT-IR spectra of the CHIFA before and after Ni$^{2+}$, Cu$^{2+}$, Cr$^{3+}$ and Zn$^{2+}$ adsorption are compared. As illustrated in Fig. S11a, the intensity of O-H stretching vibrations at 3414 cm$^{-1}$ slightly shifted to upper wave numbers after the adsorption of Ni$^{2+}$, Cu$^{2+}$, Cr$^{3+}$ or Zn$^{2+}$, which can be attributed to the complexation of metal ions with the ionized O-H group of “free” hydroxyl groups and bonded O-H bands of carboxylic acids.[19] Meanwhile, the band at 1356 cm$^{-1}$, originated from O-H bending vibrations, almost vanished after the Ni$^{2+}$, Cu$^{2+}$, Cr$^{3+}$ or Zn$^{2+}$ adsorption, due to the complexation of hydroxyl group with Ni$^{2+}$, Cu$^{2+}$,
Cr$^{3+}$ or Zn$^{2+}$ on the adsorption sites. Furthermore, the band at 1715 cm$^{-1}$, originated from C=O stretching vibration significantly decreased and shifted to upper wave numbers at 1558 cm$^{-1}$ after the adsorption of Ni$^{2+}$, Cu$^{2+}$, Cr$^{3+}$ or Zn$^{2+}$, which indicated involvement of binding metal ions. Besides, the wavenumber difference between asymmetric and symmetric vibrations of COO group at 1400-1600 cm$^{-1}$ could be used to confirm the point-point interaction type.$^{[20]}$ To gain insight into the mechanism and the interaction of indole with Cu$^{2+}$, UV absorption was performed. Fig. S11b shows the absorption spectra of 5-Hydroxyindole-3-acetic acid (5-HI-COOH) in the absence and presence of equimolar Cu$^{2+}$, together with the difference spectrum 5-HI-COOH-Cu$^{2+}$ _minus_ 5-HI-COOH. The difference spectrum 5-HI-COOH-Cu$^{2+}$ (red line) reveals a negative band at 218 nm and a positive band at 230 nm attributable to a Cu$^{2+}$-5-HI-COOH interaction. An analogous UV difference spectrum with a negative/positive band pair around 220/230 nm has been observed for an indolyl model compound of the cation-π interaction,$^{[21]}$ a cation-π interaction between a positively charged His imidazole ring and a nearby Trp indole ring has also been reported to produce an analogous band pair.$^{[22]}$ The similarity of the UV difference spectrum of 5-HI-COOH-Cu$^{2+}$ with those reported previously for other types of cation-π interactions indicates that the Cu$^{2+}$-5-HI-COOH interaction in 5-HI-COOH-Cu$^{2+}$ is also categorized as a cation-π interaction.
**Simulation method**

The Density functional theory (DFT) calculation was utilized to investigate the adsorption mechanism. All the calculations reported here were fulfilled with Materials Studio DMol3 program (Accerlrys. USA). For the exchange correlation term of the energy functional, the generalized gradient corrected functional GGA and PW91 functional as implemented, were applied for all the geometry optimizations. The double numerical plus polarization (DNP) basis sets was employed. All the energy values were determined for 298 K. No restrictions on symmetries were imposed on the initial structures. The frequency analysis was performed on all DFT structures to ensure the absence of imaginary frequency and verify the existence of a true minimum. The computed interaction enthalpies at 298 K for the complexes were defined as,

\[
-\Delta E = - \left[ E_{\text{complex}} - (E_{Cu^2+} + E_A) \right]
\]  

(1)
where A represents CHIFA.

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