

Supporting Information

Fabrication of efficient surface ion-imprinted materials based on rice husk ash for Cu²⁺ ion detection in crafish and adsorption from tap water

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SI. General information

Unless stated otherwise, all analytical grad chemicals and solvents used in this paper were purchased from commercial vendors. The salts used in stock solutions of metal ions were SnSO₄, K₂SO₄, Ba(NO₃)₂, Ca(NO₃)₂·4H₂O, Cr(NO₃)₃·9H₂O, ZnSO₄·7H₂O, CoSO₄·7H₂O, MgSO₄, Cd(NO₃)₂·4H₂O, Hg(NO₃)₂·H₂O, Sr(NO₃)₂, Al(NO₃)₃·9H₂O, MnSO₄·4H₂O, Ni(NO₃)₂·6H₂O, CuSO₄·5H₂O. The morphology of the materials were characterized by scanning electron microscopy (SEM, JSM-IT500). The specific surface area and pore-size distribution of the materials were recorded using an ASAP2010 (Micromeritics Inc., USA) BET-BJH instrument at 77 K within the P/P₀ range of 0.05-0.2. The samples were degassed at 150 °C for 4 h under vacuum prior to the N₂ adsorption/desorption measurements. Fourier transform

infrared spectra (FTIR) were recorded on an AVATAR 360 spectrometer (Nicolet, USA) using the KBr disk method within the range of 4000–400 cm^{-1} . The concentrations of metal ions were determined with atomic absorption spectrometer (Hitachi Z-8100, Japan). X-ray photoelectron spectroscopy (XPS) measurements were carried out by a Thermo VG Multilab 2000 spectrometer with an Al Ka X-ray source. Fluorescence spectra was determined by a Hitachi F-4600 fluorescence spectrophotometer.

SII. Determination of Detection Limit

The detection limit was calculated based on fluorescence titration as a function the solubility of Cu^{2+} at λ_{em} 611 nm. The fluorescence emission spectrum of free probe RHA-CIIM was measured over 10 times to determine standard deviation for blank measurement. A linear plot was constructed with F/F_0 against the concentration of Cu^{2+} for determining the slope. Using the slope the detection limit was calculated from the following equation.^{1,2}

$$\text{LOD}=3\sigma/K$$

where k is the slope of the fitting line, the mean standard deviation σ of F/F_0 was determined after 10 repetitive measurements.

SIII. Preparation of RH-CIIM

SIII-1. Preparation of P-3

To prepare **P-3**, **P-1** (5 mmol, 2.49g) was fully dissolved in 30 mL ethanol under nitrogen protection, then a mixture of **P-2** (7.5 mmol, 2.75g) and ethanol (5mL) was added, and the resulting mixture was stirred in an oil bath at 80°C for 10 h.³

SIII-2. Synthesis of RHA@MCM-41, RHA-CNIM and RHA-CIIM.

RHA@MCM-41 was prepared according to the methods reported in the literature.⁴ **P-3** and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ formed prepolymerization units, and then through dehydration condensation reaction cross-linked on the surface of RHA@MCM-41 to prepare RHA-CIIM. The resultant route is shown in Fig 1. 0.06 g $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ was dissolved in 5 mL ethanol and 20 mL of the as-prepared **P-3** ethanol solution stirred at room temperature for 30 minutes. After that, add

0.1g RHA@MCM-41 and stir the mixture at 80°C for 24 h. Freshly prepared RHA-CIIM are first washed three times with ethanol to eliminate unreacted reactants, then several times with EDTA until Cu^{2+} is no longer detectable in the filtrate. Then wash with DW, vacuum dry at 60°C, you can get the required product. At the same time, RHA-CNIM was synthesized by a similar method without Cu^{2+} .

SIV. General procedures of the fluorometric determination of Cu^{2+} using the proposed ion-imprinted polymer.

In cuvette, 1992 μL distilled water was added, then 4 μL free probe RHA-CIIM (5mg/mL) was added, finally 0.4 μL , 0.8 μL , 1.2 μL , 1.6 μL , 2.0 μL , 2.4 μL , 2.8 μL , 3.2 μL , 3.6 μL , 4.0 μL , 4.4 μL , Cu^{2+} (5 mg/mL) was gradually added, respectively, and the fluorescence signal was recorded at $\lambda_{\text{ex}} = 330 \text{ nm}$, $\lambda_{\text{em}} = 611 \text{ nm}$.

SV. Adsorption experiments

All batch experiments were repeated three times and performed in a 100 mL conical flask containing 10 mg of the adsorbent and 50 mL of 250 mg/L Cu(II) solution at pH 6, which placed on a rotary shaker with speed of 150 rpm 120 min at room temperature. The Cu(II) and other metal ions concentration were analyzed by using the AAS method. The Cu^{2+} uptake capacity of the RHA-CIIM were evaluated under different conditions, such as pH, Cu^{2+} initial concentration, and time in a batch mode. For the pH-effect study, pH was adjusted by adding HCl or NaOH at different concentrations (0.01-1.0 mol/L) to reach pH 1-6. Isotherm tests were performed with initial Cu^{2+} concentrations ranged from 5 to 250 mg/L at 308K. Adsorption kinetics was conducted at a time range of 1-180 min. All experiments were conducted in triplicates. The q_t and q_e (mg/g) represent the adsorption quantity of Cu^{2+} at different time t (min) and equilibrium, which were calculated using Eqs.⁵

$$q_{t,e} = \frac{(C_0 - C_{t,e}) \times V}{m}$$

Where $C_{t,e}$ and C_0 (mg/L) are Cu^{2+} concentration at time t at equilibrium and initial, m (g) is the mass of sorbent and V (L) is solution volume.

SVI. Adsorption isotherms and kinetics models

SVI-1. Detailed description of isotherms models

Langmuir model describes a monolayer coverage in which all adsorption sites on the adsorbent are identical. Freundlich isotherm is established on the assumption that the adsorption is a multilayer one and the adsorption surfaces are heterogeneous. While the Temkin isotherm model assumes that the energy of the adsorption decreases with increasing the coverage of adsorption sites with adsorbate. The three models are described as follows ⁶:

$$\text{Langmuir: } q_e = \frac{K_L q_{\max} C_e}{1 + K_L C_e} \quad (\text{S1})$$

$$\text{Freundlich: } q_e = K_F C_e^n \quad (\text{S2})$$

$$\text{Temkin: } q_e = \frac{Rt}{b} \ln K_t + \frac{Rt}{b} \ln C_e \quad (\text{S3})$$

Where C_e (mg/L) is the equilibrium Cu^{2+} concentration. q_{\max} and q_e (mg/g) stand for the maximum and equilibrium uptake capacity of Cu^{2+} by RHA-CIIM. K_L (L/mg) represent Langmuir constant. K_F ($\text{mg}^{1-n}\text{L}^n/\text{g}$) and n are Freundlich constants. R (8.314 J/mol. K) and t (308 K) are the gas constant and temperature, respectively. Rt/b (B) (J/mol) and K_t (L/g) stand for Temkin constants.

SVI-2. Detailed description of kinetics models

To analyze the adsorption process of Cu^{2+} onto RHA-CIIM, pseudo-first-order and pseudo-second-order kinetic models were used to fit the experimental kinetics data.

The linear forms of the two models are expressed as follows ⁷:

pseudo-first-order: $q_t = q_e(1 - e^{-k_1 t})$ (S4)

pseudo-second-order: $q_t = \frac{k_2 t q_e^2}{1 + k_2 t q_e}$ (S5)

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

SVII. Crayfish digestion procedure

The material was broken down in a microwave digestion system after a mixture of 9 mL of concentrated HNO_3 solution was added to the digestion tube. Leave the microwave digestion tank covered for a full day. After that, the crayfish were broken down in three batches using a microwave digestion system that contained 6 mL of HNO_3 (65%) and 4 mL of H_2O_2 (30%). Three stages make up the microwave digesting system: the programming temperature rises from 130°C (hold for 5.0 minutes) to 160°C (hold for 10 minutes), and then to 180°C (hold for 15 minutes).⁸

Table S 1 Comparison of the LOD of RM-CIIP toward Cu^{2+} with other particle-based sensors.

Sensor Name	LOD	Ref
f-sporopollenin	0.741 μM	[9]2021
BODIPY based magnetic nanomaterial	1 μM	[10]2013

Au nanoparticle	5 μM	[11]2015
l-Cysteine-capped ZnS QDs	7.1 μM	[12]2009
Aza chalcone	10 μM	[13]2015
ZnO@ZnS core-shell nanoparticle	15 μM	[14]2014
AuNP	20 μM	[15]2010
Glutathione-capped Zn _x Hg _{1-x} Se QDs	20 μM	[16]2009
Sp-APTES-monoBODIPY	0.49 μM	[17]2022
DHIH	0.52 μM	[18]2015
Ru@FITC-MSN	0.36 μM	[19]2020
Diphenylcarbazine (DPC)	0.16 μM	[20]2015
Chemosensor NRC	0.18 μM	[21]2011
inorganic-organic chemosensing material MS-NSP	0.19 μM	[22]2022
waste cotton fabric WCF	7.8 μM	[23]2022
Fe ₃ O ₄ @SiO ₂ @TiO ₂ -APTMSmonoBODIPY	0.47 μM	[24]2022
{[Cd(HL)]·CH ₃ OH} _n	5.7 μM	[25]2024
morpholine-modified polyacrylamide derivatives (MMPAm)	17.3 μM	[26]2024
copper ion-imprinted materials (RHA-CIIM)	0.063 μM /4.03 $\mu\text{g/L}$	This work

Table S2 The RSD of RHA-CIIM

F/F ₀ =0.9993-0.1028[Cu ²⁺]			
[Cu ²⁺] (mg/L)	[Cu ²⁺] (mg/L)	F/F ₀	RSD
0.60	0.6135	0.9362	2.1%
	0.5905	0.9386	
	0.6085	0.9367	
	0.6034	0.9373	
	0.6305	0.9345	
	0.5976	0.9379	

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