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Poly-L-lysine functionalized magnetic graphene for immobilized metal affinity purification of histidine-rich protein

Jiawei Liu*, Yingying Liu, Yixun Liang, Fen Ma, Quan Bai*

Key Laboratory of Synthetic and Natural Functional Molecule of the Ministry of Education, Modern Separation Science Key Laboratory of Shaanxi Province, College of Chemistry & Materials Science, Northwest University, Xi'an, 710069, P. R. China

*Corresponding author:

E-mail addresses: jwliu@nwu.edu.cn, baiquan@nwu.edu.cn.

Preparation of MG composite

Briefly, 30 mL of GO suspension (30 mg) is transferred into a three-necked flask under N_2 atmosphere for 20 min. Then 0.280 g $FeCl_3 \cdot 6H_2O$ and 0.147 g $FeSO_4 \cdot 4H_2O$ (Fe^{3+}/Fe^{2+} ions molar ratio of 2:1) are dissolved in 5 mL of water, and slowly added into the above dispersion under strong mechanical stirring. Afterwards, the mixture is adjusted to be pH 9 with ammonia monohydrate, and the reaction is further taken place at 50°C for 1 h. The black product is collected by magnet, washed with water for three times to remove impurities and dried under vacuum at room temperature for 12 h.

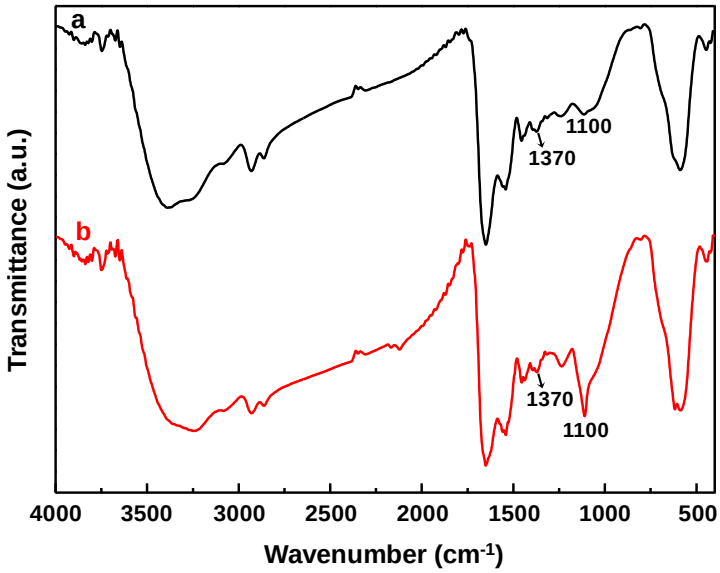

Fig. S1 FT-IR spectra of (a) MGPLA and (b) MGPLA-Cu composite.

By comparing the FI-IR spectra of both MGPLA and MGPLA-Cu composite, it is clearly seen that the absorption band of -COO^- groups at 1100 cm^{-1} is strengthened after the Asp ligands chelate with copper ions. This indicates the successful immobilization of Cu^{2+} ions onto the composite through chelation of Asp and copper ions.

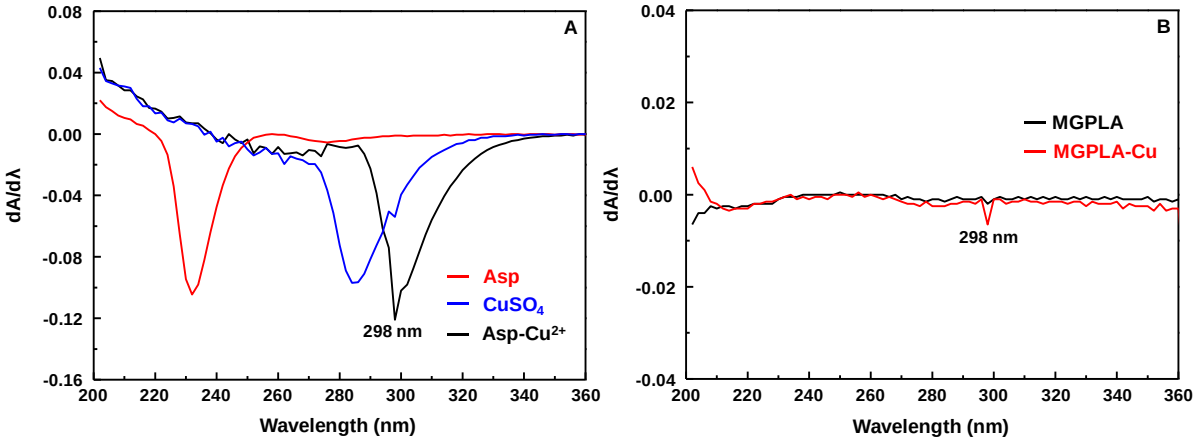

Fig. S2 The derivative UV-Vis spectra of (A) Asp, $CuSO_4$ and Asp-Cu^{2+} mixture aqueous solutions (0.1 mol L^{-1}) and (B) MGPLA and MGPLA-Cu aqueous dispersions (0.1 mg mL^{-1}).

To further demonstrate the chelation of Asp ligands with copper ions, the derivative UV-Vis spectra are measured in the wavelength range of 200-360 nm. As shown in Fig. S2A, Asp ligand in aqueous solution shows a negative peak at 230 nm, which is derived from n-σ* transition of C-N skeleton. In addition, Cu^{2+} ions in aqueous solution displays a negative peak at 284 nm. After mixing the isopyknic Asp and Cu^{2+} solutions, the Asp-Cu mixture shows a new negative peak at 298 nm, indicating that Asp ligands chelate copper ions through coordination forces between carboxyl groups and Cu^{2+} ions. In the spectrum of MGPLA-Cu aqueous dispersion (Fig. S2B), similar negative peak at around 298 nm is also found. However, this peak is absent in the spectrum of MGPLA dispersion. This observation clearly indicates that the copper ions have been successfully immobilized onto the composite through chelation of carboxyl groups ($-COO^-$) with Cu^{2+} ions.

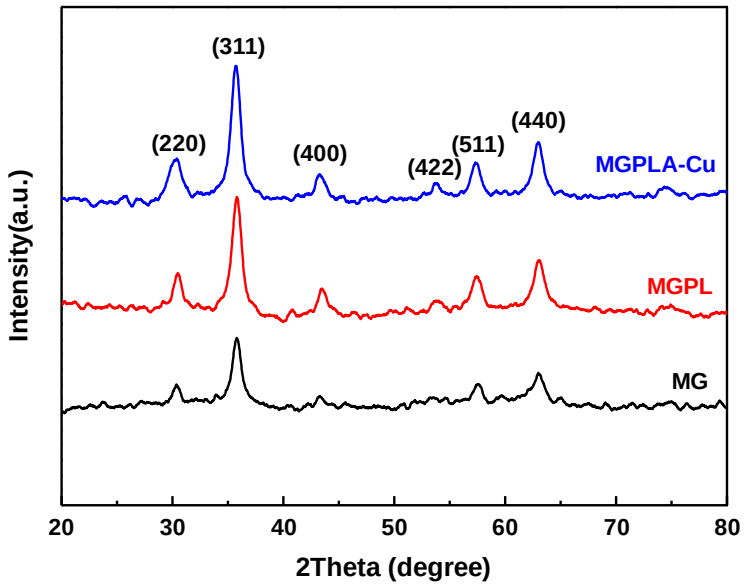

Fig. S3 XRD patterns of MG, MGPL and MGPLA-Cu composites.

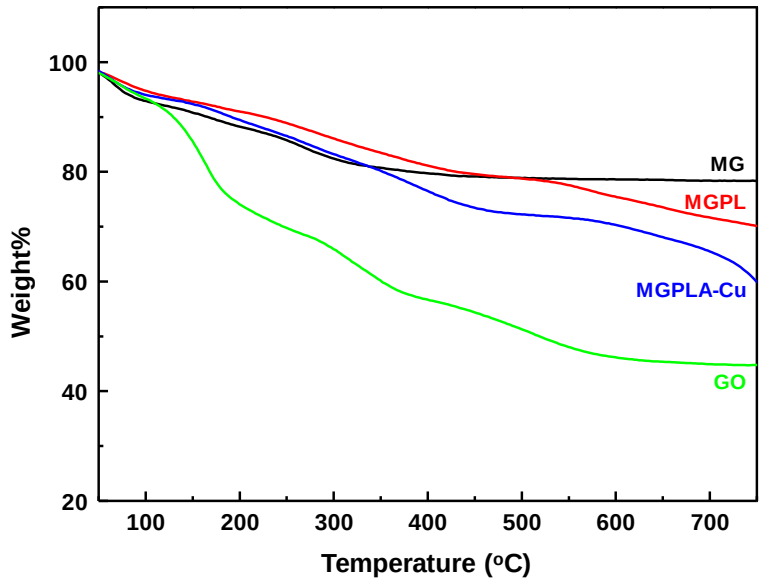

Fig. S4 TGA curves of GO, MG, MGPL and MGPLA-Cu composites.

The immobilization density of metal affinity groups on the surface of MGPLA-Cu composite is determined by TGA and BET data using equation (S1) as follows:

$$\text{Metal affinity groups density } (\mu\text{mol m}^{-2}) = \frac{\frac{W_{\text{MGPLA-Cu}}}{100\text{-}W_{\text{MGPLA-Cu}}} \times 100\text{-}W_{\text{MGPL}}}{M_{\text{Asp-Cu}} \times S_{\text{MGPLA-Cu}} \times 100} \times 10^6 \quad \text{(S1)}$$

where $W_{\text{MGPLA-Cu}}$ is the weight loss of 33.2% between 100 and 750°C related to the decomposition of MGPLA-Cu composite, and W_{MGPL} is the weight loss of MGPL composite in the same temperature range. $M_{\text{Asp-Cu}}$ is the molecular weight of the immobilized Asp-Cu groups (196 g mol^{-1}) and $S_{\text{MGPLA-Cu}}$ is the specific surface area of MGPLA-Cu composite and its BET surface area is determined as 86.6 m^2 g^{-1} from the nitrogen adsorption-desorption isotherm (data are not shown). Therefore, the immobilized density of metal affinity groups on MGPLA-Cu composite is calculated to be about 14.5 μmol m^{-2}.

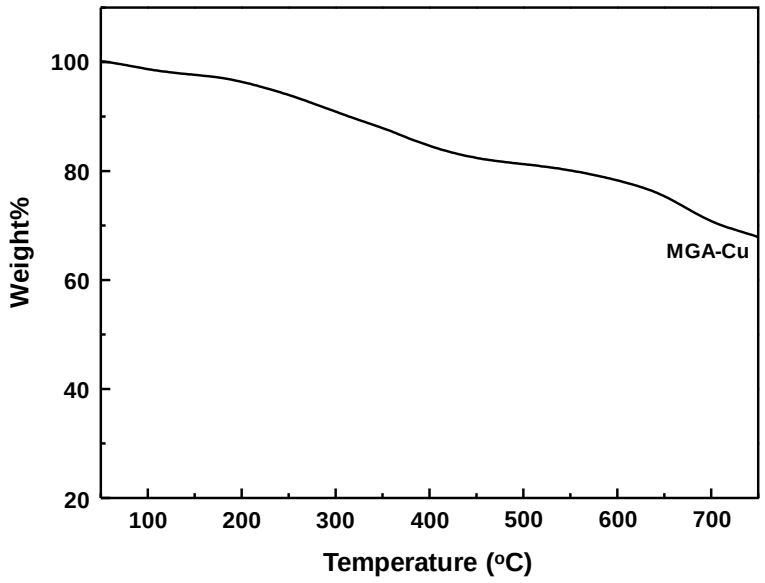

Fig. S5 TGA curve of MGA-Cu composite.

Similarly, the immobilized density of metal affinity groups on MGA-Cu composite without PLL chains is also determined based on equation S2:

$$\text{Metal affinity groups density } (\mu\text{mol m}^{-2}) = \frac{\frac{W_{\text{MGA-Cu}}}{100\text{-}W_{\text{MGA-Cu}}}\times 100\text{-}W_{\text{MG}}}{M_{\text{Asp-Cu}}\times S_{\text{MGA-Cu}}\times 100}\times 10^{6} \quad \text{(S2)}$$

where $W_{\text{MGA-Cu}}$ is the weight loss of MGA-Cu composite (28.6%) between 100 and 700°C from its TGA curve (Fig. S5), and W_{MG} is the weight loss of MG composite (19.6%). the $S_{\text{MGA-Cu}}$ value of MGA-Cu composite is determined to be 89.5 $m^2\ g^{-1}$ (data are not shown). Therefore, the immobilized density of metal affinity groups on MGA-Cu composite is determined to be 11.6 μmol m^{-2}.

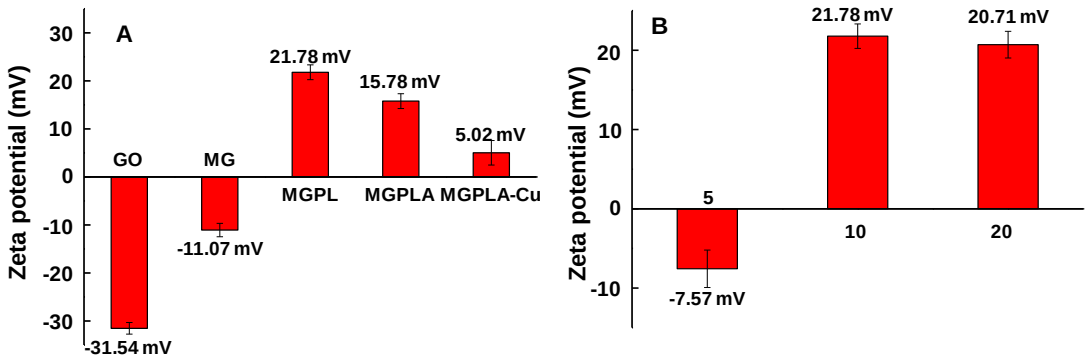

Fig. S6 (A) Zeta potentials of GO, MG, MGPL, MGPLA and MGPLA-Cu composite. (B) Zeta potentials of MGPL composites with various PLL/GO mass ratios.

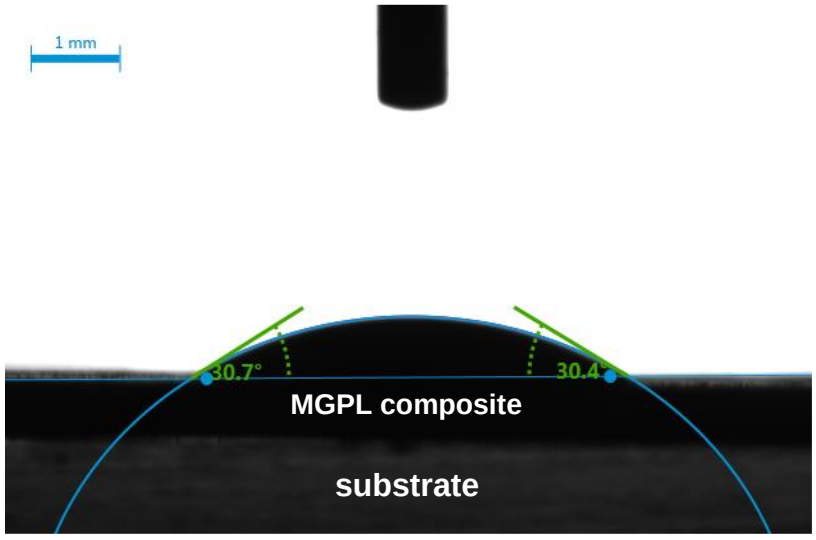

Fig. S7 Photographs of water droplets in air on the MGPL composite film. The measurement is carried out on DSA25 static contact angel analyzer (Kruss, Germany).

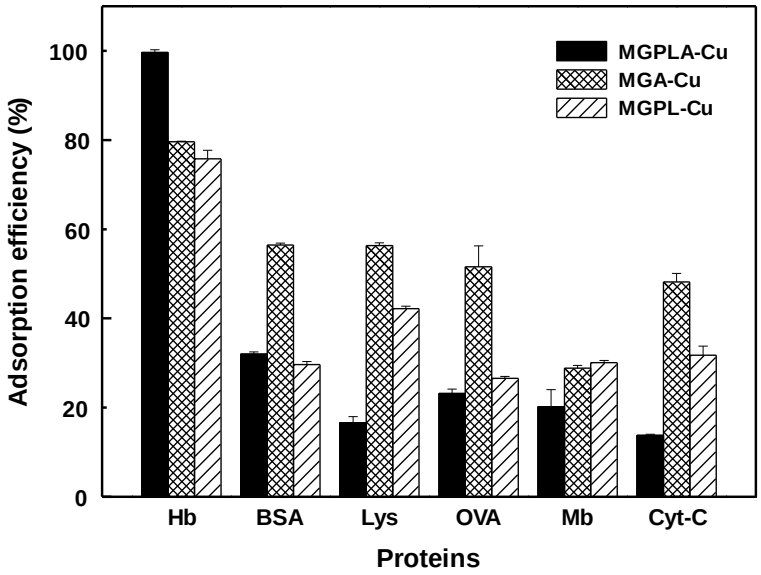

Fig. S8 Adsorption selectivity of MGPLA-Cu, MGA-Cu and MGPL-Cu composites toward six protein models. Adsorption condition: protein sample concentration and volume: 200 mg L^{-1} and 1.0 mL, pH 8, sorbent dosage: 1.0 mg, adsorption time: 30 min.

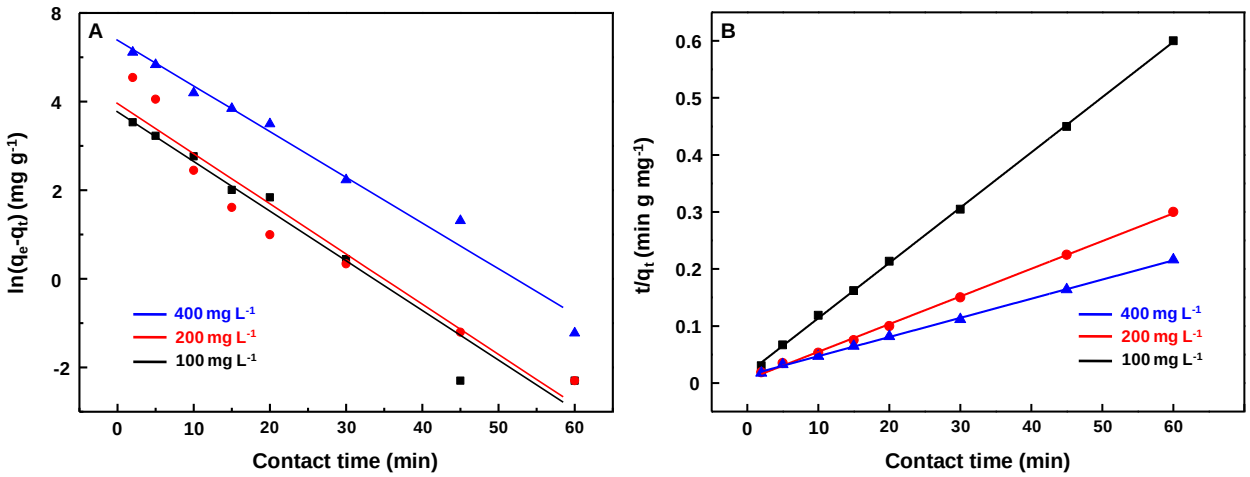

Fig. S9 Linear fitting plots of (A) ln(q_e-q_t) versus t based on pseudo-first-order model; and (B) of t/qt versus t based on pseudo-second-order model.

Table S1 Calculated parameters of pseudo-first-order and pseudo-second-order kinetic models for Hb adsorption on MGPLA-Cu composite with different initial concentrations.

c_0 (mg L^{-1})	$q_{e,exp}$ (mg g^{-1}) [a]	Pseudo-first-order model			Pseudo-second-order model		
		$q_{e,cal}$ (mg g^{-1}) [b]	k_1 (min^{-1})	R^2	$q_{e,cal}$ (mg g^{-1}) [b]	k_2 (g mg^{-1} min^{-1})	R^2
100	99.8	43.3	0.2582	0.9580	103.1	0.00563	0.9997
200	199.9	52.3	0.2607	0.9373	204.1	0.00394	0.9993
400	277.7	218.0	0.2374	0.9820	285.7	0.00091	0.9993

[a]: Equilibrium adsorption capacity obtained from experiment.

[b]: Equilibrium adsorption capacity calculated according to kinetic models

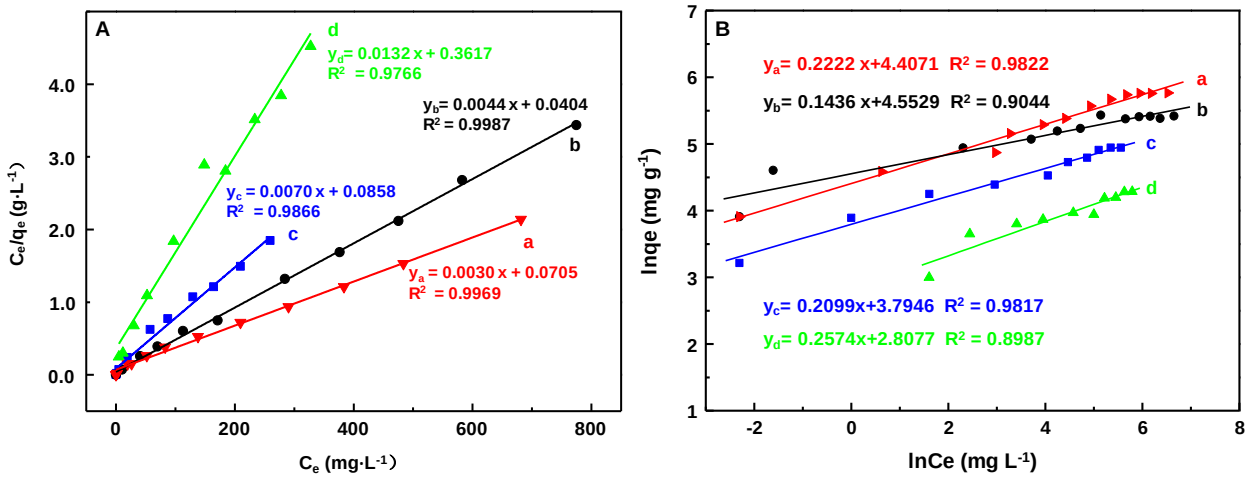

Fig. S10 (A) Linear plots of C_e/q_e versus C_e for Langmuir model and (B) linear plots of ln q_e versus C_e for Freundlich model. Hb on MGPLA-Cu composite (a) and MGA-Cu composite (b); BSA on MGA-Cu composite (c) and MGPLA-Cu composite (d).

Table S2 Adsorption parameters of Langmuir and Freundlich isotherm models for Hb and BSA adsorption on MGPLA-Cu and MGA-Cu composite.

Adsorbent	Protein	Langmuir model parameters			Freundlich model parameters		
		q_m (mg g^{-1})	b (L mg^{-1})	R^2	K_F ($mg^{1-1/n}$ $L^{1/n}$ g^{-1})	$1/n$	R^2
MGPLA-Cu	Hb	334	0.0425	0.9969	82.0	0.222	0.9822
	BSA	76	0.0364	0.9766	16.6	0.257	0.8987
MGA-Cu	Hb	227	0.1090	0.9987	94.9	0.144	0.9044
	BSA	143	0.0815	0.9866	44.5	0.210	0.9817

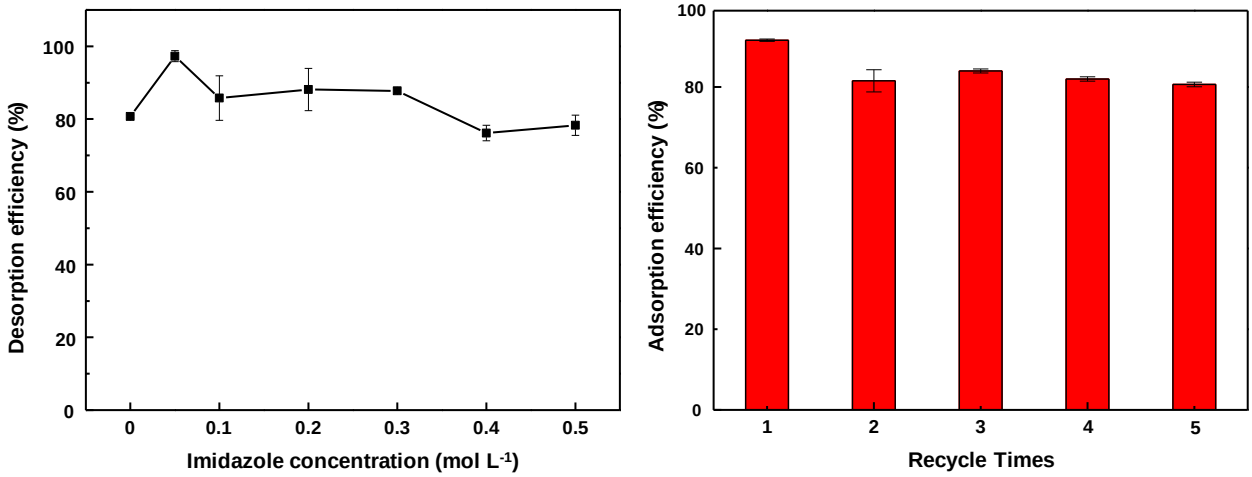

Fig. S11 (A) The effect of imidazole concentration on desorption efficiency of Hb from MGPLA-Cu composite. (B) Reusability of MGPLA-Cu composite for Hb adsorption-desorption process. Adsorption conditions: protein sample concentration and volume: 200 mg L^{-1} and 1.0 mL, pH 8, sorbent dosage: 1.0 mg, adsorption time: 30 min. Desorption conditions: elution buffer: 0.2 mol L^{-1} carbonate buffer at pH 10, desorption time: 30 min.