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Supplementary Information

Enhanced Adsorption of Cu(II) Ions on the Chitosan Microspheres Functionalized with Polyethylenimine-conjugated Poly(glycidyl methacrylate) Brushes

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S1. Experimental

1.1 Grafting density of PGMA brushes onto the CCS microspheres

The grafting yield (GY) and grafting density (GD) of the PGMA brushes onto the CCS microspheres via SI-ATRP can be precisely controlled by varying reaction time and the initial monomer concentration. The GY and GD values were determined using the previously-reported equations.[1,2] The GY were determined by measuring the increase in the mass percentage of the CCS-*g*-PGMA microspheres as follows:

$$GY = \frac{W_g - W_o}{W_o} \times 100\% \quad (1)$$

where W_o and W_g were the weights of the dry CCS microspheres before and after the grafting of PGMA brushes, respectively. The GD of PGMA brushes were determined by the following equation:

$$GD = \frac{(W_g - W_o)/M}{W_o} \times 100\% \quad (2)$$

where M is the molecular weight of the GMA repeat unit (i.e., 142.15 g·mol^{-1}) of the PGMA chains. The GY and GD values were the mean values from at least three replicate measurements.

1.2 Effect of solution pH

To determine the optimal solution pH for the CCS-*g*-PGMA2-*c*-PEI microspheres from 4 h of ATRP reaction, the adsorption profiles of Cu(II) ion in an initial solution pH range of 1.0 –6.0 was investigated. An aliquot 100 mg of the CCS microspheres was immersed in 200 mL of Cu(II) ions with an initial concentration of 0.2 mmol·L^{-1} (i.e. 13 mg· L^{-1}), and the adsorption was allowed to proceed at 150 rpm and 25^{o}C for 24 h. The solution pH was adjusted by adding 0.1 mol·L^{-1} HNO_3 or NaOH solution every 2 h to remain relatively constant throughout the adsorption experiment. The equilibrium adsorption capacity was calculated by the following

equation:[3]

$$q_e = \frac{(C_o - C_e) \cdot v}{m} \tag{3}$$

where q_e is the equilibrium adsorption capacity (mg·g^{-1}), C_o and C_e are the concentrations of the initial Cu(II) solution and the final solution at equilibrium, respectively, m is the mass of the CCS microspheres (g), and v is the solution volume (L), which remained constant throughout the adsorption period.

1.3 Adsorption kinetics

To determine the adsorption kinetics of Cu(II) ions, a aliquot 100 mg of CCS-*g*-PGMA2-*c*-PEI microspheres was immersed in 200 mL of Cu(II) solution with an initial concentration of 0.2 mmol·L^{-1} (i.e. 13 mg· L^{-1}). The initial solution pH values was 5.0, and no pH adjustment was performed throughout the adsorption process. The adsorption of Cu(II) ions on the pristine and functionalized CCS microspheres was allowed to proceed at 25^{o}C at 150 rpm for a predetermined period. The residual concentration of Cu(II) ions was analyzed by taking 1.0 mL aliquot of the Cu(II) solution at different time intervals. The adsorbed amounts of Cu(II) ions per unit weight of the microspheres at time t, q_t (mg·g^{-1}), were calculated from the following equation:[4]

$$q_t = \frac{(C_o - C_t) \cdot V}{m} \tag{4}$$

where C_o and C_t correspond to the initial concentration of Cu(II) ions and the Cu(II) concentration at time t (mg·L^{-1}), respectively. v is the volume of the residual volume at time t, and m is the weight of the microspheres added.

1.4 Adsorption isotherms

The adsorption isotherms were obtained by varying adsorption temperatures of 25, 35, 45, and 55 ^{o}C. The adsorption solution pH was adjusted at 5.0 ± 0.1

throughout the experimental periods with a series of initial concentration of Cu(II) from C_0 = 0.1 - 2.2 mmol·L^{-1} (i.e. 6.5 – 140 mg· L^{-1}). At a predetermined temperature, an aliquot 100 mg of the CCS-*g*-PGMA2-c-PEI microspheres were added into 200 mL of Cu(II) solutions under continuous stirring at 150 rpm for 2 h. The adsorption amount of Cu(II) ions onto the microspheres at equilibrium was calculated from the above Equation 3.

1.6 Competitive adsorption of the coexisting heavy metal ions

To determine the effect of coexisting heavy metal ions on the adsorption behavior of Cu(II) ions on the microspheres, the competition adsorption experiment was conducted in a quinary ion system with Pb(II), Cu(II), Mg(II) and Ca(II) ions as the coexisting heavy metal ions. Typically, a 100 mg aliquot of the CCS-*g*-PGMA2-c-PEI microspheres was added to 200 mL of the quinary heavy metal ion solution at 25^{o}C and at 150 rpm for 24 h. The initial concentration of each heavy metal ion was 0.2 mmol·L^{-1}, i.e., 41, 13, 8 and 4.9 mg·L^{-1} for Pb(II), Cu(II), Ca(II) and Mg(II) ions, respectively. The solution pH value remained constant at 5.0 ± 0.1 throughout the adsorption periods by adjusting with 0.1 mol·L^{-1} HNO_3 or NaOH solution for every 2 h.

1.7 Regeneration and recycle of the CCS-*g*-PGMA2-*c*-PEI microspheres

To regenerate the Cu(II)-adsorbed CCS microspheres for recycle use, the desorption of the CCS microspheres was performed in a 1 mol·L^{-1} EDTA solution. The adsorption experiments were carried out by adding 100 mg of the microspheres in 200 ml of 0.2 mmol·L^{-1} (i.e., 13 mg·L^{-1}) Cu(II) solution with pH at 5.0 at 25 ^{o}C for 2 h. The desorption of the Cu(II)-loaded CCS microspheres was conducted in 50 mL of 1 mol·L^{-1}EDTA solution at 25 ^{o}C at 150 rpm for 1 h. The sorption-desorption experiments were conducted for five cycles to evaluate the regeneration capacity of

the functionalized CCS microspheres.

S2. Results and Discussion

Table S1 Comparison adsorption of Cu(II) ions on the PEI-modified adsorbents

Adsorbents	Equilibrium time (min)	C_0 (ppm)	pH values	q_{max} (mmol·g^{-1})	Refs
PP-*g*-PEI	180	20-100	6	1.88	5
PEI-modified magnetic porous powder	10	100-600	6.5	2.47	6
PEI-modified magnetic graphene oxides	30	10-350	5	2.46	7
PEI-coated Fe_3O_4	60	50	5.5	2.50	8
PEI-modified biomass	240	20-500	5.5	1.44	9
PEI-immobilized PMMA microspheres	30	50-600	5.5	0.22	10
PEI-grafted resin	1200	128	5	2. 60	11
PEI-modified aerobic granular sludge	180	10-500	6	1.11	12
PEI-*c*-PGMA-modified CCS microspheres	120	6.5-140	5	3.58	This study

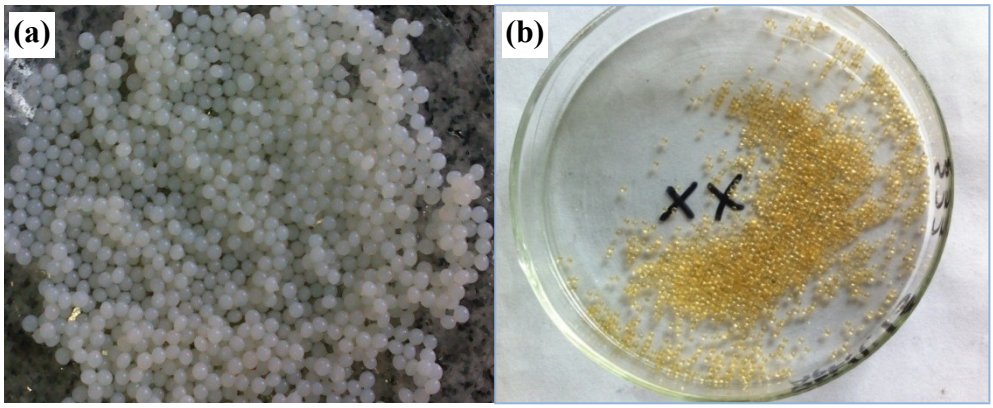

Fig. S1 The optical images of the (a) wet hydrogel and (b) dry crosslinked chitosan (CCS) microspheres.

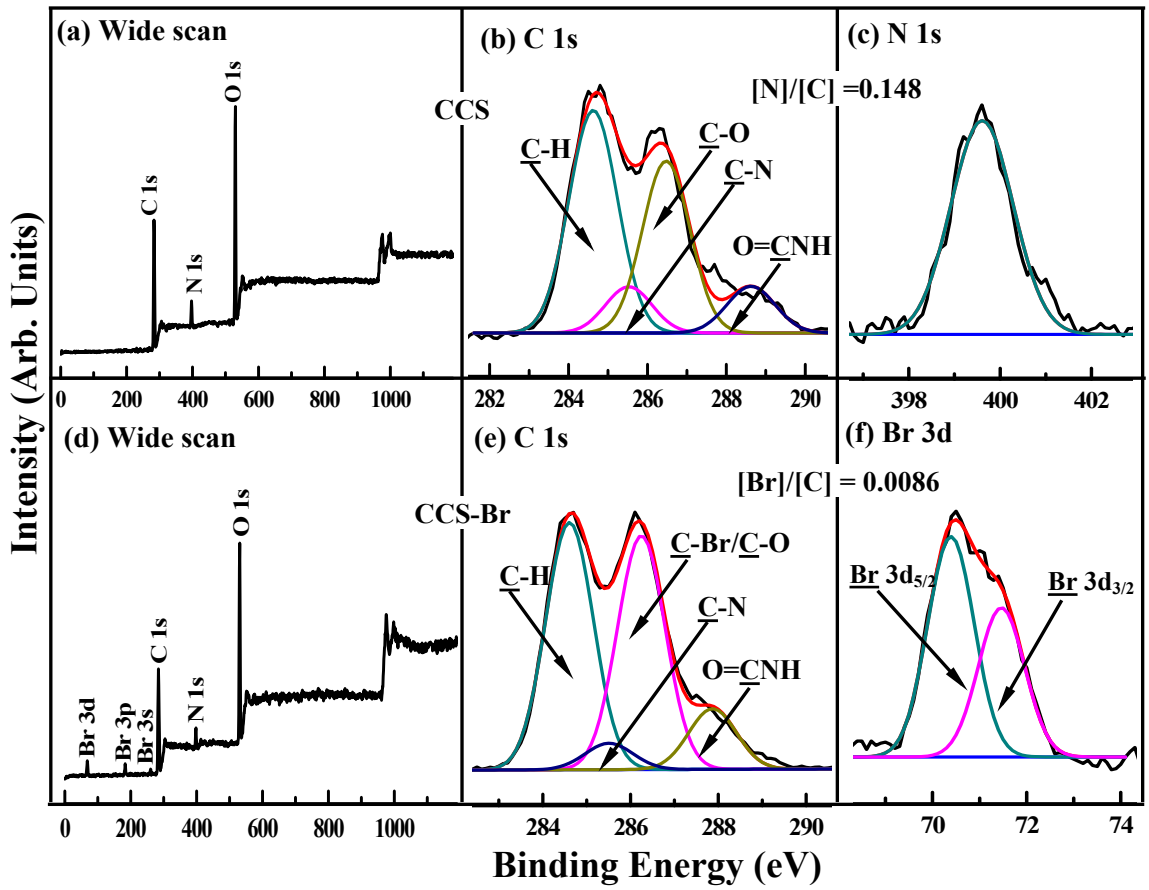

Fig. S2 The wide scan, C 1s and N 1s (or Br 3d) core-level XPS spectra of the surfaces for the (a,b,c) CCS and (d,e,f) CCS-Br microspheres.

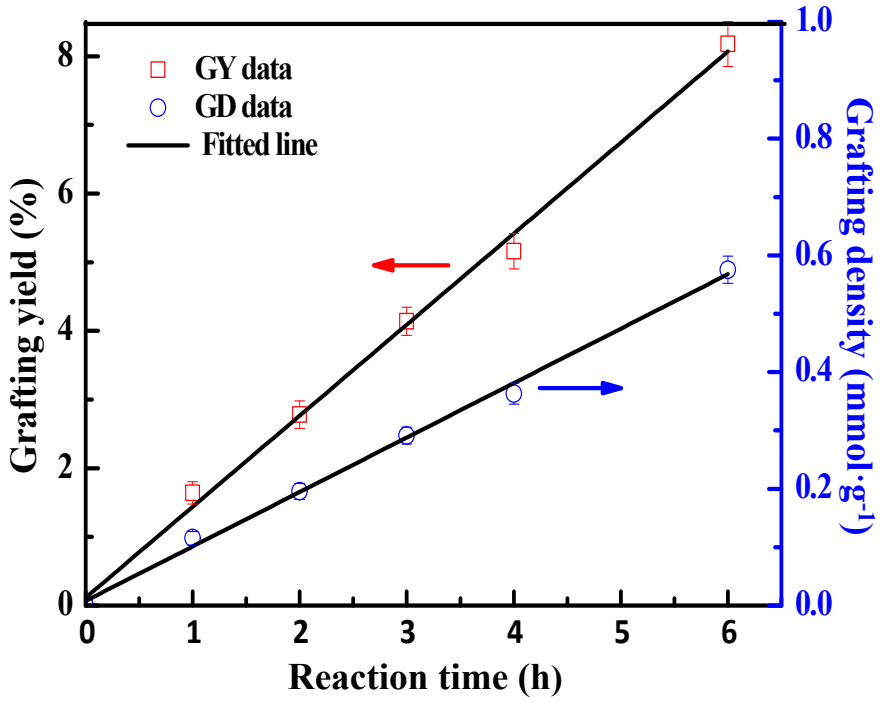

Fig. S3 A linear relationship of the grafting yield (GY) and grafting density (GD) for the PGMA brushes formed on the surfaces of the CCS-*g*-PGMA microspheres as a function of ATRP reaction time.

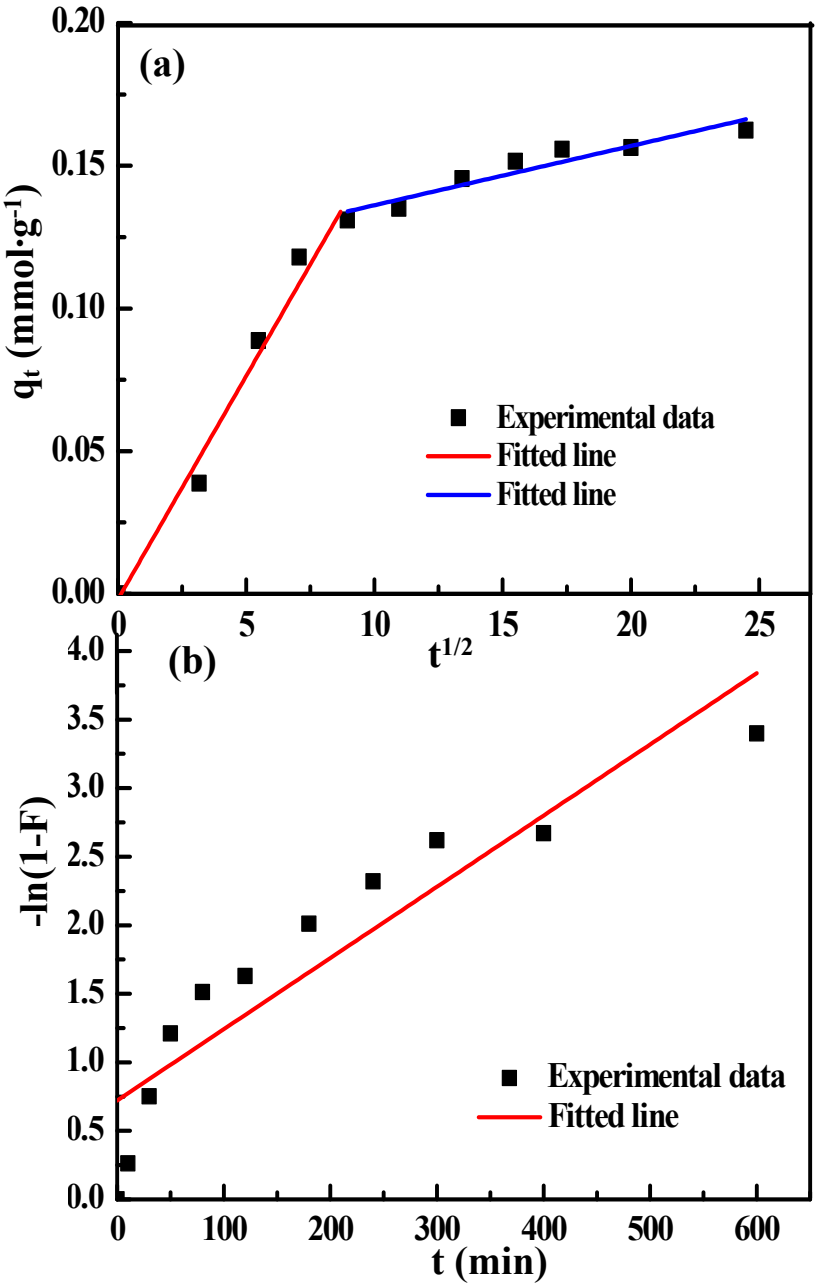

Fig. S4 The diffusion-based model-fitted adsorption kinetics of Cu(II) ions on the pristine CCS microspheres at the initial pH value of 5.0: (a) Weber-Morris and (b) Boyd. Experimental conditions: C_0 = 0.2 mmol·L^{-1} (i.e. 12.7 mg· L^{-1}), v = 200 mL, T = 298.15 K, and m = 100 mg.

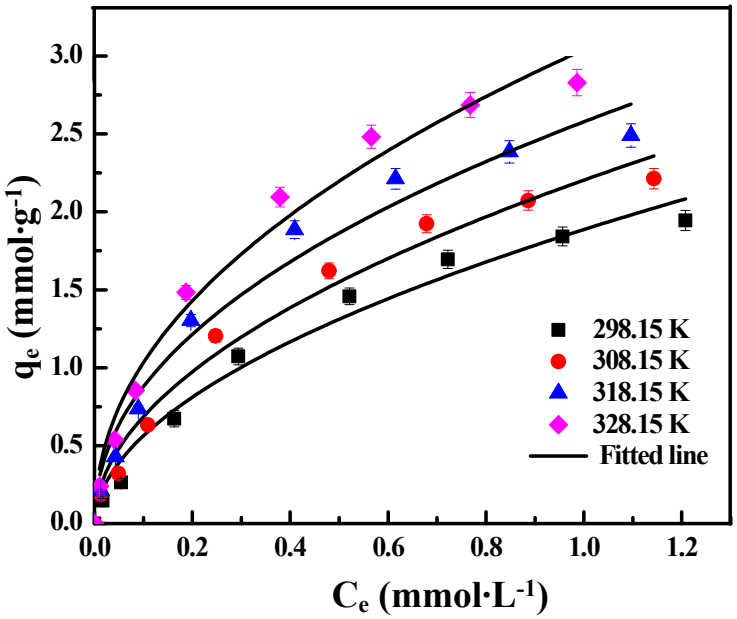

Fig. S5 Freundlich-fitted adsorption isotherms of Cu^{2+} ions on the CCS-*g*-PGMA2-*c*-PEI microspheres at different adsorption temperatures of 298.15, 308.15, 318.15 and 328.15 K. Experimental conditions: C_0 = 0.1 - 2.2 mmol·L^{-1} (i.e. 6.35 – 139.7 mg· L^{-1}), *v* = 200 mL, m = 100 mg, adsorption time = 2 h, and pH = 5.0.

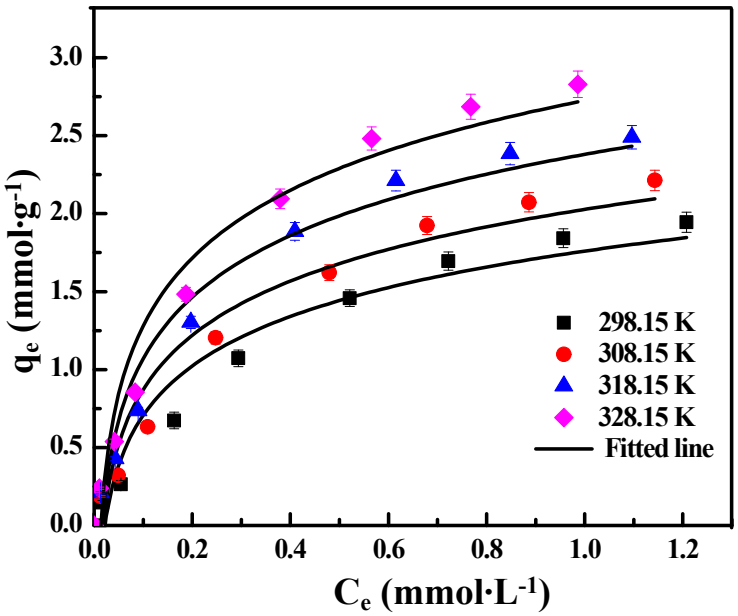

Fig. S6 Temkin-fitted adsorption isotherms of Cu^{2+} ions on the CCS-*g*-PGMA2-*c*-PEI microspheres at different adsorption temperatures of 298.15, 308.15, 318.15 and 328.15 K. Experimental conditions: C_0 = 0.1 - 2.2 mmol·L^{-1} (i.e. 6.35 – 139.7 mg· L^{-1}), *v* = 200 mL, m = 100 mg, adsorption time = 2 h, and pH = 5.0.

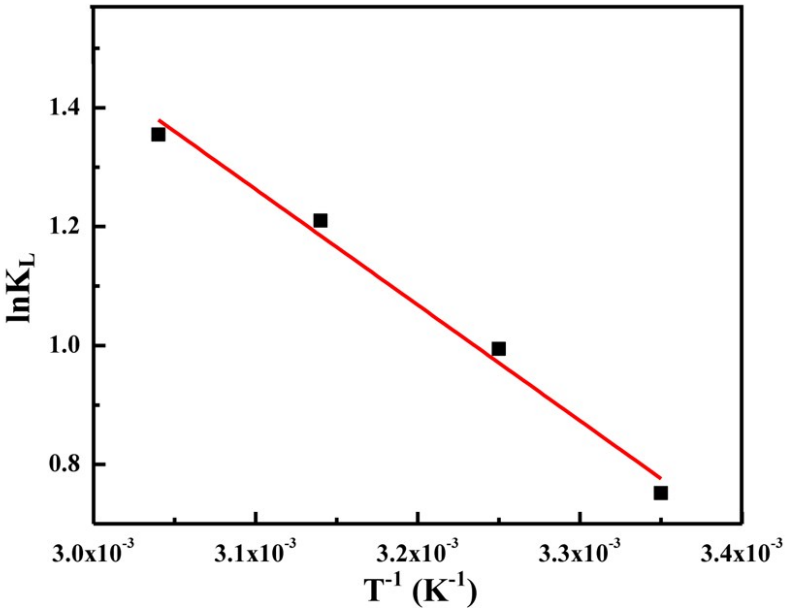

Fig. S7 Van′t Hoff plot for the adsorption of Cu^{2+} ions on the CCS-*g*-PGMA2-*c*-PEI microspheres.

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