Magnetic cellulose-chitosan hydrogels prepared from ionic liquids as reusable adsorbent for removal of heavy metal ions

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Experimental section

Chemicals. Paper pulp was provided by ChenMing Co. Ltd. (Shandong, China). (cellulose content: 83.3 wt%; hemicelluloses content: 14.7 wt%; lignin content: 0.7 wt%; ash content: 1.2 wt%). Chitosan (with a deacetylation degree of 90%) was purchased from Sinopharm Chemical Reagent. 1-butyl-3-methylimidazolium chloride (bmimCl) was obtained from Lihua Co. Ltd. (Henan, China). All other reagents used were analytical grade and used as received.

Preparation of the magnetite cellulose-chitosan hydrogels microspheres. The hydrogels were prepared via sol-gel method. The cellulose, chitosan and bmimCl were dried at 80 ℃ for 24 h in a vacuum oven before use. Cellulose (0.7g) and chitosan (1.4g) were dissolved in bmimCl (30g) at 100 ℃ for 30min to obtain a 7 wt% clear and viscous solution. Then, Fe_3O_4 particles (0.7g) was added to the solution and homogenized by continuous agitation for 20min. After that, the mixture was dispersed in 100mL vacuum pump oil with 5 wt% Span 80 under the agitation of 1000 rpm for 4 h at 100 ℃ and cooled down to room temperature at the rate of 5 ℃/10 min. During stirring, ethanol was added to the suspension to further regenerate the hydrogels microspheres from ionic liquids (ILs). After stewed for 12 h, the upper oil phase was poured out, and the microspheres were washed five times with ethanol followed by five washings with deionized (DI) water to remove the residual ILs. Finally, the reconstituted hybrid hydrogels microspheres were stored in DI water at about 2 ℃.

Characterization. The Fourier transform infrared (FTIR) spectra of all the samples were measured on a Nicolet iN 10 IR spectrometer (Thermo Fisher Scientific Inc, USA) over the frequency range of 4000-400 cm^{-1} at a resolution of 4 cm^{-1}. The KBr disk method was carried out, and the samples were dried in the vacuum oven for 24 h before testing. XRD patterns were recorded on the X-ray diffractometer (D8-Advance, Bruker) with Cu Ka radiation ($\lambda = 1.5406$ Å) at 40 kv and 30 mA in the range of 10-80^{o} at room temperature. Magnetization measurement of the microspheres was performed with a vibrating sample magnetometer (VSM, Lake Shore, 7410, USA) at room temperature under ambient atmosphere. The morphology of the microspheres was determined by scanning electron microscopy (SEM) (S-4800, Hitachi, Japan) with an accelerating voltage of 10 kV. Prior to image, the samples were dried in the air and sputter-coated with gold thereby making the samples conductive.

Adsorption and desorption measurements.

Adsorption of metal cations. Aqueous solutions of Cu^{2+}, Mn^{2+}, Zn^{2+}, Pb^{2+}, Fe^{2+} and Ni^{2+} were prepared by dissolving the corresponding nitrates in DI water, respectively. Adsorption assays were performed batchwise in 25 mL serum bottle by contacting 50 mg adsorbent with 10 ml metal solutions and stirred for 24 h to reach equilibrium at room temperature. The pH of the solution was adjusted with 1 mol/L HCl solution. The initial and the obtained solutions through magnetic separation after adsorption were exactly analyzed by the inductively coupled plasma optical emission spectroscopy (ICP-OES, Optima 7000, PerkinElmer, USA). The amount of metal retained in the adsorbent phase q_e (mg/g) was calculated by Equation (1):

$$q_e = (C_i-C_e)V/m \cdots\cdots\cdots (1)$$

where C_i and C_e are the initial and final (equilibrium) concentrations of the metal ions in solution (mg/L), respectively; V is the solution volume (L), and m is the mass of sorbent (g, wet weight).

Desorption study. Desorption studies were performed by dispersing the used adsorbent into 5 mL DI water with different pH value (ranged from 1 to 7) and stirred for 24 h to reach equilibrium at room temperature. The used adsorbent was obtained by magnetic separation from the adsorption solution (by contacting 50 mg of the adsorbent with 10 ml of 100 ppm Cu^{2+} solution (pH=7) for 24 h) and washed with DI water three times to remove the electrostatic attracted Cu^{2+}. The amount of metal detached from the sorbent phase (mg/g) was calculated by Equation (2)

$$q_{de} = C_{de}V/m \cdots\cdots\cdots (2)$$

where C_{de} is the equilibrium concentrations of the metal ions in the desorption solution (mg/L), V is the solution volume (L), and m is the mass of sorbent (g, wet weight).

Adsorbent recycling.

After desorption, the adsorbents were separated, regenerated and reused for adsorption from the solution with Cu^{2+} concentration of 79.2 mg/L, which was the equilibrium solution after adsorbing for 24h (the initial Cu^{2+} concentration was 100 mg/L). We have repeated the above procedure up to seven cycles. All the experiments for adsorption, desorption and recycling were carried out at least twice in our lab. The results are well reproducible and the average was taken for each test.

Table S1 Analysis of heavy metals adsorption with magnetic cellulose-chitosan beads

	Metals					
	Cu	Fe	Pb	Zn	Mn	Ni
C_0 (ppm)	99.0	99.6	99.8	97.1	94.1	97.7
C_e (ppm)	79.2	57.6	87.4	95.3	92.4	95.5
q_e (mg/g) [a]	3.76	7.91	2.36	0.35	0.28	0.4
q'_e (mg/g)[b]	44.7±5	94.1±7	28.1±3	4.2±1	3.3±0.8	4.7±1
Q_e (mg/g)[c]	89.4±10	188±14	56.2±6	8.4±2	6.6±1.6	9.4±2

[a] 10 mL of metal solution was stirred with 50 mg adsorbent (hydrogels) at 25 ℃ for 24h. The weight was calculated according to the wet weight of the adsorbent.
[b] q'_e is the adsorption capacity which was calculated based on the dried weight of the adsorbent. The moisture content of the adsorbent was 91.6%. $q'_e = q_e/(1-91.6\%)$.
[c] Q_e is the adsorption capacity that was calculated based on the dried weight of chitosan. The weight of chitosan accounts for 50 wt% of the dried weight of the adsorbent. The weight was calculated according to the dry weight of the adsorbent. $Q_e = 2q'_e$.

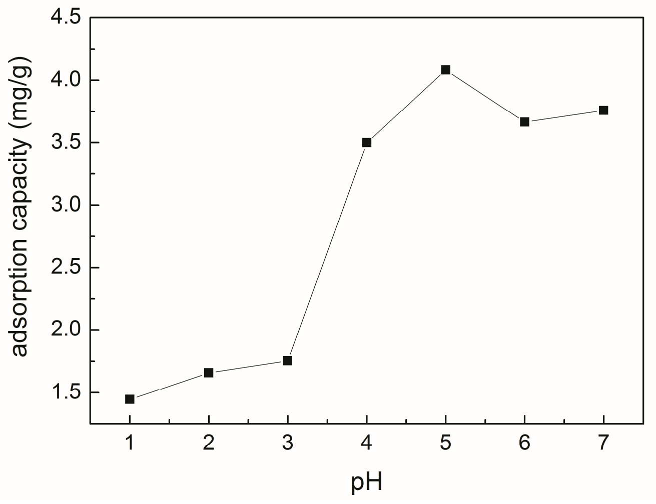

Fig. S1. The effects of pH on the adsorption of Cu(II)

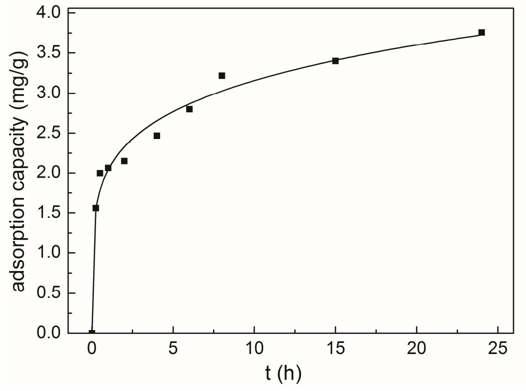

Fig. S2. The effects of contact time on the adsorption of Cu(II)

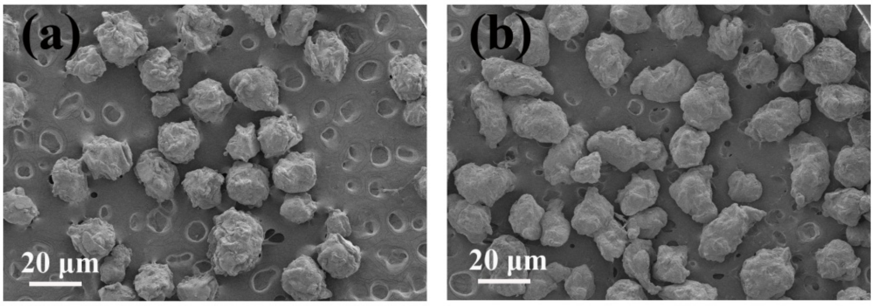

Fig. S3. SEM images of the microspheres before the adsorption (a), and after recycling 3 times (b).

Table S2. Adsorption capacities and experimental conditions of chitosan composites for Cu (II)

Adsorbent	q_e (mg/g)	pH	T (℃)	Ref.
Chitosan hydrogels	44. 7	5	25	Our adsorbent
Chitosan/cotton fiber	24.78	6.5	25	Zhang et al. (2008)[1]
Chitosan/cellulose	26.50	-	25	Sun et al. (2009)[2]
Chitosan/perlite	196.07	5.0	-	Kalyani et al. (2005)[3]
Chitosan/perlite	104	4.5	25	Shameem et al. (2008)[4]
Chitosan/ceramic alumina	86.2	4.0	25	Veera et al. (2008)[5]
Chitosan/alginate	66.67	4.5	-	Wan Ngah et al. (2008)[6]
Chitosan/PVC	87.9	4.0	-	Srinivasa et al. (2009)[7]
Chitosan/PVA	47.85	6.0	-	Wan Ngah et al. (2004)[8]
Chitosan/sand	8.18	-	-	Wan et al. (2010)[9]

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