Electronic Supplementary Information

Lignin-based Pickering HIPEs for macroporous foams and their enhanced adsorption of copper(II) ions

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Materials

Furfural residues were purchased from Tian Guan Furfural Co. Ltd (China) and used with further cleaning with water and drying. HCl, NaOH, Na_2S, H_2SO_4, and concentrated ammonia solution were bought from Guangzhou Chemical Factory (China) and used without purification. Melamine was obtained from the Sinopharm Chemical Reagent Co. Ltd., China. 37.0 wt. % formaldehyde aqueous solution and toluene Guangdong Guangzhou Chemical Factory Co. Ltd., China. Triethanolamine (TEA, Tianjin Fuyu Chemical Reagent Co. Ltd., China) and acetic acid (Jiangsu Qiangsheng Chemical Reagent Co. Ltd., China) were used to control the pH value of solutions. $CuSO_4{\cdot}5H_2O$ (A.R. grade reagents) was supplied by Aladdin. Water used in all experiments was purified by deionization and filtration with a Millipore (MA, USA) purification apparatus to a resistivity higher than 18.0 MΩ · cm.

Preparation of lignin particles

Alkaline lignin was obtained from the Kraft pulping process which was reported in our previous work.[1] Lignin particles were successfully synthesized by adjusting the pH value of aqueous lignin solutions. A typical preparation procedure was as follows: The aqueous dispersions of lignin with different solid contents (0.05-1 wt. %) were prepared by adding different amounts of lignin powder to a fixed amount of deionized water. Secondly, the pH value of the lignin dispersions was modified by adding concentrated ammonia solution (37 wt. %), until lignin was completely dissolved. The pH value was around 11 this time. The resulting solution was filtered to remove any impurities before use. Stable and homogeneous lignin solutions were obtained, which is similar to black liquor in paper making. Finally, the pH value of the lignin solution was adjusted to around 3 by adding HCl (1 M). Lignin particles were formed and dispersed in the solution. The particle dispersion was then used for the preparation of Pickering emulsion.

Fabrication of porous PMF foams templating from lignin particle-stabilized high internal phase Pickering emulsions

First of all, the pre-MF monomer was synthesized as follow: 1.75 g of melamine and 3.5 ml of 37.0 wt % formaldehyde aqueous solution were mixed in a 50 mL two-necked round bottom flask connected to a reflux condenser and equipped with stirring rod. Then, the pH value of the solution was adjusted to 9.0-9.5 by 2.5 mL of triethanolamine (TEA) under mechanical stirring. The mixture was heated to 55-60 ^{o}C. After 30 min, the MF pre-polymer solution was obtained. The continuous aqueous phase was prepared by mixing certain volume tatio of prepolymer solution and lignin particles dispersion, and the pH was adjusted around 3 by adding HCl (1 M).

Illustration for the preparation of polyHIPEs is shown in Scheme S1. HIPEs are normally prepared by stirring the continuous phase vigorously under continued stirring at 400 rpm while slowly adding the toluene droplet phase. Once all of the toluene phase had been added, the mixture was stirred at 1000 rpm viscous and homogeneous HIPEs were obtained. Subsequently, these lignin particle-stabilized high internal Pickering emulsions were transferred into an oven and polymerized at 60 ^{o}C for 4 h. The products were purified with ethanol to remove the internal toluene, and air-dried at room temperature for 24 h to constant weight. Finally, the porous PMF foams were obtained. The detailed experimental compositions are shown in Table S1.

Adsorption experiments

Adsorption of copper(II) at different initial solution pH

The influences of different initial solution pH to the adsorption of copper(II) by PMF foams was investigated. The range of pH was 3.0–5.5, and the initial concentration of Cu(II) ions in each aqueous solution was 385.0 mg · dm^{-3}. PMF foams was weighed and immerged in Cu(II) solutions with different initial pH under continuous stirring at room temperature for 24 h. The Cu(II) concentrations were analyzed with ethylenediamine as developing agent at a wavelength of 557 nm by Vis spectrophotometer. The amount of adsorption, q (mg/g), was calculated according to the following equation:

$$q = \frac{(C_0 - C_e)V}{m}$$

where C_0 and C_e (mg/dm^3) are the initial and final Cu(II) concentrations, V (dm^3) is the volume of the Cu(II) solution, and m (g) is the weight of the polymers in the dried adsorbents.

Adsorption equilibrium experiments

The adsorption equilibrium experiments of PMF foams were carried out at 30 ^{o}C and pH 5.5. The initial concentration of Cu(II) was ranged from 20.0 to 400.0 mg · dm^{-3}. The magnetic adsorbents were weighed and immerged in Cu(II) solutions with various initial concentrations under continuous stirring for 24 h, respectively. The same analysis method as mentioned above has been employed to detect the initial and final Cu(II) concentrations by Vis spectrophotometer. The amount of adsorption was calculated based on Eq. (1).

Kinetics adsorption experiments

The kinetics adsorption experiments were also measured at 30 ^{o}C and pH 5.5. The initial Cu(II) concentration of solution is 385.0 mg/g. PMF foams was weighed and immerged in Cu(II) solutions under continuous stirring. At desired time intervals, 0.002 dm^3 of sample solution was taken out and filtrated to analyze the Cu(II) concentration (C_{ti}). Meanwhile, an equal amount of deionized water is added into the bulk solutions to keep the volume of the solutions constant. The adsorption of Cu(II) ions at time t_i, $q(t_i)$ (mg/g), was calculated from the following equation,

$$q(t_i) = \frac{(C_0 - C_{ti})V_0 - \sum_2^{i-1} C_{t_{i-1}} V_s}{m}$$

Where C_0 and C_{ti} (mg/dm^3) are the initial Cu(II) concentration and the concentrations at time t_i (min), respectively. V_0 and V_s (dm^3) are the initial volume of the Cu(II) solution and that of the bulk solution taken out every time for Cu(II) concentration analysis, respectively. Here, V_s is equal to 0.002 dm^3. m (g) is the weight of the polymers in the dried adsorbents.

Characterization

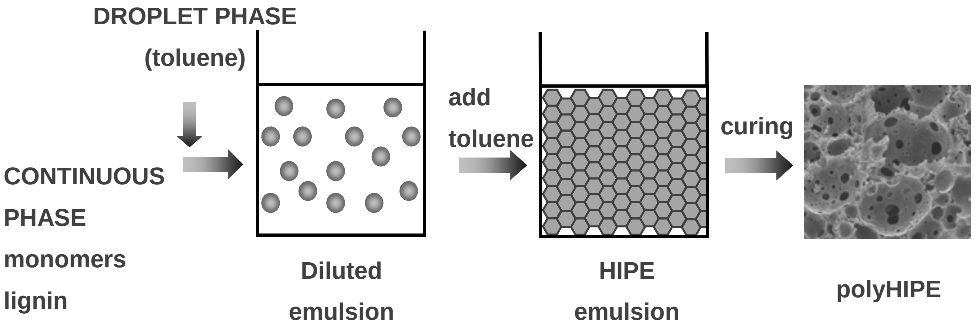
Pickering emulsions were observed with a microscope (Carl Zeiss, German). The average diameter of the emulsion droplets were determined with a laser scattering particle size distribution analyzer (Malvern mastersizer 2000). Fourier transform infrared (FTIR) spectra of the samples were tested on German Vector-33, which was recorded using KBr pellets for solid samples. Morphology of the foams was analyzed via Scanning electron microscopy (SEM), which was carried out with a Zeiss EVO 18 $_0$electron microscope equipped with a field emission electron gun and energy dispersive spectrometer (EDS). The Zeta potential of aqueous lignin colloidal particles was measured using a Malvern Zeta sizer Nano ZS90. UV adsorbance of lignin and the Cu(II) concentrations was analyzed with a Hitachi U-3010 ultraviolet and visible analyzer. The pH values were monitored using a pH meter (PHB-2, Leici, China).

Table S1. Parameters of lignin particle-stabilized Pickering HIPE templates for PMF foams.

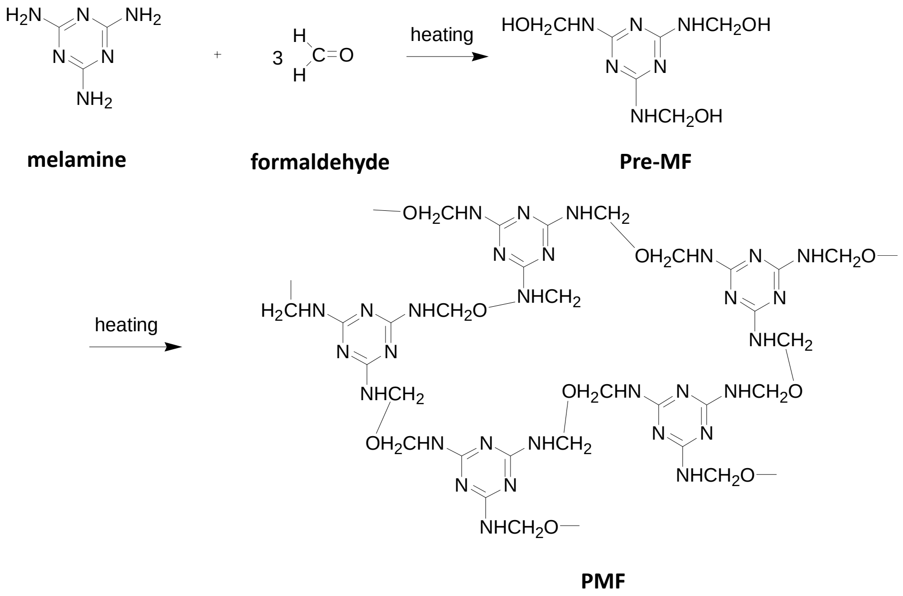
Sample	Aqueous phase			Oil phase (toluene) /mL	Inter phase fraction /vol/	Monomer concentration /wt%	Droplet size/μm
	Water /mL	Lignin /wt%	Pre-MF /mL				
HIPE 1	1.875	1.0	0.625	7.5	75	25	106±43
HIPE 2	1.5	1.0	0.5	8.0	80	25	114±50
HIPE 3	1.125	1.0	0.375	8.5	85	25	134±53
HIPE 4	0.75	1.0	0.25	9.0	90	25	152±62
HIPE 5	0.75	1.0	0.75	8.5	85	50	146±57
HIPE 6	0.375	1.0	1.125	8.5	85	75	119±45
HIPE 7	1.125	0.5	0.375	8.5	85	25	123±48
HIPE 8	1.125	2.0	0.375	8.5	85	25	119±20
HIPE 9	1.125	4.0	0.375	8.5	85	25	105±49

Table S2. Cu(II) uptakes of various adsorbents.

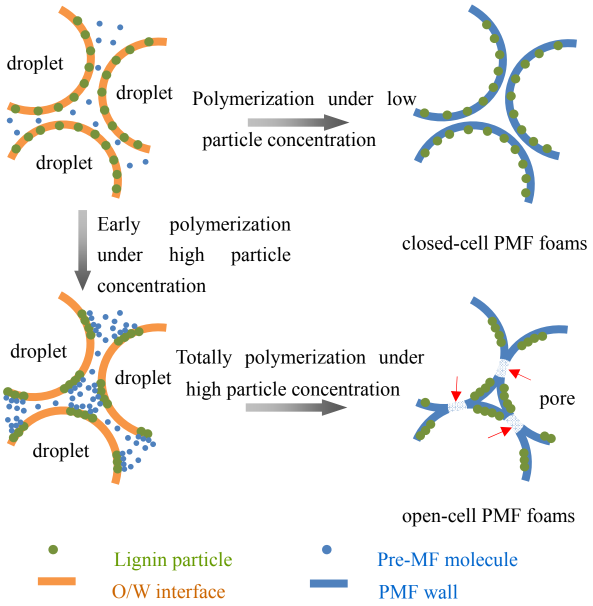
Adsorbents	q (mg/g)	Reference
PMF foams	73.2	This study
Manganese-coated activated carbon	39.5	[2]
Magnetic porous ferrospinel $MnFe_2O_4$	60.5	[3]
Drying bed activated sludge	62.5	[4]
Aspergillus terreus	15.2	[5]
Citric acid modified Barley straw	31.71	[6]
Graphene oxide	117.5	[7]
Surface carboxymethylated CS beads	130.0	[8]
Citrus maxima peel	83.7	[9]
Porous chitosan–tripolyphosphate beads	208.3	[10]



Scheme S1. Formation of polyHIPEs by lignin particle-stabilized toluene-in-water Pickering HIPE polymerization technique.



Scheme S2. The reaction between melamine and formaldehyde to form pre-MF and PMF.



Scheme S3. Schematic of the formation of different foams with closed-cell structure or open-cell structure.

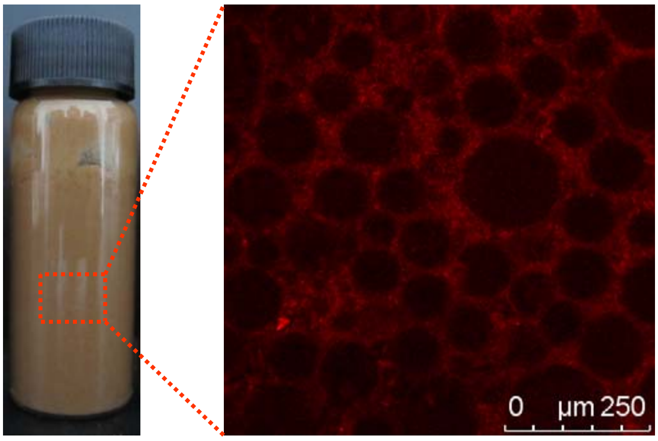


Figure S1. The left picture is the appearance of the lignin particle-stabilized Pickering HIPE with an 85 vol % internal phase fraction. The right picture is the fluorescence micrograph of the corresponding Pickering HIPE.

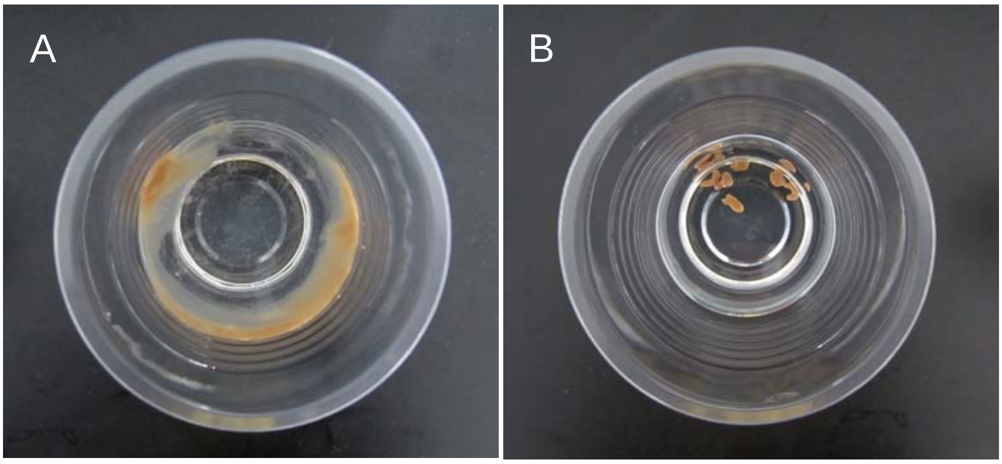


Figure S2. Digital photographs of a drop of HIPEs dispersing in (a) water and (b) toluene. This drop test was used to determine the type of the emulsions. In toluene, the emulsion floated on the surface of toluene. However, the emulsion collapsed immediately in water. It indicates that the lignin particle-stabilized HIPEs were an O/W emulsion.

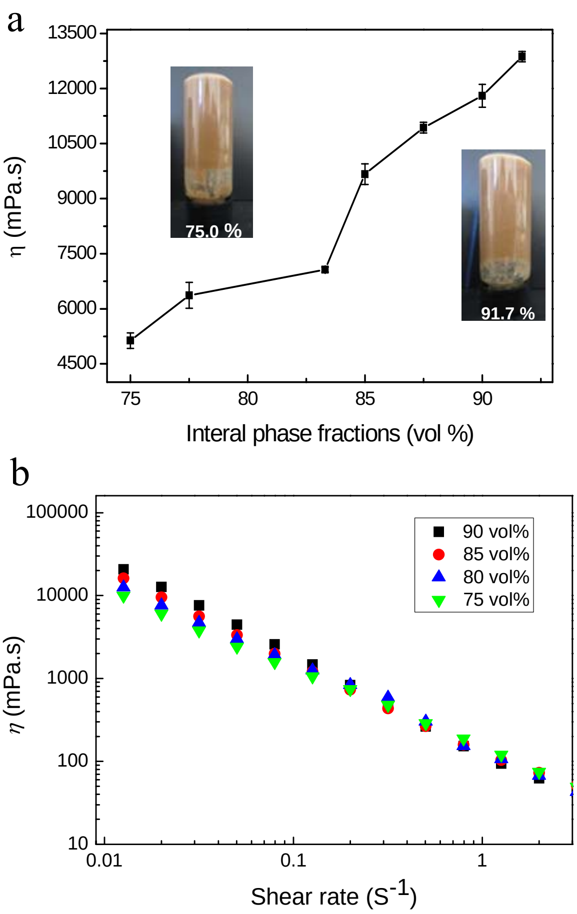


Figure S3. (a) Viscosity by a rotational viscometer and (b) rheology by an AR2000 stress controlled rheometer (TA Instruments) of toluene-in-water Pickering HIPEs stabilized by lignin particles with the different internal phase fractions. Insets in (a) are photographs of the typical gel emulisons, left: 75.0%; right: 91.7%. The concentration of lignin particles is fixed as 1 wt% to water.

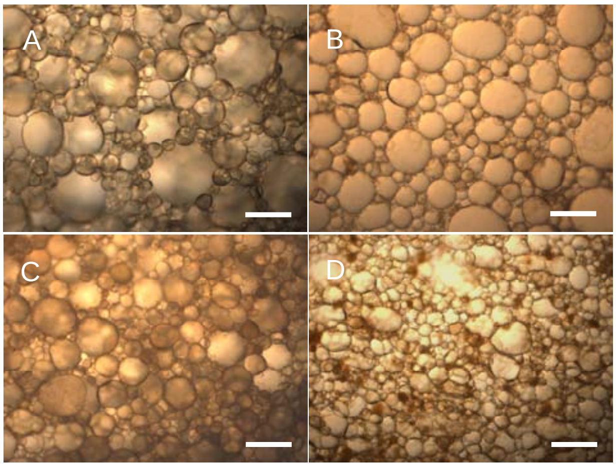


Figure S4. Optical microscopic images of toluene-in-water Pickering HIPEs stabilized by lignin particles of different concentrations: (A) 0.5, (B) 1.0, (C) 2.0, (D) 4.0 wt%. All scale bars present 100 μm.

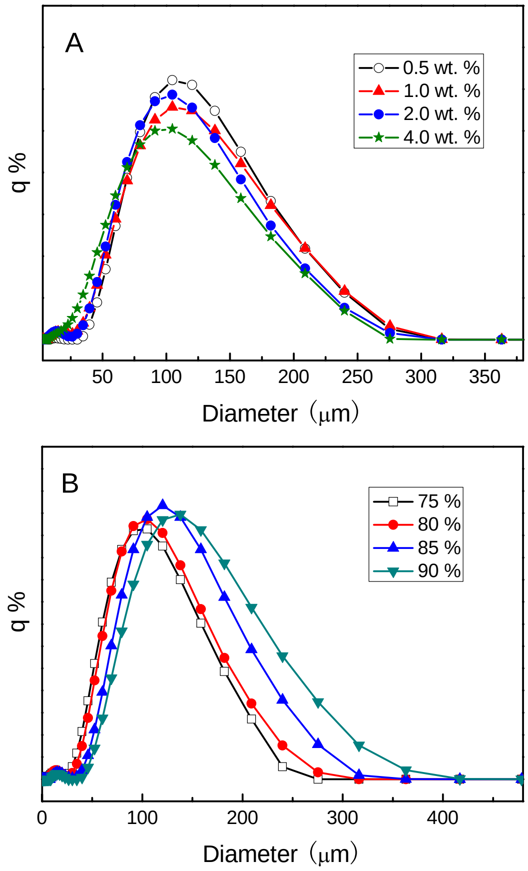


Figure S5. The size distribution graphs of HIPEs: (A) the different lignin particle concentrations and (B) the different interal phase fractions.

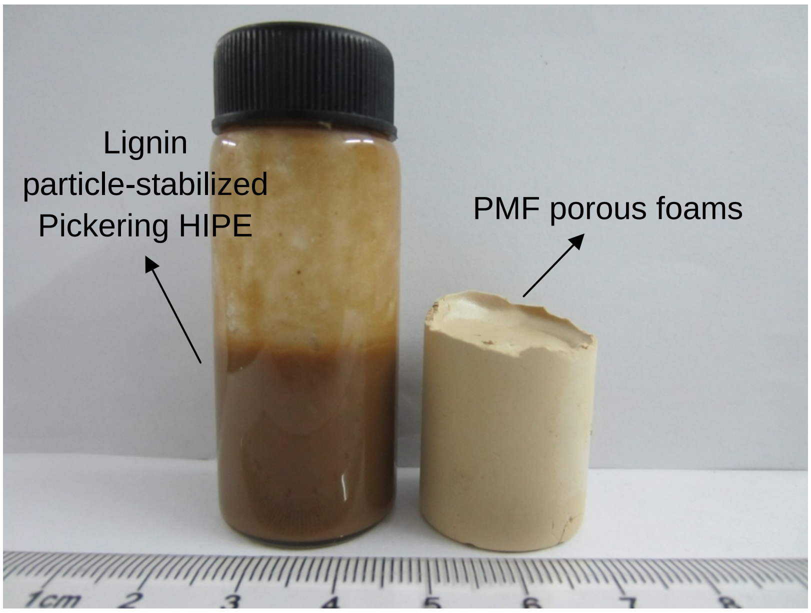


Figure S6. Digital photograph: left, Pickering HIPE and right, porous PMF foam. The foam kept the same volume and shape without any change after polymerization.

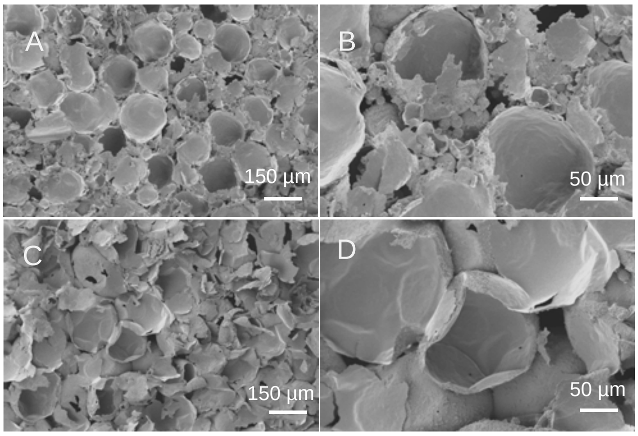


Figure S7. SEM images of closed-cell PMF foams prepared from (A,B) HIPE 1 and (C,D) HIPE 2 in Table S1.

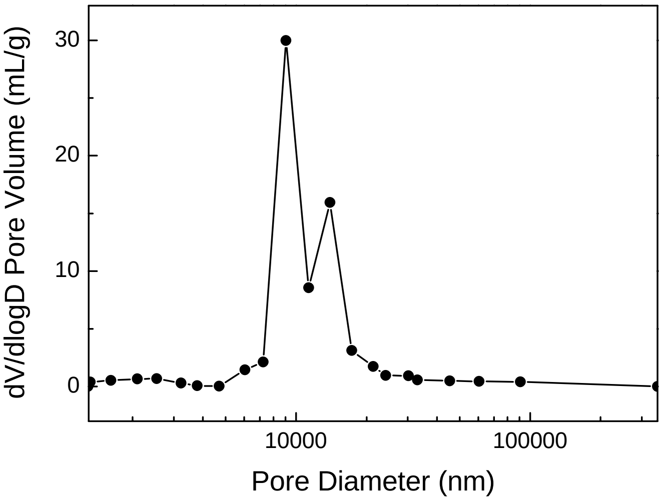


Figure S8. The pore size distribution of HIPE 6 foam. The median pore diameter is about 11.1 μm and the porousity is 91.9 %.

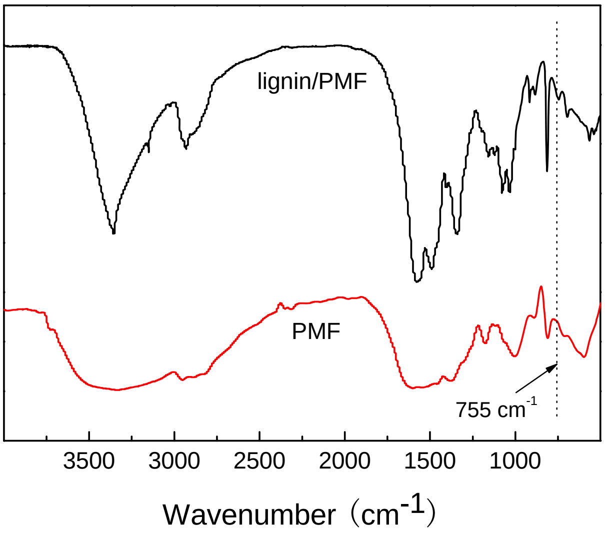


Figure S9. FTIR spectra of lignin/PMF complex and pure PMF. The lignin/PMF complex was obtained as follow: The lignin particles and pre-MF monomers were mixed under the acidic condition at 60 °C for 4h; Then the product was soaked in the ammonia solution for 2 h. From the FTIR spectra, the 1705 cm^{-1} peak of the soaked product is typical for hemicelluloses, an impurity mixed in lignin. The 755 cm^{-1} peak for C-H of the benzene ring could be observed at the lignin/PMF complex (the lignin is a heterogeneous and amorphous polymer of a phenolic nature, containing benzene ring at its chemical structure), which cannot be found for pure PMF, indicating that there is a chemical reaction between the lignin particles and PMF monomers.

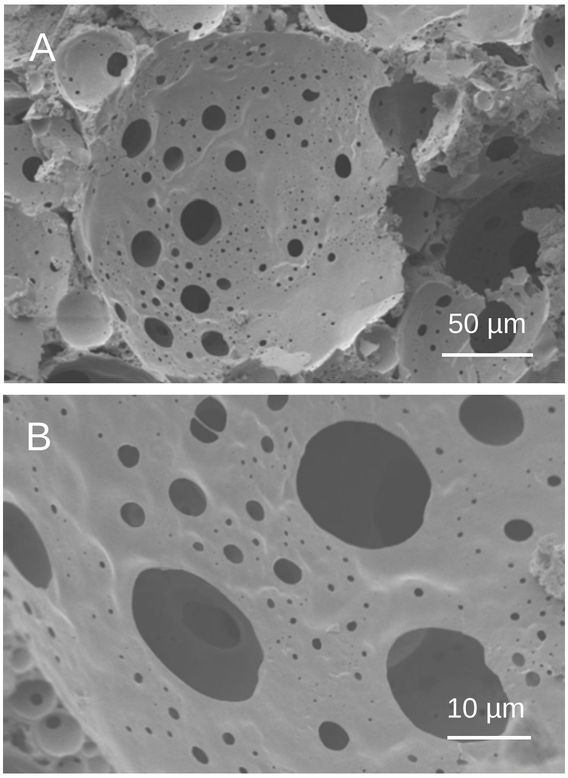


Figure S10. SEM images of HIPE 6 foam before adsorption of Cu(II) ions.

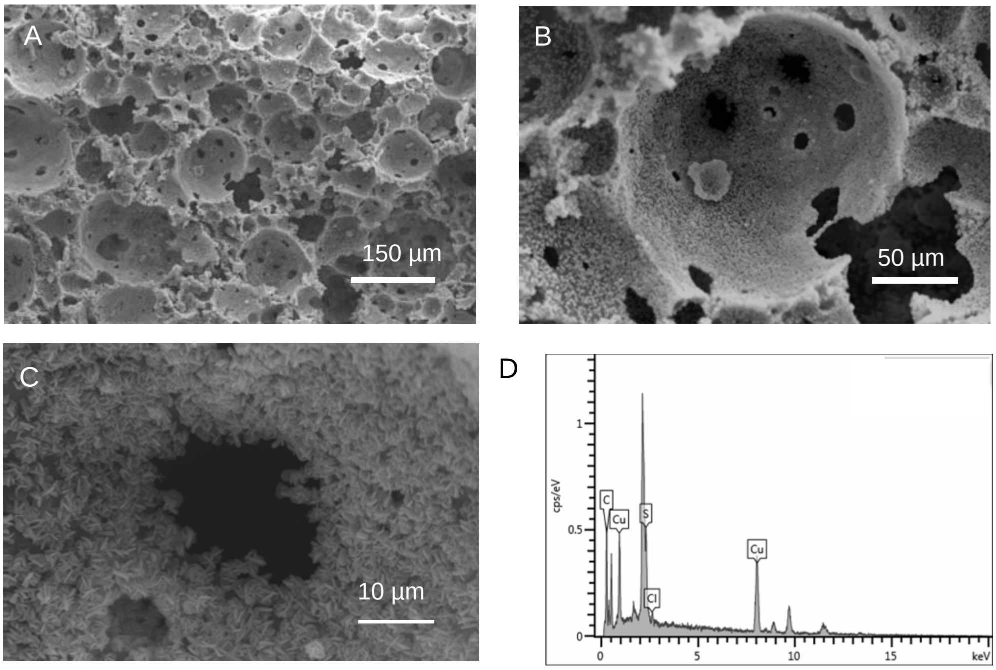


Figure S11. (A-C) SEM photographs in the different magnification and (D) EDS spectrum of HIPE 6 foam after adsorption of Cu (II) ions. The EDS spectrum of the foam indicated that there was the Cu element, which proved that Cu(II) ions were adsorbed by the interconnected porous PMF foam.

Reference

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