Supporting Information

Hypercrosslinked microporous polymer sorbents for the selective removal and regeneration of soluble acid catalyst and degradation products in the acid-catalysed hydrolysis of α-cellulose

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Experimental

Materials

Benzene, dimethoxymethane, iron(III) chloride, 1,2-dichloroethane, para-toluenesulfonic acid, glucose, xylose, 2-hydroxymethylfurfural, furfural. Methanol, ethanol and hexane were all purchased from VWR Chemicals and were used as received

Characterization

The textural properties and pore size distribution of the hypercrosslinked polymer were measured using a porosity analyser (Micromeritics 3Flex) at -196 °C. The sample (~100 mg) was degassed under vacuum (0.2 mbar) at 120 °C overnight and then further degassed for 4 h (0.003 mbar) in-situ at 120 °C prior to measurement. Surface areas were calculated using the Brunauer Emmett-Teller (BET) method.[18] The total volume of pores was calculated from the volume of N_2 adsorbed at P/P_0 0.97, while the micropore volume was determined using the t-plot method. All UV-Visible spectroscopy were measured at 25 °C using a UV-Vis spectrometer (Agilent Technologies, UV-Vis 01) over a 200-900 nm spectral range, using a cuvette with a path length of 0.1 mm. Concentrations were determined using UV by the plotting of calibration curves for each combination of material and solvent used.

CHNS/O analysis of MOPs was determined using an Elementar VarioMICRO Cube. Samples (~2 mg) was weighed and sealed in an aluminium boat prior to analysis. Each samples was measured at least three times. and the oxygen content was determined by subtraction (%O = 100 - %C - %H - %N - %S - %ash).

FTIR spectra were collected on a benchtop Cary 630 FTIR spectrometer (Agilent Technologies) using a Ge ATR crystal. The spectral range used was 650 – 4000 cm^{-1} with 128 scans taken per sample at a resolution of 4 cm^{-1}.

The continuous flow experiments were conducted using a high performance liquid chromatography (HPLC) pump (Alltech HPLC pump, Model 426) and a column (8 mm x 30 mm) filled with the hypercrosslinked benzene polymer. During the experiments, the column was stored at 30 °C in a HPLC column thermostat (Spark Holland SPH99). The sugar stream

was eluted through the column at 0.1 mL/min, before passing through the UV-Visible spectrometer, which was setup to continuously take a measurement every minute. Removal of all material during continuous flow experiments was calculated up to the beginning of the breakthrough curve.

Preparation of Organosolv lignin

Organosolv fractionation process was applied to extract lignin from poplar wood using a 10 L stainless steel batch reactor (Par Instruments & Co.; model number: 4552) following a similar procedure to that reported recently by Ferrini *et al.*[19] Specifically, poplar wood (500 g) was loaded into the reactor together with a solvent mixture of 2-propanol and water (7:3 v/v, 4140 mL total). Subsequently, the reaction mixture was stirred (100 rpm) overnight at 40 ºC. The reactor was then heated to 200 ºC (~ 3 ºC/min). Once the desired temperature was reached, it was kept constant for a further 3 h. In sequence, the mixture was left to cool down to room temperature. The pulp was then separated from the reddish-brown solution (liquor) by filtration, the solvent mixture partially evaporated at 45 °C under vacuum using a rotoevaporator, and deionised water was added to precipitate the lignin. In this way, apolar lignin was separated by precipitation from the remaining solvent mixture and the more polar carbohydrate derived products, and finally dried for 5 days at 40 ºC using a vacuum oven, yielding 87.9 g of reddish-brown solid Organosolv lignin.

Synthesis of hypercrosslinked polymers

In a typical polymerisation, the monomeric material (either benzene or organosolv lignin) (20 mmol) was added to a two-necked round bottom flask fitted with a reflux condenser. The flask was then charged with dimethoxymethane (60 mmol for benzene, 80 mmol for organosolv lignin) and anhydrous 1,2-dichloroethane (50 mL) before purging with N2 for a minimum of 30 min. Under continuous N2 flow, the iron(III) chloride catalyst (60 mmol for benzene; 80 mmol for organosolv lignin) was quickly added. The reactor was then sealed and heated under reflux at 80 °C overnight. Benzene polymers were then washed briefly with methanol in a Büchner funnel before further washing via Soxhlet extraction in methanol for 24 h. Organosolv polymers were washed with acetone and an aqueous HCl solution (1 M) before Soxhlet extraction in methanol for up to 48 h. Finally, residual solvent was removed from the polymers in a vacuum oven under reduced pressure at at least 60 °C, overnight.

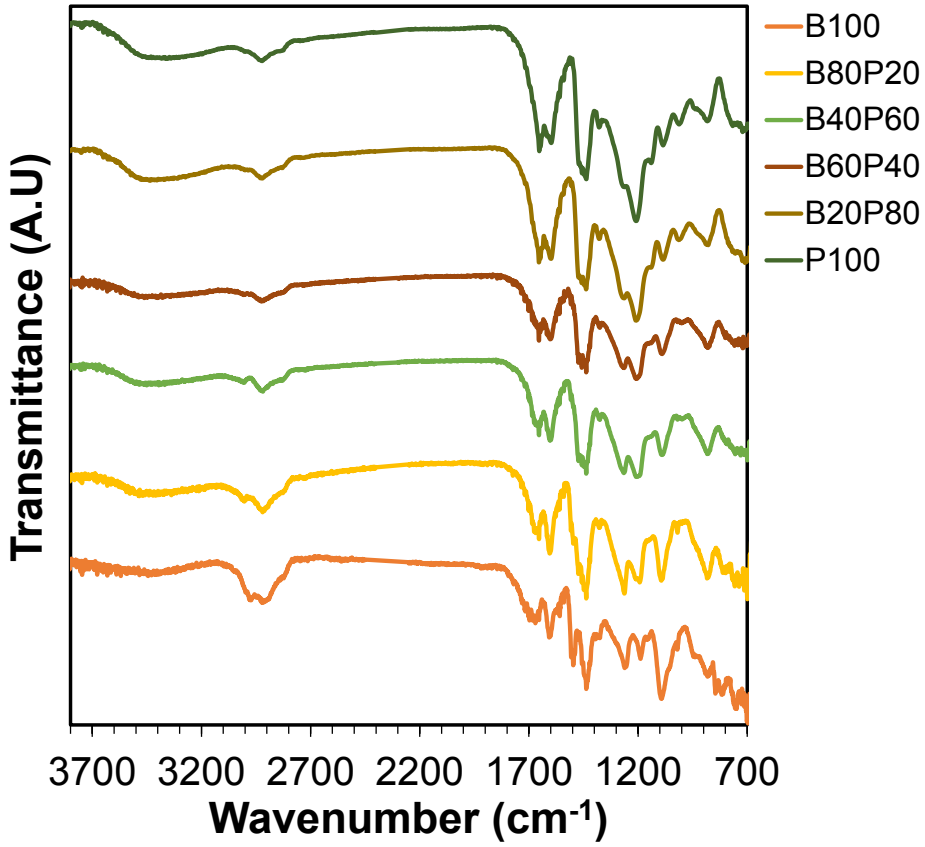

Figure S1. FTIR Spectra of all benzene and phenol MOPs. Atmospheric CO2 peaks at 2,341 were removed from all spectra for clarity.

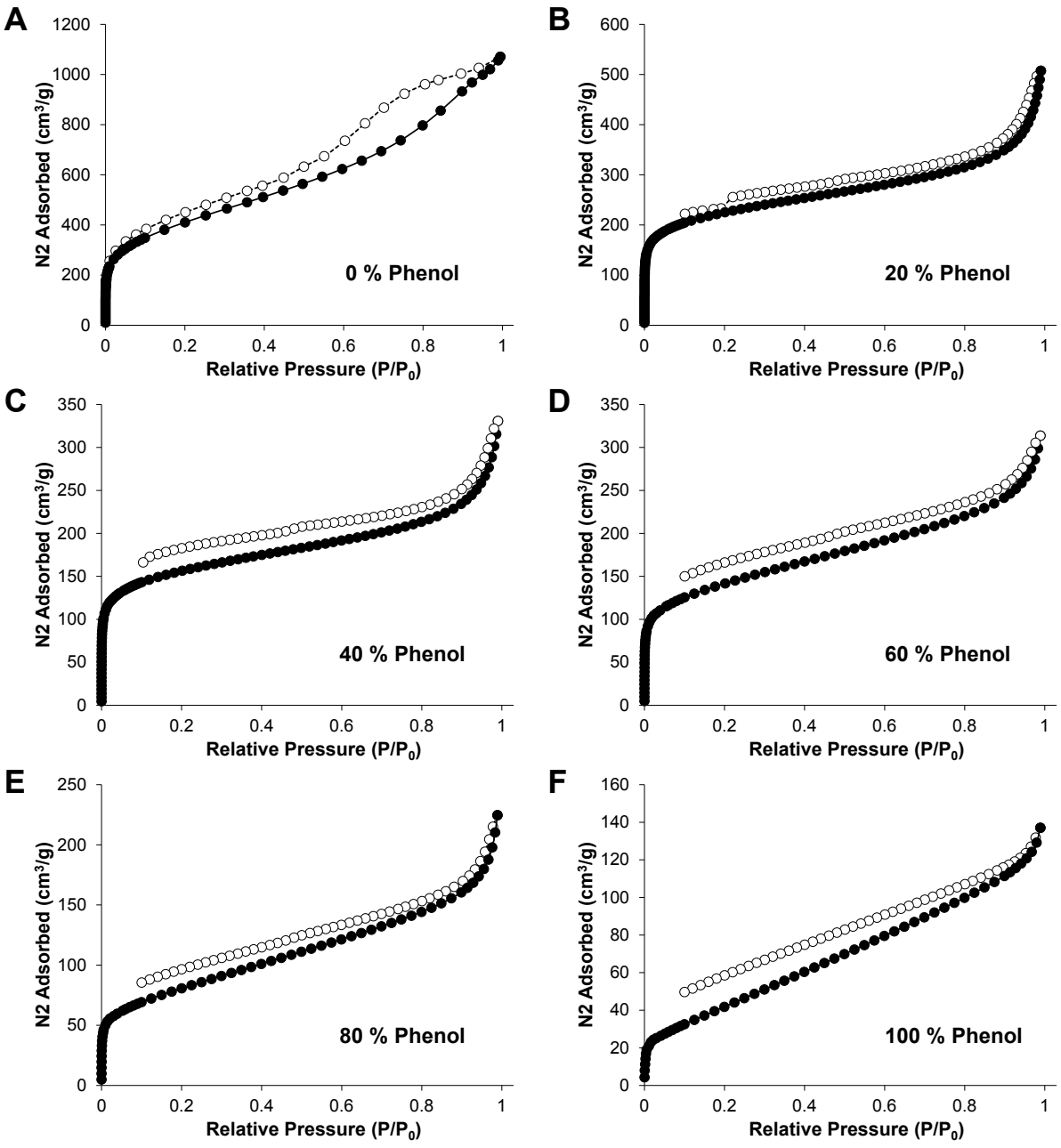

Figure S2. N_2 sorption isotherms of all benzene-phenol MOPs.

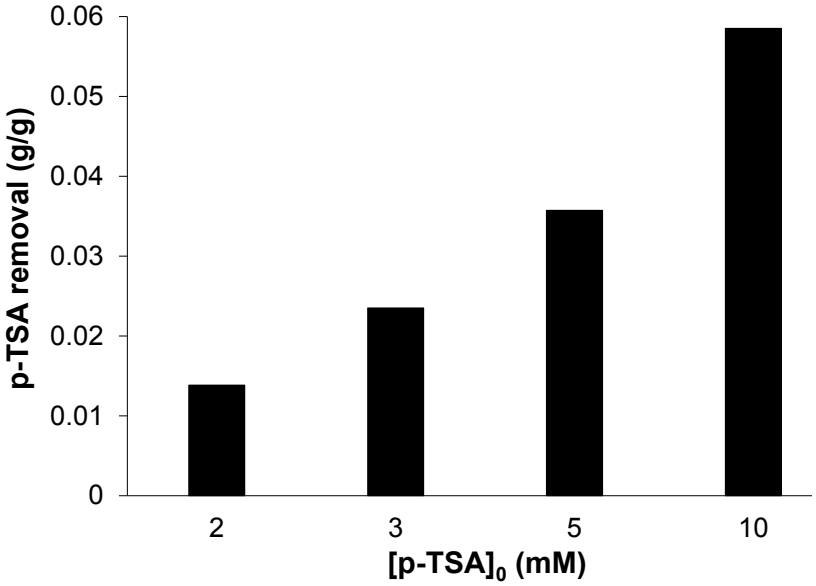

Figure S3. Adsorption of p-TSA from solutions of varying concentration; total p-TSA removed per gram of B100 MOP sorbent

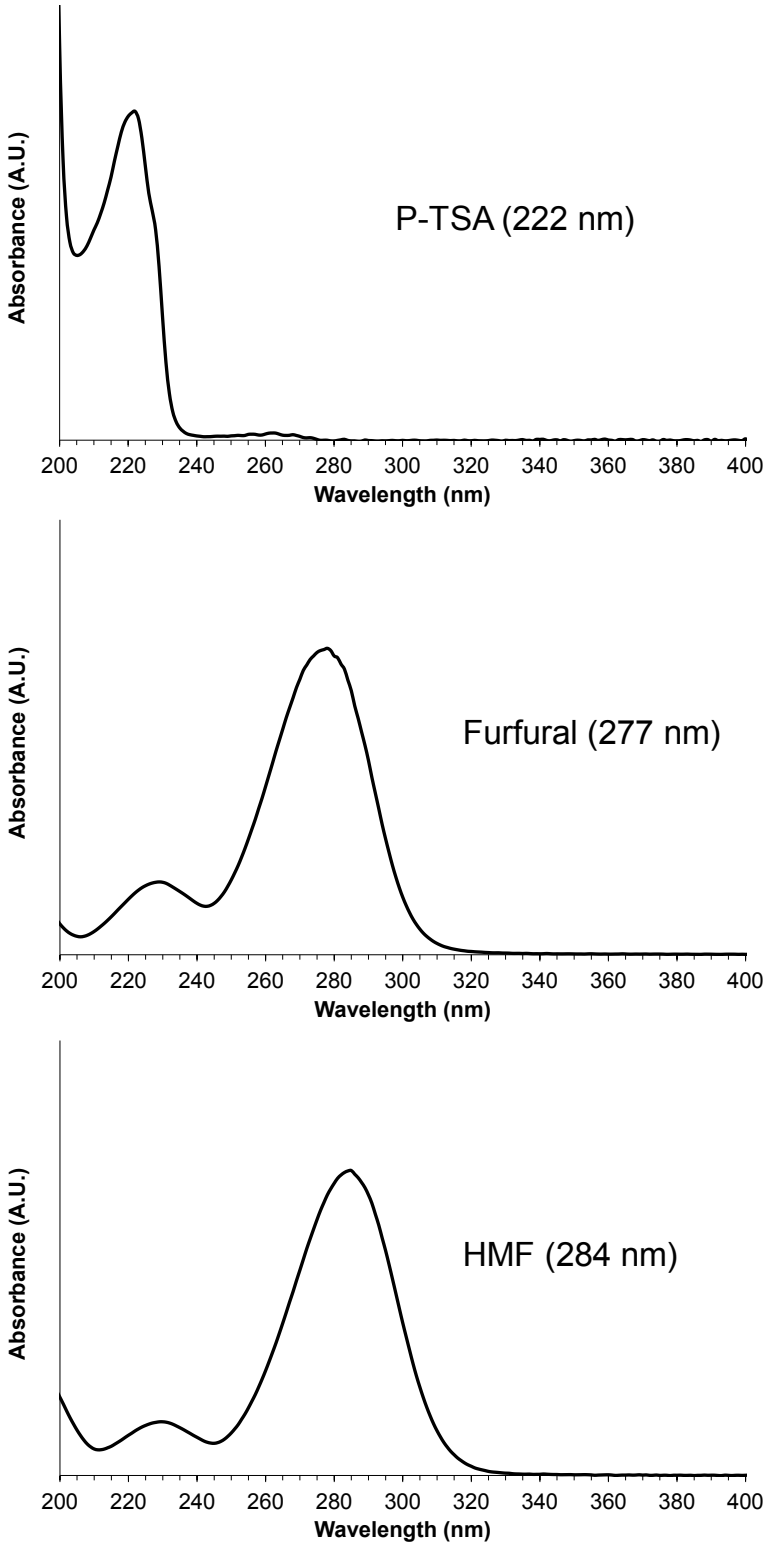

Figure S4. UV-Vis spectra of p-TSA, furfural and HMF

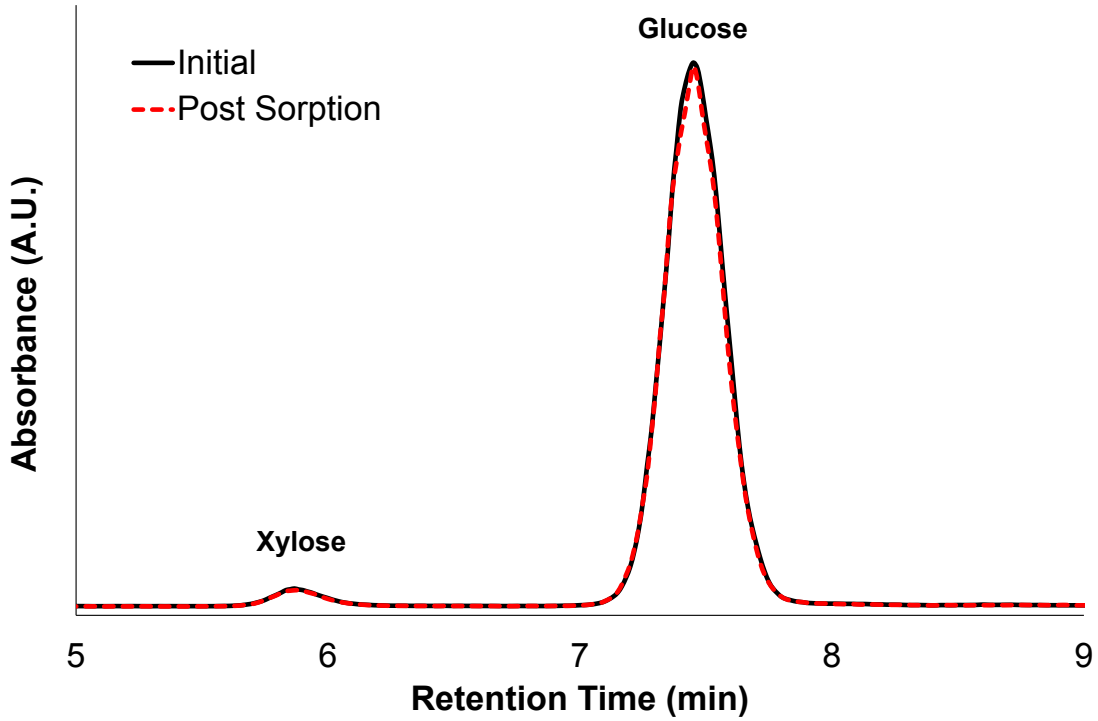

Figure S5 HPLC chromatograms of sugar solutions (4 mg/mL) both before and after exposure to the B100 MOP, showing no change in absorbance intensity.

Table S1. Concentration of glucose and xylose in solutions both prior to and after 1 h of exposure to polymer B100 (5 wt.%), measured via high performance liquid chromatography (HPLC).

Sample	Glucose conc. (mg/mL)[a]	Xylose conc. (mg/mL)[a]
Initial solution	3.23	0.57
After 1h exposure to B100 (5 wt.%)	3.16	0.49
After 1h exposure to B100 (5 wt.%) Repeat	3.28	0.59

[a]As determined via HPLC analysis using calibration curves