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The design and synthesis of efficiency adsorption materials for 1,3-propanediol: physical and chemical structure regulation

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Supplementary materials

1. The synthetic section

1.1 Preparation of physical structure regulated resins

1.1.1 Preparation of physical structure resins of temperature regulated

10 g CMPS (crosslinking degree 7 %, chlorine content 18.9 %) was added to 250 mL three-mouth flask, and then 60 mL nitrobenzene was added to dilate overnight, and 2 g $AlCl_3$ was rapidly added at room temperature, stirred for 30 minutes. Then heated to the specified temperature (40 ℃, 80 ℃, 100 ℃, 120 ℃ and 135 ℃) to start the timing. The reaction was stopped after 4 h and the crosslinked resin was filtered out. Under ultrasonic conditions, the resin was washed with ethanol and pure water for several times. The cleaned resin was moved into a blast drying oven at 70 ℃ and dried for 24 hours to obtain PS-W series (PS-W40, PS-W80, PS-W100, PS-W120 and PS-W135) resins.

1.1.2 Preparation of physical structure resins of time regulated

10 g CMPS (crosslinking degree 7 %, chlorine content 18.9 %) was added to 250 mL three-mouth flask, and then 60 mL nitrobenzene was added to dilate overnight, and 2 g $AlCl_3$ was rapidly added at room temperature, stirred for 30 minutes. Then heated to 60 ℃ to start the timing. After a period of reaction (0.5 h, 1 h, 4 h, 8 h and 12 h), the reaction was stopped and the crosslinked resin was filtered out. Under ultrasonic conditions, the resin was washed with ethanol and pure water for several times. The cleaned resin was moved into a blast drying oven at 70 ℃ and dried for 24 h to obtain PS-S series (PS-S0.5, PS-S1, PS-S4, PS-S8 and PS-S12) resins.

1.2 Preparation of chemical functional group modified resins

1.2.1 Preparation of aminated resin

Added 10 g dried CMPS into 500 mL three-mouth flask, 100 mL DMF, and swelled under mechanical stirring for 12 h. Anhydrous K_2CO_3 (10.50 g) and 2 eq of ethylenediamine were added slowly at room temperature. The reaction lasted for 24 h at 353 K, followed by cooling, filtration, anhydrous ethanol and pure water ultrasonic elution until the eluent was colorless. The resulting resin was dried overnight in a vacuum at 343 K to obtain the amine resin PS-EDA.

1.2.2 Preparation of gallic acid modified resin

5 g CMPS and 75 mL DMF were added to 250 mL three-mouth flask to swell overnight. At room temperature, 5.1 g gallic acid (30 mmol) and 2.1 g$NaHCO_3$ (25 mmol) were added, stirred for 30 min and heated to 80 ℃ for 24 h. After the reaction, the resin was filtered and cleaned repeatedly with ethanol and pure water under ultrasonic conditions. The cleaned resin was moved into a 70 ℃ air-blast drying oven to get PS-GA resin.

1.2.3 Preparation of boronic acid modified resins

Added 1 g CMPS and 15 mL DMF to 100 mL three-mouth flask and swelled overnight. At room temperature, 6 mmol phenylboronic acid or phenylboronic acid pinacol ester and 6 mmol base ($NaHCO_3$ or $CsCO_3$) were added, stirred for 30 min and heated to 80 ℃ for 24 h. After the reaction, the resin was filtered and cleaned several times with ethanol and pure water under ultrasonic conditions. The cleaned resin was moved into the air-blast drying oven at 70 ℃ to get PS-SB or PS-SBZ resins.

PS-SBZ deprotection scheme as follows: 1 mmol modified PS-SBZ resin was added to 100 mL three-mouth flask, 30 mL methanol and 0.14 g ammonium chloride (2.5 mmol) were added. A 7 mL water solution of 0.64 g sodium periodate (3 mmol) was slowly added with a constant pressure drip funnel. Stir the reaction at room temperature for 18 h, filtered the resin, washed it, put the cleaned resin into constant temperature drying, and got PS-SBT resin. Detailed synthesis conditions were shown in Table. 1.

2. Quantitative analysis of residual chlorine and boronic acid content of modified resins

2.1 Quantitative determination of residual chlorine of modified resins

The residual chlorine content of resin was determined by Volhard method.[1] The specific determination method is as follows: accurately weighed 0.2 g resin into the crucible, added 1 g NaOH and 1 g KNO_3 to stir evenly, then covered the surface with a layer of KNO_3, put the crucible in muff furnace and decomposed it under 873 K for 4 h. After the muff furnace was cooled, the sample was taken out, dissolved in pure water (can be added with an appropriate amount of concentrated nitric acid to assist dissolution) and then added phenolphthalein indicator. Added concentrated nitric acid into the system to adjust pH to acidity, and 2 mL nitrobenzene to protect chloride ion. After adding an excess of 0.1M silver nitrate standard solution and alum iron as an indicator, titrate with potassium thiocyanate standard solution and the chlorine content was calculated.

2.2 Boronic acid content of modified resins [2]

Accurately weighed 30 mg of boronic acid modified resin into a 15 mL closed tube and added 1 mL pinacol solution (dissolved in DMF in advance at a concentration of 10 g/L).The reaction system was placed in a constant temperature oscillating chamber at 30 ℃ and 180 r/min for adsorption for 18 h, and then the adsorption equilibrium solution was taken out to prepare samples for gas chromatography to be measured. Each sample was reported twice.

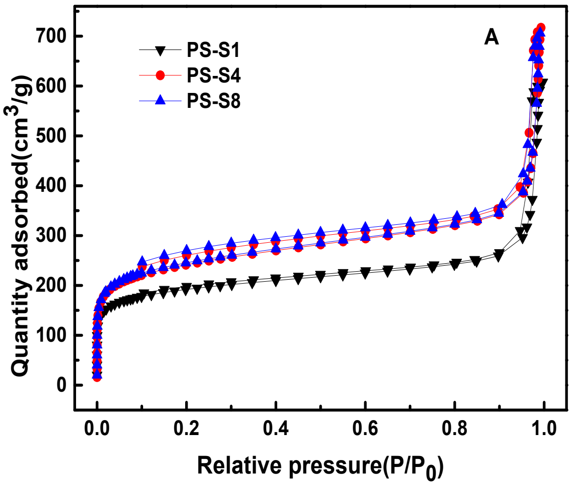
$$C_b=(C_{p0}-C_{pe})V_p/M_pW_r \qquad (1)$$

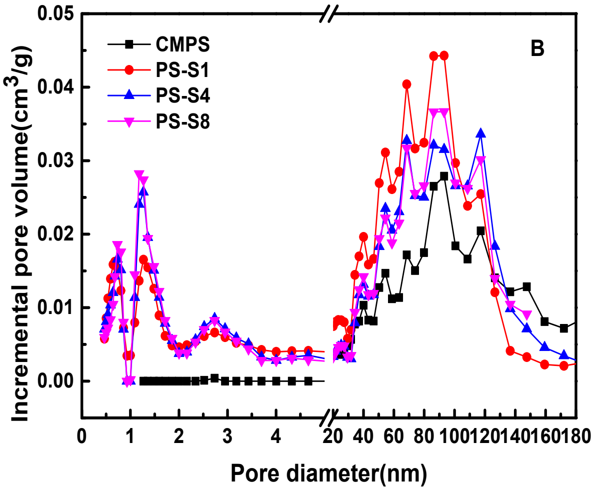
Where C_b (mmol/g) is the boronic acid payload; C_{p0} (mg/L) is the initial concentration of pinacol; C_{pe} (mg/L) is the pinacol concentration after adsorption; V_p (L) is volume of pinacol; W_r (g) is the quality of boronic acid modified resin.

References
1 Carlitz, L. Duke Math. J. 1973, 40(4), 893-901. doi:10.1215/S0012-7094-73-04083-0.
2 Y.-X. Jia, W. Sun, C. Yin, C. Xu, S. Yu and M. Xian, *Journal of Chemical Technology & Biotechnology,* 2019, 94(4), 1259-1268.

3. The characterization section

3.1 The pore structure diagram of physical structure resins





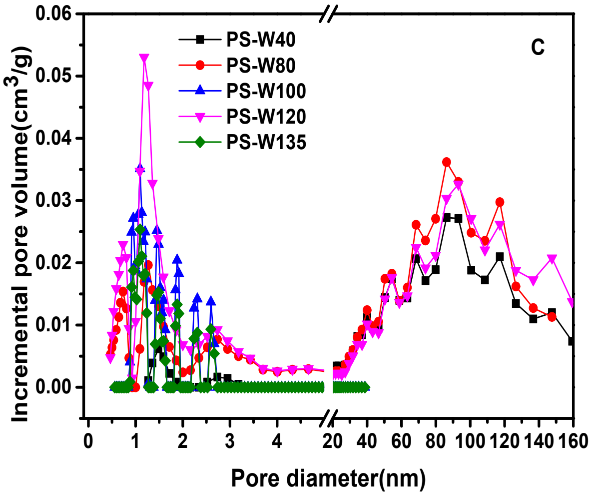


Fig. S1 Nitrogen adsorption-desorption curves of PS-S series resins(A) and the distribution of pore volume with the pore diameter of PS-S series resins(B) and PS-W series resins(C).

3.2 Thermogravimetric analysis

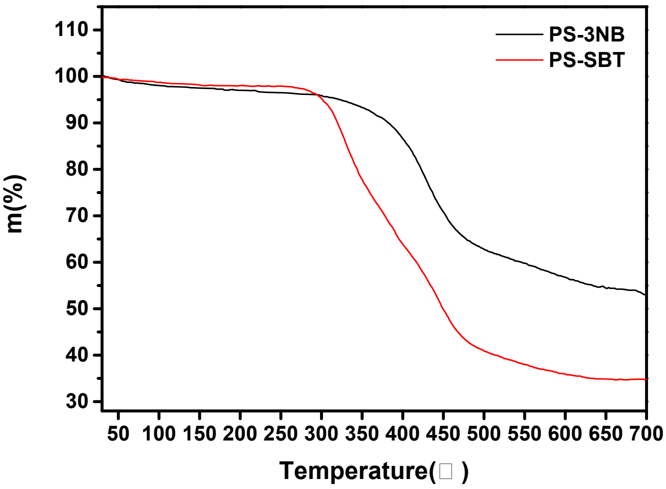


Fig. S2 Thermogravimetric analysis of PS-SBT and PS-3NB resin.

3.3 PS-SBT cyclic adsorption capacity of 1,3-propanediol

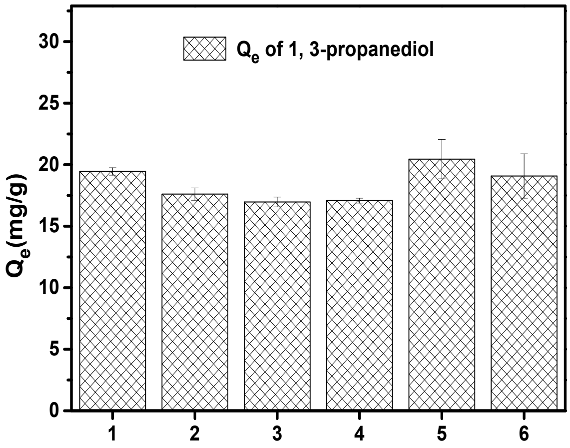
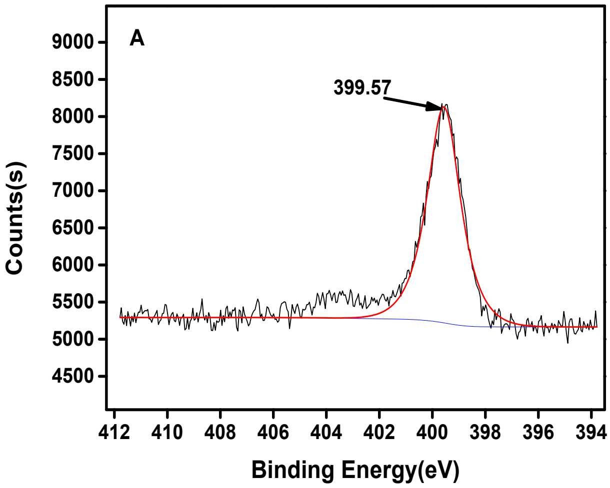


Fig. S3 Adsorption capacity of PS-SBT to 1,3-propanediol in six cycles.

3.4 Nitrogen element XPS characterization of PS-3NB



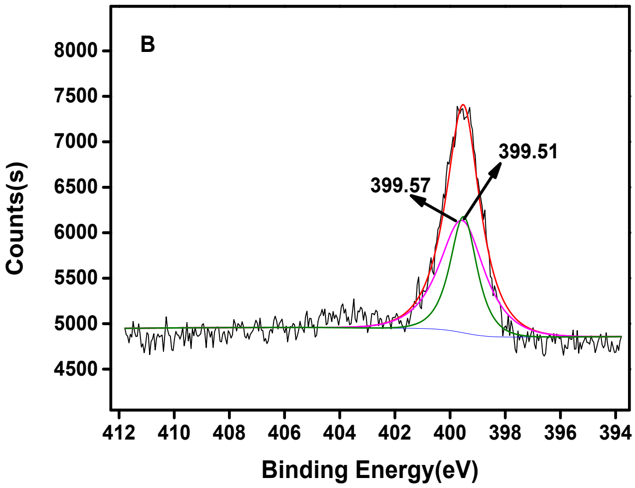


Fig. S4 XPS high resolution nitrogen (N_{1s}) spectra of: (A) N_{1s} before adsorption 1,3-propanediol in PS-3NB; (B) N_{1s} after adsorption 1,3-propanediol in PS-3NB.

3.5 IR spectra of boronic acid modified resin PS-SBT before and after adsorption

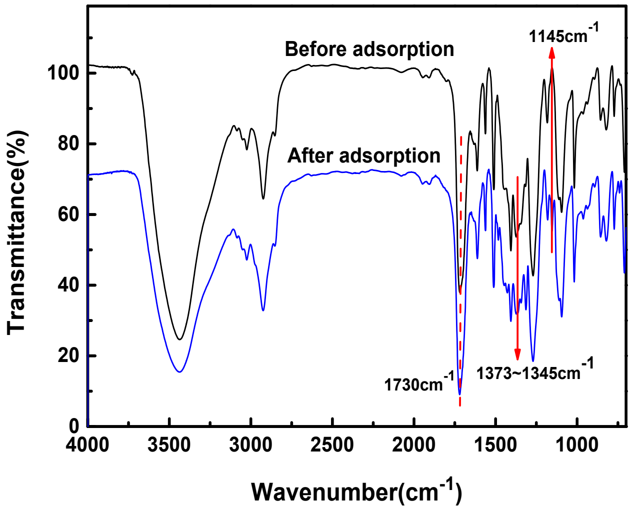


Fig. S5 IR spectra (wavenumbers from 700~4000 cm^{-1}) of boronic acid modified resin PS-SBT before and after adsorption.

3.6 Thermodynamic enthalpy, entropy and Gibbs free energy parameters

Table. S1 Energy change during thermodynamic adsorption

Resin	Temperature (K)	*ΔH* (kJ/mol)	*ΔG* (kJ/mol)	*ΔS* (J/mol K)
PS-SBT	293	0.5065	-3.7125	-10.942
	303		-3.6880	-10.500
	313		-3.7785	-10.454
CHA-111	293	-0.8121	-2.7624	-12.200
	303		-2.8718	-12.158
	313		-2.9458	-12.006