Supporting information
Hydroxyl modified hypercrosslinked polymers: targeting highly efficient adsorption separation towards aniline

Zishuai Wei, Qibin Chen, Honglai Liu*

State Key Laboratory of Chemical Engineering and School of Chemistry & Molecular Engineering, East China University of Science and Technology, Shanghai, 200237, P.R. China

Derivation for K_C

The derivation for K_C from K_L and K_F were calculated according to equations (1) and (2) separately:[1]

$$K_C = M_w \times 55.5 \times 1000 \times K_L \quad (1)$$

$$K_c = K_F \times \rho \times \left(\frac{10^6}{\rho}\right)^{\left(1-\frac{1}{n}\right)} \quad (2)$$

the factor 55.5 and M_w are the number of moles of pure water per liter (dividing 1000 $g \cdot L^{-1}$ by 18 $g \cdot mol^{-1}$) and the relative molecular mass of aniline (93.13 $g \cdot mol^{-1}$), respectively. Where ρ is the density of pure water (assumption on 1.0 $g \cdot mL^{-1}$).

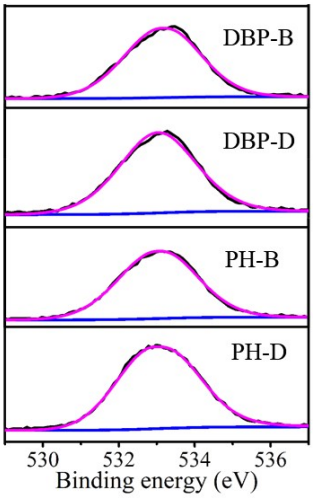

Figure S1. XPS O1s scan spectra of DBP-B, DBP-D, PH-B and PH-D.

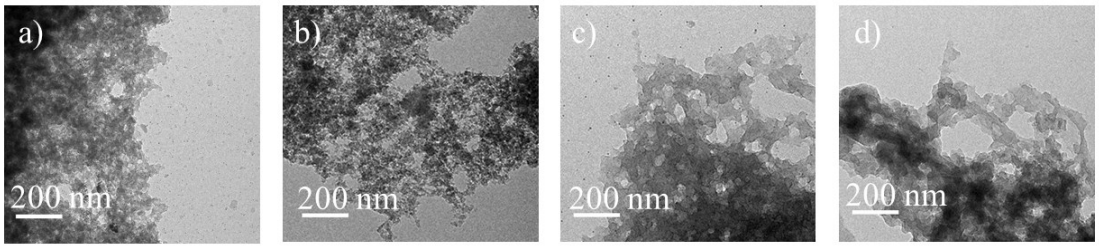

Figure S2. TEM images of DBP-B (a), DBP-D (b), PH-B (c) and PH-D (d).

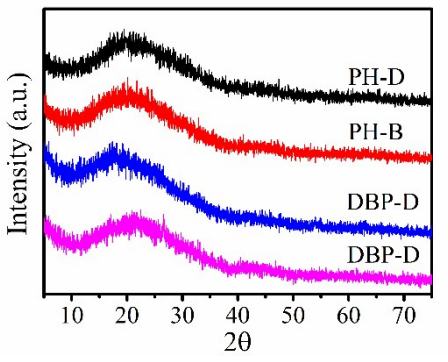

Figure S3. The XRD patterns of PH-D, PH-B, DBP-D and DBP-B.

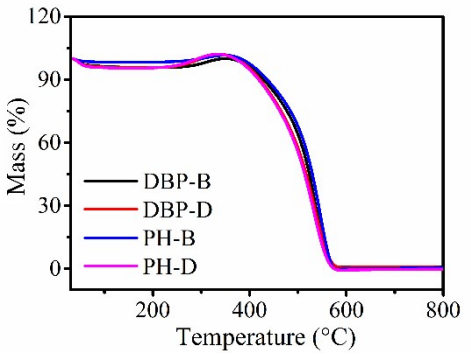

Figure S4. TGA curves of PH-D, PH-B, DBP-D and DBP-B.

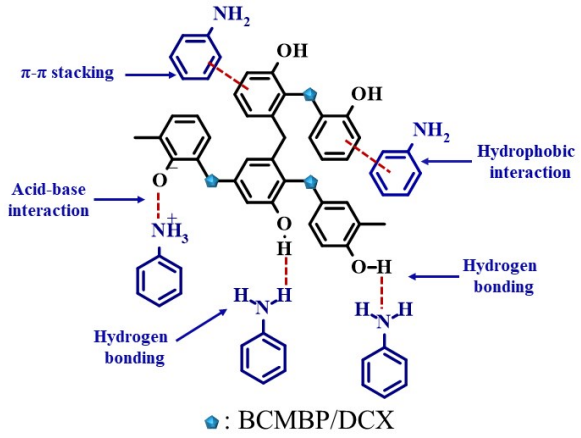

Figure S5. Possible interaction of the polymers with aniline.

Table S1. Correlated parameters of the equilibrium data for the adsorption of aniline on PH-D, PH-B, DBP-D and DBP-B at 303 K according to the Langmuir, Freundlich, R-P and Temkin model.

HCPs	PH-D	PH-B	DBP-D	DBP-B
Langmuir model				
K_L ($L \cdot mg^{-1}$)	0.01319	0.01135	0.00987	0.00799
q_{max} ($mg \cdot g^{-1}$)	158.202	171.193	205.009	227.690
R^2	0.9917	0.9919	0.9949	0.9926
Freundlich model				
K_F/ ($mg \cdot g^{-1} \cdot L^{1/n} \cdot mg^{-1/n}$)	16.6819	14.8156	14.0962	11.5051
n^{-1}	0.3560	0.3851	0.4207	0.4649
R^2	0.9972	0.9985	0.9957	0.9995
R-P model				
a	5.7670	6.4060	3.5014	7.6542
b	0.1880	0.2544	0.0736	0.4223
n	0.7376	0.6954	0.7656	0.6023
R^2	0.9976	0.9987	0.9974	0.9997
Temkin model				
K_t ($L \cdot mg^{-1}$)	0.1351	0.1114	0.0918	0.0776
b ($J \cdot mol^{-1}$)	73.7658	66.8695	54.5575	49.7323
B	34.1674	37.6911	46.2139	50.6791
R^2	0.9888	0.9885	0.9904	0.9809

Table S2. Comparison of the q_{max} of aniline on four HCPs with some other adsorbents in the literature.

Adsorbents	q_{max}/(mg·g^{-1})	Reference
EFAC	27.10 (298K)	2
SD-β-CD	84.03 (288K)	3
PMAA/SiO_2	132.7 (293K)	4
g-C_3N_4	71.9(298K)	5
HCP-P-5%	169.2 (303K)	6
Modified jute fiber	125 (298K)	7
SA-HCLP	171.2 (303K)	8
PHBA-HCLP	184.8 (303K)	8
NAC3	125.3 (298K)	9
EC	114.1 (303K)	10
PS-DBP-HCP	198.8 (298K)	11
PS-AI-HCLR	200.6 (308K)	12
PS-PH-HCP	178.4 (303K)	13
coconut shell-AC	133.6 (298K)	14
AZO-POP-1	1059.68 (293K)	15
HCPs	769.23 (298K)	16
DBP-B	227.7 (303K)	This work

Table S3. Correlated parameters of the equilibrium data for the adsorption of aniline on DBP-B at three different temperatures (303, 313 and 323 K) according to the Langmuir and Freundlich model.

	Langmuir			Freundlich		
	K_L/ ($L \cdot mg^{-1}$)	q_{max} / ($mg \cdot g^{-1}$)	R^2	K_F/ ($mg \cdot g^{-1} \cdot L^{1/n} \cdot mg^{-1/n}$)	n^{-1}	R^2
303K	0.00799	227.690	0.9926	11.505	0.4649	0.9995
313K	0.00652	222.320	0.9941	8.8540	0.4942	0.9983
323K	0.00539	218.843	0.9933	6.7868	0.5246	0.9982

Table S4. Thermodynamic parameters for the adsorption of aniline on DBP-B.

	Langmuir			Freundlich		
	ΔG ($KJ \cdot mol^{-1}$)	ΔH ($KJ \cdot mol^{-1}$)	ΔS ($J \cdot mol^{-1} \cdot K^{-1}$)	ΔG ($KJ \cdot mol^{-1}$)	ΔH ($KJ \cdot mol^{-1}$)	ΔS ($J \cdot mol^{-1} \cdot K^{-1}$)
303 K	-26.775	-16.044	35.421	-23.555	-21.465	6.928
313 K	-27.130	-16.044	35.421	-23.651	-21.465	6.928
323 K	-27.485	-16.044	35.421	-23.692	-21.465	6.928
R^2		0.99999			0.99896	

Table S5. Correlated parameters of the kinetic data for the adsorption of aniline on DBP-B at three different temperatures (303, 313 and 323 K) according to the pseudo-first-order kinetic model and the pseudo-second-order kinetic model.

	pseudo-first-order			pseudo-second-order		
	K_1/	q_e/ (mg·g^{-1})	R^2	K_2/ (g· mg^{-1}·min^{-1})	q_e/ (mg·g^{-1})	R^2
303K	0.1475	177.67	0.9961	9.96×10^{-4}	198.56	0.9856
313K	0.4419	162.53	0.9963	4.29×10^{-3}	176.68	0.9783
323K	2.1876	142.22	0.9938	2.34×10^{-2}	153.85	0.9980

Table S6. Intra-particle diffusion parameters for the adsorption of aniline from aqueous solution by DBP-B at 303 K.

	K_d (mg/(g·min$^{1/2}$))	I (mg·g^{-1})	R^2
the first linear portion	45.82	-13.229	0.9761
the second linear portion	3.19	152.611	0.9781

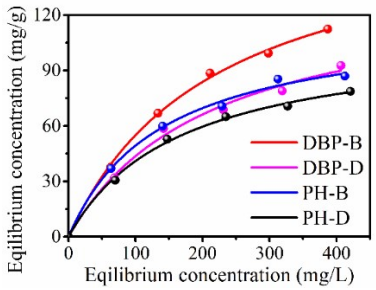

Figure S6. Equilibrium adsorption data of DBP-B, DBP-D, PH-B and PH-D for phenol at 303 K, fitted with Langmuir model.

Reference

1. Tran, H. N.; You, S. J.; Chao, H. P. Thermodynamic parameters of cadmium adsorption onto orange peel calculated from various methods: A comparison study. J. Environ. Chem. Eng., 2016, 4, 2671-2682.

2. H. Y. Li, L. X. Liu, J. G. Cui, J. L. Cui, F. Wang, F. Zhang, High-efficiency adsorption and regeneration of methylene blue and aniline onto activated carbon from waste edible fungus residue and its possible mechanism, RSC Advances, 2020, 10, 14262.

3. Q. Hu, D. W. Gao, H. Y. Pan, L. L. Hao, P. Wang, Equilibrium and kinetics of aniline adsorption onto crosslinked sawdust-cyclodextrin polymers, RSC Advances, 2014, 4, 40071.

4. F. Q. An, X. Q. Feng, B. J. Gao, Adsorption property and mechanism of composite adsorbent PMAA/SiO_2 for aniline, Journal of Hazardous Materials, 2010, 178, 499-504.

5. R. Hu, X. K. Wang, S. Y. Dai, D. D. Shao, T. Hayat, A. Alsaedi, Application of graphitic carbon nitride for the removal of Pb(II) and aniline from aqueous solutions, Chem. Eng. J., 2015, 260, 469-477.

6. W. Kuang, Y. N. Liu, J. H. Huang, Phenol-modified hyper-cross-linked resins with almost all micro/mesopores and their adsorption to aniline, J. Colloids Interfaces Sci., 2017, 487, 31-37.

7. D. W. Gao, Q. Hu, H. Y. Pan, J. P. Jiang, P. Wang, High-capacity adsorption of aniline using surface modification of lignocellulose-biomass jute fibers, Bioresour. Technol., 2015, 193, 507-512.

8. X. M. Wang, X. Mao, J. H. Huang, Hierarchical porous hyper-cross-linked polymers modified with phenolic hydroxyl groups and their efficient adsorption of aniline from aqueous solution, Colloids and Surfaces A, 2018, 558, 80-87.

9. C.Y. Chen, X.H. Geng, W.L. Huang, Adsorption of 4-chlorophenol and aniline by nanosized activated carbons, Chem. Eng. J., 2017, 327, 941-952.

10. D. Jiang, J. A. Yang, D. H. Wang, Green Carbon Material for Organic Contaminants

Adsorption, Langmuir, 2020, 36, 3141-3148.

11. Y. Wang, Y. Q. Gan, J. H. Huang, Hyper-Cross-Linked Phenolic Hydroxyl Polymers with Hierarchical Porosity and Their Efficient Adsorption Performance, Ind. Eng. Chem. Res., 2020, 59, 11275-11283.

12. X. Zeng, J. H. Huang., Anisole-modified hyper-cross-linked resins for efficient adsorption of aniline from aqueous solution, J. Colloids Interfaces Sci., 2020, 569, 177-183.

13. Y. Q. Gan, G. Chen, Y. F. Sang, F. Zhou, R. L. Man, J. H. Huang. Oxygen-rich hyper-cross-linked polymers with hierarchical porosity for aniline adsorption, Chem. Eng. J., 2019, 368, 29-36.

14. C. Chen, X. Geng, W. Huang, Adsorption of 4-chlorophenol and aniline by nanosized activated carbons, Chem. Eng. J., 2017, 327, 941-952.

15. J. X. Zhou, X. S. Luo, X. X. Liu, Y. Qiao, P. F. Wang, D. Mecerreyes, N. Bogliotti, S. L. Chen, M. H. Huang. Azo-linked porous organic polymers: robust and time-efficient synthesis via $NaBH_4$-mediated reductive homocoupling on polynitro monomers and adsorption capacity towards aniline in water, J. Mater. Chem. A, 2018, 6, 5608-5612.

16. Y. Liu, X. L. Fan, X. K. Jia, B. L. Zhang, H. P. Zhang, A. B. Zhang, Q. Y. Zhang. Hypercrosslinked polymers: controlled preparation and effective adsorption of aniline, J. Mater. Sci., 2016, 51, 8579-8592.