Supporting Information

Removal of Various Pollutants from Wastewaters Using an Efficient and Degradable Hypercrosslinked Polymer

Zujin Yang [1,3], Yuxin Chai[1], Qiuru Li[2], Hongbing Ji[2,3,4]*

[1] School of Chemical Engineering and Technology, Sun Yat-sen University, Zhuhai 519082, China; yangzj3@mail.sysu.edu.cn; yuxin_1230@qq.com
[2] Fine Chemical Industry Research Institute, The Key Laboratory of Low-carbon Chemistry & Energy Conservation of Guangdong Province, School of Chemistry, Sun Yat-sen University, Guangzhou 510275, China; jihb@mail.sysu.edu.cn; 1045757624@qq.com
[3] Huizhou Research Institute of Sun Yat-sen University, Huizhou 516216, China; yangzj3@mail.sysu.edu.cn; jihb@mail.sysu.edu.cn
[4] School of Chemical Engineering, Guangdong University of Petrochemical Technology, Maomen 525000, China; jihb@mail.sysu.edu.cn

Adsorption Model Fitting

After adsorption, the concentration of aniline in the solution at a regular time interval was determined and the amount of the compound adsorbed by mass unit of adsorbent at t (q_t, mg/g) was calculated by *Eq* (1) described in Section 2.3. The experimental data of the kinetic study are fitted by the following models:

(1) The pseudo-first order kinetic model was widely used for adsorption process, and its equation is expressed as [1]:

$$q_t = q_e(1 - e^{-k_1 t}) \quad (1)$$

where q_t and q_e are adsorbed amount of aniline adsorbed at time t and at equilibrium (mg/g), respectively, and k_1 is the rate constant of pseudo-first-order adsorption process (L/min). The slope and intercept of plots of ln (q_e - q_t) versus t can be used to determine the first-order rate constant k_1 and equilibrium adsorption amount q_e.

The pseudo-second order kinetic equation based on equilibrium capacity is represented as [1]:

$$q_t = q_e^2 k_2 t / (1 + q_e k_2 t) \quad (2)$$

where k_2 is the equilibrium rate constant of pseudo-second-order adsorption(g/mg/min). If the plot of t/q_t versus t gives a linear relationship, and then k_2 and q_e can be calculated from the slope and intercept of the line.

Fittings of experimental results to the Freundlich [1] and Langmuir [1] isotherms were determined in order to describe the equilibrium data of aniline adsorption on the HTC-HCP.

The Langmuir equation is given as

$$q_e = q_m K_L C_e / (1 + K_L C_e) \quad (3)$$

where c_e (mg/L) and q_e (mg/g) are the concentration of adsorbate and adsorbed amount of the compound adsorbed at time t, respectively. K_L is Langmuir adsorption constant and q_m (mg/g) is the theoretical maximum adsorption amount to form monolayer on the polymer, respectively.

The Freundlich isotherm is used to describe multilayer adsorption with interaction between the adsorbed molecules, and is determined as:

$$q_e = K_f C_e^{1/n} \quad (4)$$

where K_f is Freundlich constant that is an indicator of adsorption concentration and $1/n$ is the Freundlich coefficient related to the magnitude of the adsorption driving force.

The values of q_m and K_L increases with the increase of temperatures in the range of 25 to 35 °C, which reveals the endothermic nature of the adsorption process. The values of K_L at the different temperatures are fitted according to the isothermal equation (*Eq*. (5)) and the van't Hoff equation (Eq. (6)) [1]:

$$\Delta G^o = -RT \ln K \quad (5)$$

$$\ln K_L = -\Delta H^o / RT + \Delta S^o / R \quad (6)$$

where R (8.314 J mol^{-1} K^{-1}) is the gas constant, T (K) is the absolute temperature, and K_L (L mol^{-1}) is the Langmuir constant. $\Delta G°$, $\Delta H°$, and $\Delta S°$ are the changes in Gibbs free energy, enthalpy and entropy, respectively. $\Delta H°$ and $\Delta S°$ were calculated from the slope and the intercept of plotting ln K_L against $1/T$.

Figures and Tables

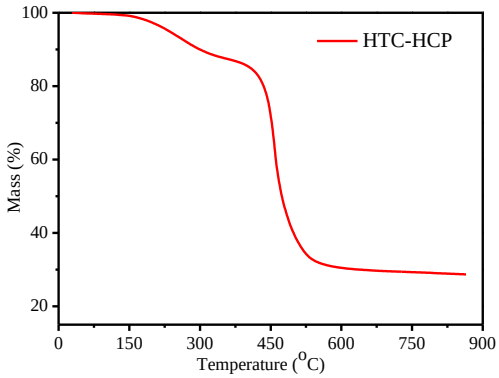


Figure S1. TGA of HTC-HCP

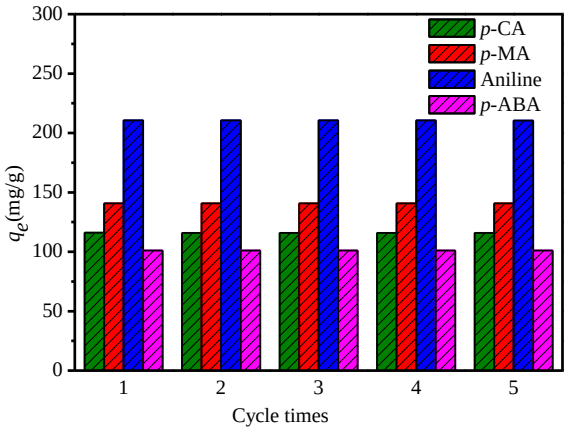
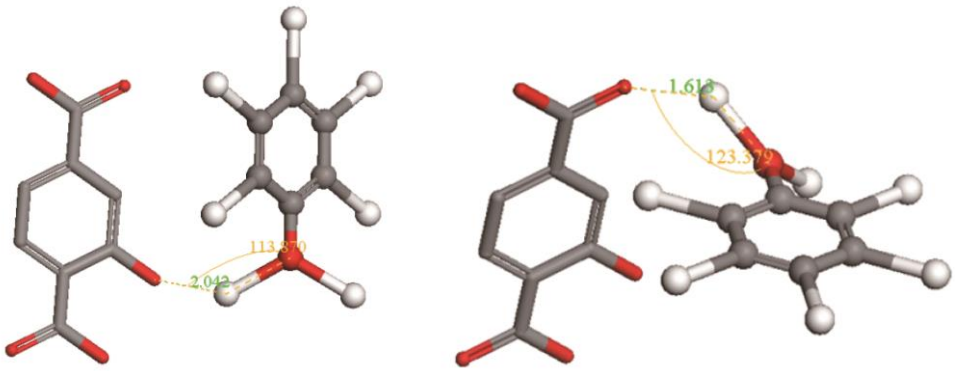


Figure S2. Effect of regeneration cycles on the adsorption capacity of aniline, *p*-MA, *p*-CA, and *p*-ABA via HTC-HCP. Adsorption conditions: HTC-HCP (0.1 g), initial concentration (100 mg/L), V_0 (100 mL), 25 °C, 200 r/min, pH = 7, 720 min.



(a) HPC/aniline BE_2 = -24.57 kJ/mol (b) HPC/aniline BE_2 = -27.24 kJ/mol

Figure S3. Optimized structure of HTC/aniline by the DMol3.

Table S1. Comparison of the maximum uptake of Ni^{2+}, Cu^{2+}, Cd^{2+}, and Pb^{2+} on various adsorbents.

Adsorbent	Solution conditions	q_{max} (mg/g) Ni^{2+}	Cu^{2+}	Cd^{2+}	Pb^{2+}	Refs.
Carbon nanotube/diatomite	pH = 6, T = 30 °C	-	-	-	60	[2]
Cellulose/chitosan composite	pH = 5, T = 25 °C	-	33.03	31.47	33.16	[3]
MNPs-COOH	pH = 5, T = 25 °C	25.89	41.91	58.22	177.16	[4]
P(AAm/CA)no imprinting hydrogel	pH = 6, T = 25 °C	12.20	10.92			[5]
P(AMPSG/AAc/NVP/HEMA) hydrogel	pH = 5, T = 25 °C			27.76	22.79	[6]
Chemical treated cherry kernels	pH = 6, T = 25 °C	12.33		19.67	17.86	[7]

Table S2. Thermodynamic parameters for the adsorption of aniline via HTC-HCP

Adsorbate	Temperature (°C)	$\triangle G$ (kJ/mol)	$\triangle H$ (kJ/mol)	$\triangle S$ (J/mol·K)
aniline	25	-5.57	-94.91	342.77
	30	-5.70		337.48
	35	-5.54		331.37

Adsorption conditions: HTC-HCP (0.1 g), initial concentration (100 mg/L), V_0 (100 mL), pH = 7, 25 °C, 200 r/min, 720 min.

Table S3. Number, type, bond length (r), bond angle (A) and BE_2 of intermolecular hydrogen

bond between HTC and aniline calculated by DMol3

Inclusion complexes	Number	Type	r (Å)	A (°)	BE_2(kJ/mol)
HTC/aniline	1	N-H…O	2.042	113.330	-24.57
HTC/aniline	1	N-H…O	1.613	123.379	-27.24

References

1. Chingombe, P.; Saha, B.; Wakeman, R. J. Sorption of atrazine on conventional and surface modified activated carbons. *J Colloid Interf Sci* **2006**, *302*, 408-416.
2. Alijani, H.; Beyki, M. H.; Shariatinia, Z.; Bayat, M.; Shemirani, F. A new approach for one step synthesis of magnetic carbon nanotubes/diatomite earth composite by chemical vapor deposition method: Application for removal of lead ions. *Chem Eng J* **2014**, 253, 456-463.
3. Xiao, M.; Hu, J. Cellulose/chitosan composites prepared in ethylene diamine/potassium thiocyanate for adsorption of heavy metal ions. *Cellulose* **2017**, 24, 2545-2557.
4. Xu, H.; Yuan, H.; Yu, J, Lin S. Study on the competitive adsorption and correlational mechanism for heavy metal ions using the carboxylated magnetic iron oxide nanoparticles (MNPs-COOH) as efficient adsorbents. *Appl Surf Sci* 2019; 473: 960-966.
5]. Mahmoud, G. A.; Hegazy, E. A.; Badway, N. A.; Salam, K. M. M.; Elbakery, S. M. Radiation synthesis of imprinted hydrogels for selective metal ions adsorption. *Desalin Water Treat* **2016,** 57, 16540-16551.
6. Yetimoğlu, E. K.; Fırlak, M.; Kahraman, M. V.; Deniz, S. Removal of Pb^{2+} and Cd^{2+} ions from aqueous solutions using guanidine modified hydrogels. *Polym Advan Technol* **2011**,*22*, 612-619.
7. Pap, S.; Radonić, J.; Trifunović, S.; Adamović, D.; Mihajlović, I.; Vojinović Miloradov, M.; Turk Sekulić, M. Evaluation of the adsorption potential of eco-friendly activated carbon prepared from cherry kernels for the removal of Pb^{2+}, Cd^{2+} and Ni^{2+} from aqueous wastes. *J Environ Manage* **2016**, 184, 297-306.