Front. Chem. Sci. Eng.

DOI 10.1007/s11705-017-1646-y

RESEARCH ARTICLE

The preparation and performance of lignin-based activated carbon fiber adsorbents for treating gaseous streams

Min Song(✉)[1], Wei Zhang[2], Yongsheng Chen[3], Jinming Luo[3], John Crittenden[3]

1 Key Laboratory of Energy Thermal Conversion and Control, Ministry of Education, School of Energy and Environment, Southeast University, Nanjing 210096, China

2 State Environmental Protection Key Laboratory of Environmental Risk Assessment and Control on Chemical Process, School of Resources and Environmental Engineering, East China University of Science and Technology, Shanghai 200237, China

3 Brook Byers Institute for Sustainable System, School of Civil and Environmental Engineering, Georgia Institute of Technology, Atlanta, GA 30332-0595, USA

© Higher Education Press and Springer-Verlag Berlin Heidelberg 2017

Received September 8, 2016; accepted March 21, 2017

E-mail: minsong@seu.edu.cn

Electronic Supplementary Materials

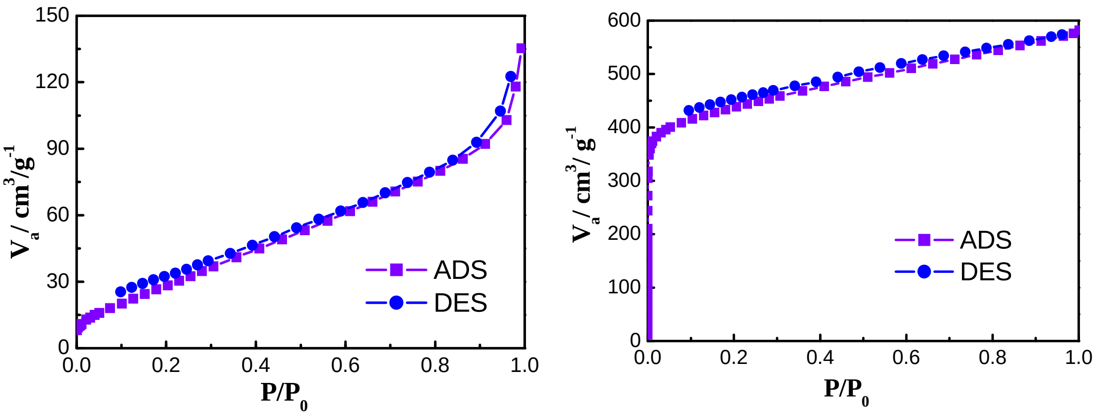

Figure S1. The nitrogen adsorption and desorption isotherms of LCF (left) and LCF-Fe (right).

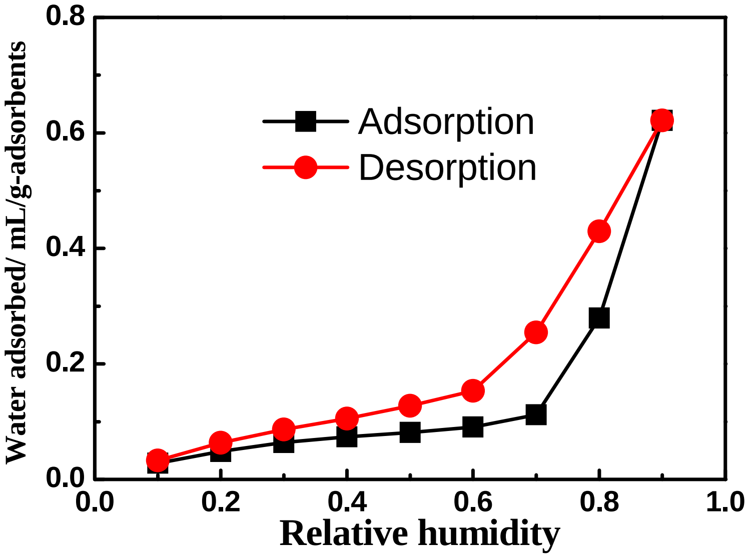

Figure S2. Adsorption and desorption isotherms of water vapor on LCF-Fe.

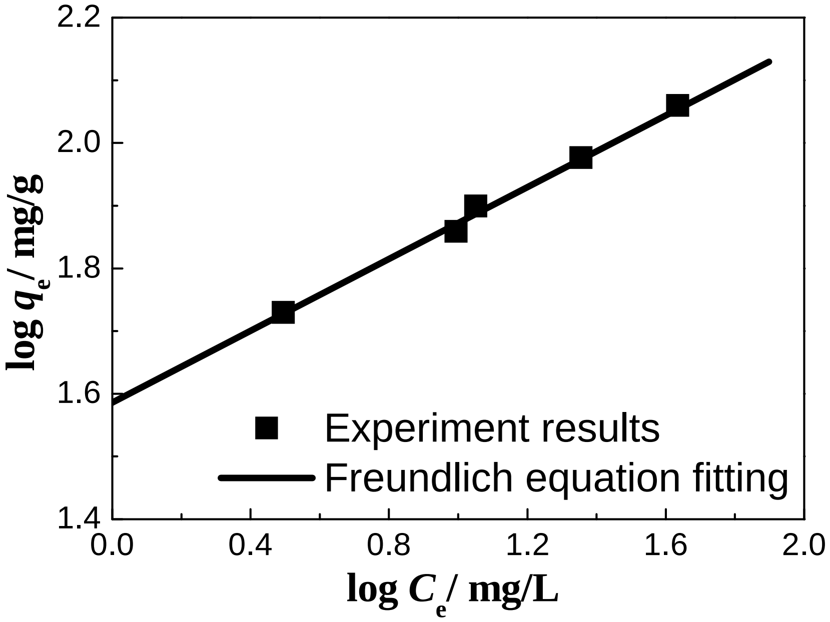

Figure S3. The aqueous phase isotherm for toluene on LCF-Fe at 20°C

Table S1. FTIR peaks assignments for LF, LF-Fe, LCF and LCF-Fe

Wavenumber/ cm^{-1}	Assignments
876	γ (C-H); the guaiacyl groups of lignin
1060	S (C-O); aliphatic -OH and -O-
1100	S (C-H); syringyl group
1210	S (C-O); phenolic hydroxyl and ether group
1260	S (C-O); guaiacyl group
1430	S (C-C); aromatic ring skeleton
1480	δa (CH, CH_2)
1560-1580	S (C=C); aromatic skeletal vibrations

Table S2. Adsorption equilibrium data for toluene-water mixed vapor on LCF-Fe

		(predicted)			(observed)
P/P_0	q_{01}	q_{02}	q_{03}	q_0	q_0
			RH=20%		
0.01	31.78934	0.132076	4.001802	35.92322	30.22873
0.02	51.38525	0.264152	4.88903	56.53843	55.57785
0.05	131.8337	0.66038	6.371289	138.8653	129.88
0.1	252.5429	1.32076	7.784397	261.648	270.4034
0.15	333.7463	1.98114	8.752161	344.4796	328.9171
		ARD/%		5.04	
			RH=50%		
0.01	29.1714	0.003518	5.602523	34.77744	28.55579
0.02	47.15352	0.007037	6.844641	54.0052	50.8443
0.05	120.9768	0.017592	8.919805	129.9142	125.1352
0.1	231.7452	0.035184	10.89816	242.6786	231.3068
0.15	306.2613	0.052776	12.25303	318.5671	302.7929
		ARD/%		7.41	
			RH=60%		
0.01	21.1589	0.001386	9.2162	30.37649	26.6876
0.02	33.8659	0.002872	11.1695	45.03827	40.3216
0.05	85.6321	0.006893	14.6531	100.2921	92.3287
0.1	162.3526	0.01286	17.3910	179.7565	170.3586
0.15	211.5638	0.01962	20.0892	231.6726	221.8562
		ARD/%		7.11	
			RH=70%		

0.01	7.6235	0.000826	16.0569	23.68123	21.5123
0.02	12.5623	0.001772	20.0265	32.59057	30.0656
0.05	35.2169	0.004253	25.9632	61.18435	51.6528
0.1	65.3871	0.007386	32.5738	97.96829	81.5623
0.15	89.6872	0.01072	37.0219	126.7198	110.8965
ARD/%				9.29	
RH=80%					
0.01	4.113915	0.000386	23.74403	27.85833	20.05587
0.02	6.649855	0.000772	29.00824	35.65887	29.34144
0.05	17.06083	0.00193	37.80298	54.86574	46.08241
0.1	32.68202	0.00386	46.18742	78.8733	72.65833
0.15	43.1907	0.00579	51.92949	95.12597	99.54701
ARD/%				12.99	

Table S3. The parameters for CPHSDM calculation

Parameters	LCL-Fe	Calgon BPL
k_f / cm/s	6.94	7.16
D_s / cm^2/s	1.41×10^{-7}	5.56×10^{-7}
D_p / cm^2/s	4.04×10^{-3}	1.5×10^{-2}
R_e	12383	399
S_c	1.83	1.83
S_t	31.91	132
D_g	3968734	482651
ε	0.104	0.473
ε_p	0.360	0.595
K	467	265
1/n	0.150	0.181
Biot	53.57	5.52

The model for predicting the adsorption of toluene and water vapor:

Applying the model is straightforward for a given RH and gas-phase concentration of toluene. The toluene loading on dry surface and the toluene concentration in condensed water are determined using the D-R equation and Henry's Law, respectively. The toluene concentration in condensed water and Freundlich parameters describing aqueous-phase adsorption of the toluene are then used to calculate the amount adsorbed onto the pores which are filled with water. In order to calculate the individual contributions to the total capacity, the volume of condensed water and the fractions of wet and dry surface need to be determined and these are found using a water vapor isotherm (as shown in Figure 5) and a pore volume-pore surface area distribution curve (as shown in Figure 2).

The toluene adsorption on the dry surface: For the dry surface, the following assumption is made to estimate adsorption capacity. Adsorption on at dry surface can be described calculating the adsorption capacity from the D-R equation times the fraction of dry surface as shown in Eq. (S1).

$$q_{o1} = q_o^{O} S_D / S_T \tag{S1}$$

where q_o^{O} is the equilibrium capacity that is determined using the D-R equation. The cumulative pore volume is calculated by using the Kelvin equation as shown in Eq. (S2)). If the contact angle α (cos α ≈ 0.6) for water is chosen, the cumulative pore volume curve calculated from the desorption isotherm of water vapor is approximately equal to that from the isotherm of nitrogen on carbon.

$$r = -2\sigma V_L \cos\alpha / (RT \ln p / p_0) \tag{S2}$$

The cumulative surface area is expressed as:

$$S = 2 \sum_{r=0}^{N} \frac{\Delta V}{\bar{r}} \tag{S3}$$

where ΔV is the increase of pore volume between r and r+Δr, and $\bar{r}$ is the average pore radius between r and r+Δr. Eq. (S3) assumes the pores are cylindrical. S_c in the adsorption step is evaluated from Figure S1. Figure S1 shows the cumulative pore volume and surface area curve that was determined from the nitrogen isotherm on LCF-Fe. V_c can be estimated from the water vapor isotherm at a given RH.

The toluene contained in the condensed water: The concentration of toluene in condensed water can be calculated from Henry's law. However, the effects of the concave meniscus of the water in the pore should be considered. The following equation was developed considering both mechanical and chemical equilibrium between two fluids with a curved interface [30]. Details of the development are provided by Crittenden et al. [31].

$$P_i = H \exp\left\{ \frac{V_i}{V_{water}} \ln\left[\frac{P_{water}}{P_{water,s}} \right] \right\} C_i \tag{S4}$$

in which, V_i, and V_{water} is the molar volumes of component i and water. The reduced pressure term $(P_{water}/P_{water,s})$ represents the RH. The concentration of toluene in the condensed water (C_i) is determined using Eq. (S4).

The adsorption capacity on wet surface: The amount of solvent adsorbed onto the wet surface q_{o3}^{O} is given as Eq. (S5):

$$q_{o3} = q_{o3}^{O} S_C / S_T \tag{S5}$$

Where q_{o3}^{O} is the adsorption capacity that would be obtained from the liquid-phase adsorption experiment. An aqueous phase isotherm for toluene at 20°C was conducted and fit to the Freundlich equation (as shown in Figure S2), yielding values of 38.7 and 0.289 for K and l/n respectively for LCF-Fe. The contribution for aqueous phase adsorption (q_{o3}) is much lower than the gas phase solvent (q_{o1}) when the RH values are lower than 50%. As for the RH = 20% calculation, the proportion of aqueous phase capacity at < 0.11 and the gas phase capacity at > 0.88 at different relative pressures are important. When the RH approaches to 50%, the values are < 0.16 and > 0.83, suggesting the small effect of the RH. However, when RH exceeds 80%, the values increase sharply to <0.85 for the aqueous phase, suggesting the obvious effect.

The total capacity is then the sum of three contributions: (1) The D-R predicted loading times the fraction of dry area; (2) the amount adsorbed onto the pore walls multiplied by the fraction of wet surface area; and (3) the volume of condensed water times the toluene concentration in the water.

The detail calculation procedure of the diffusivity of toluene molecule in the gas-phase:

$$D_{AB}=\frac{10^{-4}\left(1.084\text{-}0.249\sqrt{\frac{1}{M_A}+\frac{1}{M_B}}\right)\left(T^{1.5}\right)\sqrt{\frac{1}{M_A}+\frac{1}{M_B}}}{P_1(r_{AB})^2 f(\frac{kT}{\varepsilon_{AB}})} \tag{S6}$$

Where,

D_{AB}=gas diffusivity of organic compound A in stagnant gas B $(\frac{m^2}{sec})$

T is absolute temperature (K)

M_A, M_B represent the molecular weight of A&B, respectively(Kg/Kmol)

P_1 is absolute pressure (N/M^2)

r_{AB} is molecular separation at collision (nm) $=(\frac{r_A+r_B}{2})$

ε_{AB} is energy of molecular attraction $=\sqrt{\varepsilon_A\varepsilon_B}$

K is Boltzman's constant

$f(\frac{kT}{\varepsilon_{AB}})$ is collision function

Some of the parameters for air are:

r_B (air) = 0.3711nm $\qquad \frac{\varepsilon_B}{k}=78.6$

r_A (compound) $=1.18\,V_b^{\frac{1}{3}}$(nm)

V_b = molar volume of A @ boiling point $(\frac{m^3}{Kgmol})$

$\frac{\varepsilon_A}{k}=1.21\,(T_b)_A$ $\qquad (T_b)_A$=boiling point temperature of compound A

$\frac{\varepsilon_{AB}}{k}=\sqrt{\frac{\varepsilon_A}{k}\frac{\varepsilon_B}{k}}$ $\qquad ee=\log_{10}(\frac{kT}{\varepsilon_{AB}})$ $\qquad$ T=operating temperature (K)

$$f(\frac{kT}{\varepsilon_{AB}})=10^{(-0.14329-0.48343(ee)+0.1939(ee)^2+0.13612(ee)^3-0.20578(ee)^4+0.083899(ee)^5-0.011491(ee)^6)}$$

The calculation of toluene gas-phase diffusivity in air:

M_A =92 (Toluene) $\qquad M_B$=28.8 (air) $\qquad$ T=298K $\qquad P_1=101{,}325\,\frac{N}{m^2}$

$$\mathrm{V_b}(\mathit{Toluene})=7\times(14.8)+8\times(3.7)-1\times(15)=118.2\frac{\mathrm{cm^3}}{\mathrm{gmol}}=0.1182\frac{\mathrm{m^3}}{\mathrm{kgmol}}$$

$$\mathrm{r_A}=1.18\,\mathrm{V_b^{\frac{1}{3}}}=1.18\times(0.1182)^{\frac{1}{3}}=0.5797(\mathrm{nm}) \qquad \mathrm{r_B}\,(\mathrm{air})=0.3711\mathrm{m}$$

$$\frac{\varepsilon_\mathrm{B}}{\mathrm{k}}=78.6(\mathrm{air}) \qquad \frac{\varepsilon_\mathrm{A}}{\mathrm{k}}=1.21\,(\mathrm{T_b})_\mathrm{A}=1.21\times\,(384\mathrm{K})=464.4\ (\mathrm{Toluene})$$

$$\frac{\varepsilon_\mathrm{AB}}{\mathrm{k}}=\sqrt{\frac{\varepsilon_\mathrm{A}}{\mathrm{k}}\frac{\varepsilon_\mathrm{B}}{\mathrm{k}}}=\sqrt{(464)\times(78.6)}=191$$

$$\frac{\mathrm{kT}}{\varepsilon_\mathrm{AB}}=\frac{283}{191}=1.56 \qquad \mathrm{ee}=\log_{10}(\frac{\mathrm{kT}}{\varepsilon_\mathrm{AB}})=\log_{10}(1.56)=0.193$$

$$\mathrm{f}(\frac{\mathrm{kT}}{\varepsilon_\mathrm{AB}})=10^{(-0.14329-0.48343\times(0.193)+0.1939\times(0.193)^2+0.13612\times(0.193)^3-0.20678\times(0.193)^4+0.083899\times(0.193)^5-0.011491\times(0.193)^6)}=0.59$$

$$\sqrt{\frac{1}{\mathrm{M_A}}+\frac{1}{\mathrm{M_B}}}=\sqrt{\frac{1}{92}+\frac{1}{29}}=0.214$$

$$\mathrm{D_{AB}}=\frac{10^{-4}(1.084-0.249\times0.214)\times(298)^{1.5}\times(0.214)}{101325\times(0.475)^2\times(0.59)}=8.4\times10^{-6}\frac{\mathrm{m^2}}{\mathrm{sec}}$$

Gnielinski correlation used for the estimates of external mass transport coefficient:

$$D_g=\frac{\rho_a\times q_e\times(1-\varepsilon)}{\varepsilon\times C_0\times1000} \tag{S7}$$

$$q_e=KC_0^{\frac{1}{n}} \tag{S8}$$

$$\mathrm{Re}=\frac{\rho_{air}\times\phi\times d_p\times v_{air}}{\varepsilon\times\mu_{air}} \tag{S9}$$

$$Sc=\frac{\mu_{air}}{\rho_{air}\times D_{air}} \tag{S10}$$

$$k_f=\frac{(1+1.5\times(1-\varepsilon))\times D_g}{d_p\times\phi}\cdot(2+0.644\times\mathrm{Re}^{0.5}\times\mathrm{Sc}^{0.333}) \tag{S11}$$

where D_g is the surface solute distribution parameter; D_s is the surface diffusion coefficient (cm^2/s); D_p is the pore diffusion coefficient (cm^2/s); k_f is the external mass transport coefficient (cm/s); ρ_a is the apparent particle density of activated carbon (g/cm^3); ε is the bed porosity; ε_p is particle porosity; C_0 is the inlet concentration of toluene in air (mg/L); q_e is the equilibrium adsorption capacity of GAC for toluene at C_0 (mg/g); K and 1/n are the Freundlich equation constants; ρ_{air} is the density of air (g/cm^3); Φ is the particle shape factor; v_{air} is the superficial velocity (m/s); μ_{air} is the viscosity of air at 25 ℃ and 1 atm ((Ns)/m^2); ρ_{air} is the density of air at 25 ℃ and 1 atm (kg/m^3); D_{air} is the gas phase diffusivity (m^2/s); R_e is the Reynolds number (unitless); S_c is the Schmidt number (unitless); d_p is the adsorbent particle diameter (cm).

Estimation of the surface diffusion coefficient

$$D_s = \frac{\varepsilon_p \times C_0 \times D_{air}}{\rho_a \times q_e \times \zeta_p \times 1000} \times SPDFR \qquad \text{(S12)}$$

Where ε_p is particle porosity; C_0 is the inlet concentration of toluene in air (mg/L); D_{air} is the gas diffusivity of toluene in the air (m^2/s); ρ_a is the apparent particle density of activated carbon (g/cm^3); q_e is the equilibrium adsorption capacity of GAC for toluene at C_0 (mg/g); ζ_p is the tortuosity; SPDFR is the surface to pore diffusion flux ratio (SPDFR) =16.

Estimation of the pore diffusion coefficient

$$D_p = \frac{\varepsilon_p \times D_{air}}{((2-\varepsilon_p)^2 / \varepsilon_p)} \qquad \text{(S13)}$$

Where ε_p is particle porosity; D_{air} is the gas diffusivity of toluene in the air (m^2/s).

Estimation of other dimensionless groups

$$St = \frac{EBCT \times k_f \times (1 - \varepsilon)}{\phi \times d_p} \times 2 \qquad \text{(S14)}$$

$$Biot = \frac{k_f \times C_0 \times d_p}{2 \times D_s \times \rho_a \times q_e} \qquad \text{(S15)}$$

St is the Stanton number (unitless); EBCT is empty bed contact time (s); k_f is the external mass transport coefficient (m/s); ε is the bed porosity; Φ is the particle shape factor; d_p is the adsorbent particle diameter (cm); Boit is the Boit number (unitless); C_0 is the inlet concentration of toluene in air (mg/L); D_s is the surface diffusion coefficient (m^2/s); ρ_a is the apparent particle density of activated carbon (g/cm^3); ε is the bed porosity; q_e is the equilibrium adsorption capacity of GAC for toluene at C_0 (mg/g).