

Removal of Pollutants with Activated Carbon Produced from K_2CO_3 Activation of Lignin From Reed Black Liquors

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The activated carbon was prepared from fast precarbonization of reed lignin in the fluidized-bed followed by K_2CO_3 activation. The impregnation ratio was $\zeta = 1:1$ in this research. The effect of activation temperature upon the BET specific surface area and specific pore volume of the carbon was closely investigated. Increasing activation temperature led to an opening and widening of the porous structure below 800 °C. Above 800 °C, the excess widening of pore led to the decrease of BET surface area and micropore volume. The BET specific surface area and specific pore volume of the carbon activated at 800 °C were $s = 1217 \text{ m}^2 \text{ g}^{-1}$ and $v = 0.65 \text{ ml g}^{-1}$, respectively. The potential application of the carbon activated at 800 °C for removal of pollutants was also investigated. The Langmuir monolayer adsorption capacity q_m of this activated carbon of adsorbing phenol, nitrobenzene, and Cr (VI) can reach 136.2, 393.7 and 52.6 mg g^{-1} , respectively. The experimental results showed that it had good adsorption capacity.

Key words:

Activated carbon, reed lignin, fluidized-bed, phenol nitrobenzene, Cr (VI)

Introduction

Aromatic compounds such as phenol and nitrobenzene which are widely used as the industrial raw materials are significant water contaminants. The presence of low mass concentration of aromatic compounds affects the use (and/or) reuse of water. Most of these compounds are recognized as the toxic carcinogens.¹ Chromium is one of the most important heavy metals because of its relative high toxicity. It is present commonly as Cr(VI) and Cr(III). The former is considered as a powerful carcinogenetic agent that modifies the DNA transcription process causing important chromosomic aberration.² The effective removal of the above two kinds of pollutants is very crucial to the environmental protection and the sustainable development of local industry. Among the methods of removing the pollutants, the adsorption by activated carbons is the best and most frequently used method.³ This is due to their well-developed porosity and surface functional groups that account for their good adsorption. Many kinds of materials can be used as the precursors for producing activated carbon.^{4,5} Among them, lignin is a good precursor because of

its relatively high carbon content. There are many literature data concerning preparation of activated carbon from lignin.⁶ They mainly focus on wood lignin for preparation of activated carbon and use of $ZnCl_2$ and H_3PO_4 as the activators. Not much attention has been given to the herbaceous lignin such as reed lignin in preparation of the activated carbon. Therefore, the attempt to prepare activated carbon by fast carbonization of reed lignin in the fluidized bed followed by K_2CO_3 chemical activation is made in this work. The effect of activation temperature upon BET specific surface area and specific pore volume of the carbon is closely investigated. The adsorption of phenol, nitrobenzene and chromium (VI) by the carbon with the largest BET specific surface area is also investigated.

Experimental

Apparatus

Fig. 1 illustrates the experimental apparatus system for carbonizing lignin. A quartz glass column was used as a fluidized bed reactor. The diameter and height of the fluidized bed reactor in the bed section were 30 mm and 300 mm, respectively, and those in the expanding section were 55 mm and 90 mm respectively. The distribution plate was made of stainless steel 2 mm thick which contained

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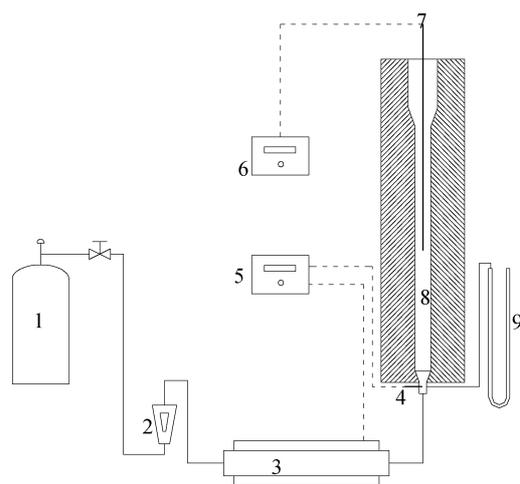


Fig. 1 – Experimental setup (1) N_2 ; (2) flow meter; (3) heating furnace; (4) thermocouple; (5) programmable thermostat; (6) programmable thermostat; (7) thermocouple; (8) fluidized bed; (9) U-tube manometer

25 holes, each 0.1 mm in diameter. The N_2 was fed into the bed through a pressure regulator, a calibrated rotameter, and a heating furnace controlled by a programmable thermostat heating at the rate of temperature change $\Delta T = 30\text{ }^\circ\text{C min}^{-1}$. A U-tube manometer was used to measure pressure drop of the bed. The fluidized-bed reactor was first heated to the preset temperature and then maintained until thermal equilibrium was achieved.

Preparation of activated carbon

The strong black liquor from reed pulping was acidulated with dilute HCl to precipitate the lignin, which was then washed with distilled water for several times and dried. The ultimate analysis of lignin on a dry basis was given in the Table 1. The result shows that the lignin has relatively high carbon content and is suitable for preparation of activated carbon.

The powder lignin of approximately 10 g was placed in the preheated ($350\text{ }^\circ\text{C}$) fluidized-bed reactor through the top and N_2 used as a protective gas at the flow rate of $Q = 8\text{ L min}^{-1}$. This condition was kept for 5 min to carbonize the raw materials and the char was taken out after the reactor was cooled to room temperature. The char was sieved to

Table 1 – Elemental analysis of lignin

Element	Content w / %
C	59.4
H	5.2
N	0.1
O (Estimated by difference)	35.3

about 0.15–0.30 mm and was impregnated with K_2CO_3 to the impregnation ratio of $\zeta = 1:1$. The mixture was then activated in the tubular furnace at different activation temperatures for 60 min. Finally, the product was washed with hot distilled water to neutralization, then filtered and dried at $120\text{ }^\circ\text{C}$.

The designations of activated carbon were made according to their preparation condition. The char carbonized in the fluidized bed at $350\text{ }^\circ\text{C}$ was labeled as PCL350, and the activated carbon activated at $800\text{ }^\circ\text{C}$ was labeled as L800.

Characterization and measurements of activated carbon

N_2 adsorption and desorption characterization: The specific surface area and porosities of the activated carbon were determined by N_2 gas adsorption-desorption with Quantachrome Autosorb Automated Gas Sorption System (Quantachrome Corporation USA). Prior to measurement, the carbons were degassed at $150\text{ }^\circ\text{C}$ overnight. The N_2 adsorption-desorption data were recorded at 77K. The N_2 adsorption-desorption isotherms of activated carbon were obtained by calculating their Brunauer-Emmett-Teller (BET) specific surface areas, assuming that the area of N_2 molecule was 0.162 nm^2 . The BET specific surface area was assessed within the range of relative pressures from 0.05 to 0.3. The micropore volume and external surface area (mesoporous surface area) were measured by t -plot method,⁷ the total specific pore volume was calculated by liquid N_2 adsorbed at a relative pressure of 0.99. Pore distribution of the carbon was determined by the methods of HK and BJH.

FT-IR Analysis: The Spectrum GX (Perkin-Elmer USA 2003) infrared spectrometer was used for the study of the surface functional groups. Disc was prepared by mixing of 0.5 mg sample with 200 mg of KBr (Merck, for spectroscopy) in an agate mortar and then by pressing the obtained mixture at 2 MPa for 1 min. The samples were scanned in the spectral range of $4000\text{--}370\text{ cm}^{-1}$.

Surface Morphology: Surface morphology was taken by HITACHI S-450 (Japan HITACHI) scanning electron microscope. The carbon samples were coated with gold with a gold sputtering device.

Adsorption test

The L800 was tested to determine its capacity for removal of pollutants from aqueous solution at $25\text{ }^\circ\text{C}$. In each experiment, 50 mg of the powdered dried activated carbon was added to the 100 ml of different pollutants at different starting concentrations and the solution with L800 was shaken under water bath at $25\text{ }^\circ\text{C}$ for 24 h. The uptake of phenol

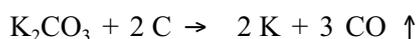
and nitrobenzene were determined by Agilent High Performance Liquid Chromatography (HP 1100) and the content of chromium in the solution was analyzed by ICP-OES (Optima DV 5300 PerkinElmer Corporation). The adsorption of phenol and nitrobenzene was carried out at pH 7, the adsorption of Cr (VI) was carried out at pH 3.

Results and Discussion

Optimization of preparing conditions of activated carbon

The thermogravimetric analysis of lignin is shown in Fig. 2. The maxima of the mass loss rate of the lignin under N_2 atmosphere appears in the temperature range of 250–350 °C, and the slight change of the mass loss of the sample occurs in the range of 350–600 °C. This experiment adopts 350 °C as the carbonization temperature to carbonize the lignin in the fluidized bed, since major part of volatile components is expelled from the lignin in the temperature range of 250–350 °C. Fig. 3 shows pressure drop and char yield of lignin as a function of carbonization time in the fluidized-bed at 350 °C during carbonization. It shows that the char yield does not change appreciably after the first 5 min of carbonization, and so is with pressure drop. This means that after the volatile matter has been removed in the first 5 min of carbonization, the volatilization is largely reduced. Therefore, it was decided to carbonize the lignin for 5 min prior to activation.

The surface area of the carbon depends largely upon the activation temperature. With the increase of activation temperature, the reaction rate between the activator of K_2CO_3 and the carbon increases fast.⁸ The reaction is shown as follows:⁹



The specific surface areas and specific pore volumes of activated carbon at different activation temperatures are shown in Fig. 4 and Fig. 5 respectively. The specific surface areas and the specific pore volumes (micropore volume, mesopore and macropore volume) of activated carbon increase between the temperature of 500 and 800 °C and the maximum specific surface areas and specific pore volume of $s = 1217 \text{ m}^2 \text{ g}^{-1}$ and $v = 0.65 \text{ mL g}^{-1}$ are observed at 800 °C. This indicates that the simultaneous pore opening and pore widening take place between the temperature of 500 and 800 °C. Above 800 °C the pore widening effect dominates the pore-opening effect, which results in a decrease of specific surface areas and micropore volume, and further increase of mesopore and macropore volume.

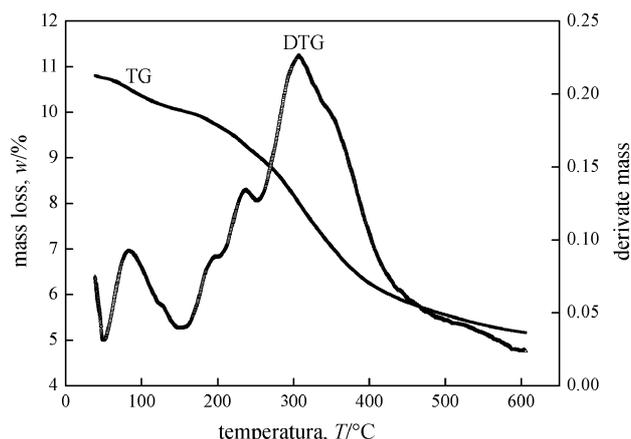


Fig. 2 – The thermogravimetric analysis of lignin

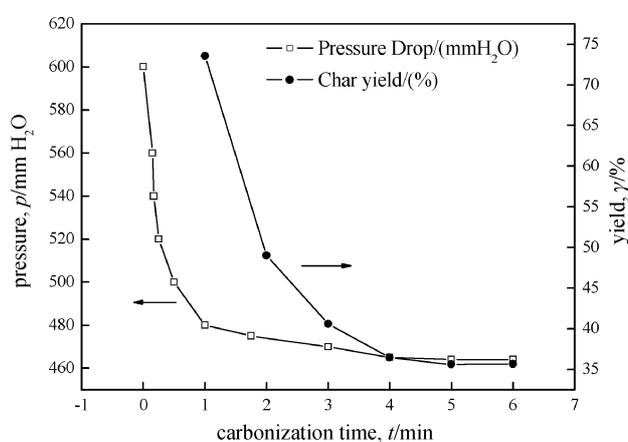


Fig. 3 – Pressure drop and char yield as function of carbonization time

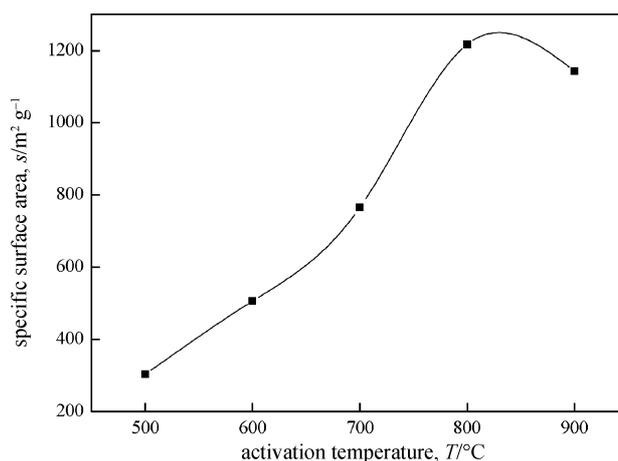


Fig. 4 – The effect of activation temperature on the specific surface area of activated carbon

By precarbonizing the lignin in the fluidized-bed at 350 °C followed by 800 °C K_2CO_3 activation, the specific surface area and specific pore volume of L800 can reach $s = 1217 \text{ m}^2 \text{ g}^{-1}$ and $v = 0.65 \text{ mL g}^{-1}$, respectively. The comparison of different preparation conditions of producing activated

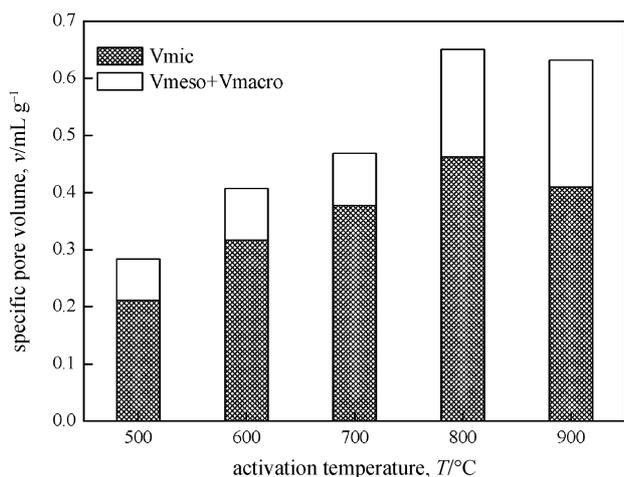


Fig. 5 – The effect of activation temperature on the specific pore volume of activated carbon

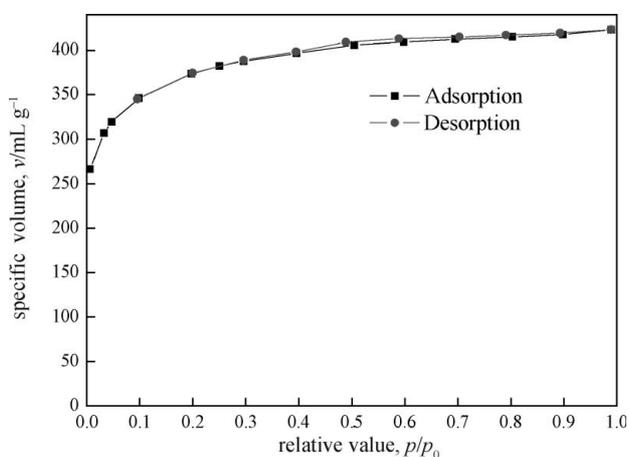


Fig. 6 – Adsorption-desorption isotherms of L800

carbon from different kinds of lignins is listed in Table 2. The specific surface area of the resulting carbon from our process is smaller than that of the carbons produced from other processes. This is probably due to different chemical activation schemes and different kinds of lignins used as a precursor.

Characterization of L800

The adsorption/desorption isotherm of L800 is shown in Fig. 6. According to Brunauer-Deming-

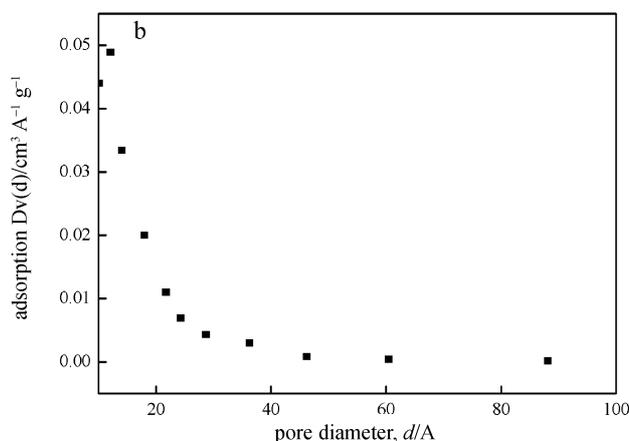
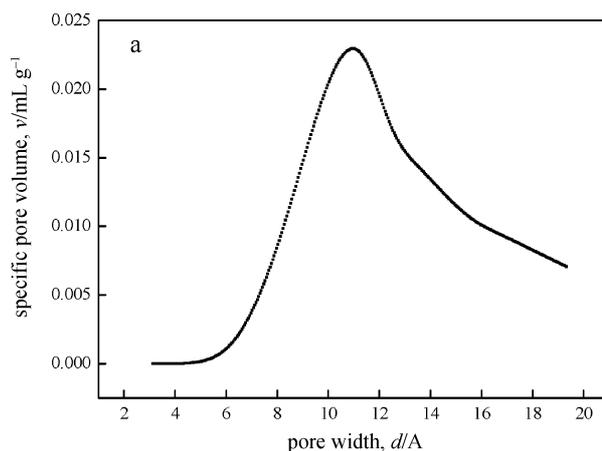


Fig. 7 – (a) Micropore distribution and (b) Cumulative specific pore volume of activated carbon in mesopore region

-Deming-Teller (BDDT) classification,¹² this carbon exhibits the typical type I isotherm. The major uptake happens at relatively low pressure, indicating the formation of highly porous materials with narrow pore size distribution that are essentially microporous material. The small upward bending at higher relative pressure in the nitrogen adsorption/desorption isotherm indicates an essentially microporous character with some contribution of wider pores (mesopores and macropores). The micropore distribution and cumulative pore volume of L800 in mesopore region are shown in Fig. 7. Large

Table 2 – Comparison of preparation conditions and the main parameters of the activated carbon from black liquid

Preparation condition	Raw material	$S_{\text{BET}} / \text{m}^2 \text{g}^{-1}$	Reference
Precarbonizing the lignin at 350 °C for 2 followed by CO ₂ gasification at 850 °C for 20 h	Eucalyptus kraft lignin	1853	10
ZnCl ₂ chemical activation at 500 °C for 1 h	Eucalyptus kraft lignin	1800	11
H ₃ PO ₄ activation at 425°C for 2 h with impregnation ratio of 1	Eucalyptus kraft lignin	1336	14
KOH chemical activation at 800 °C for 1 h with impregnation ratio of 1	Spruce wood kraft lignin	1500	6
Precarbonizing at 350 °C for 5 min. Activating the char by K ₂ CO ₃ at 800 °C for 1 h	Reed lignin	1217	This work

proportion of the pores is in the microporic range which mainly distribute in the range of 10–12 Å (1–1.2 nm). There are some proportion of mesopores (>20 Å, > 2.0 nm) in L800 which is shown in the Fig 7b. This confirms that micropores play the key role in L800 with large specific surface area. The FTIR spectroscopy of PCL350 and L800 are shown in Fig. 8. All carbon samples show wide band at about 3488–3100 cm⁻¹. This is assigned to the O-H stretching mode of hexagonal groups and adsorbed water. Two bands observed at 2920 and 2830 cm⁻¹ are assigned to the asymmetric C-H and symmetric C-H bands respectively, representing the alkyl groups such as methyl and methylene groups.¹³ With increase of temperature, the C-H becomes weak, indicating that CH₃ groups are further removed from the substituted aromatic rings at high temperature. The broad peak around 1110–1000 cm⁻¹ and sharp peak at 800 cm⁻¹ indicate the presence of Si-O in PCL350 and L800 respectively, and these peaks are in parallel with peaks from commercial-grade silica.¹⁴ Fig 9 shows morphology of L800 and PCL350. Due to the attack of chemical activator at 800 °C, L800 shows good formation of pores, while in Fig. 9b of PCL350, it shows that pore formation is poor.

Adsorption of pollutants

The activated carbon with largest specific surface area is utilized as the adsorbent for removal of water pollutants. Three target species are chosen as representative of toxic organic (phenol, nitrobenzene) and inorganic pollutant (chromium (VI)). The analyses of the adsorption isotherms of different pollutants are carried out by applying the Langmuir and Freundlich equations:

$$\text{Langmuir } 1/q_e = 1/[K_L q_m \gamma_e] + 1/q_m \quad (1)$$

$$\text{Freundlich: } q_e = K_F \gamma_e^{1/n} \quad (2)$$

Fig. 10 shows the results of Langmuir and Freundlich isotherm fit. The parameters obtained by fitting the Langmuir and Freundlich isotherms listed in Table 3. Obviously, Langmuir yields are somewhat better fitting than the Freundlich model, as reflected in the correlation coefficient (R^2). The amount of nitrobenzene adsorbed on the L800 is quite bigger than the amount of phenol adsorbed on L800, which is reflected in the value of q_m . The possible reason may be that the deactivation of nitril group upon benzenic ring favors formation of electron donor-acceptor complex between the aromatic ring and the oxygen surface groups on the surface of activated carbon. Because the adsorption of Cr (VI) is carried out at pH 3, the reduction of Cr (VI)-Cr (III) on the carbon surface is thermodynamically favored. This is probably due to the -OH groups of

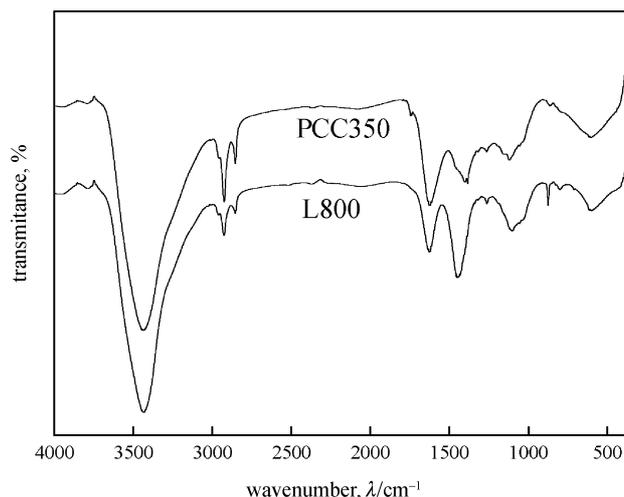
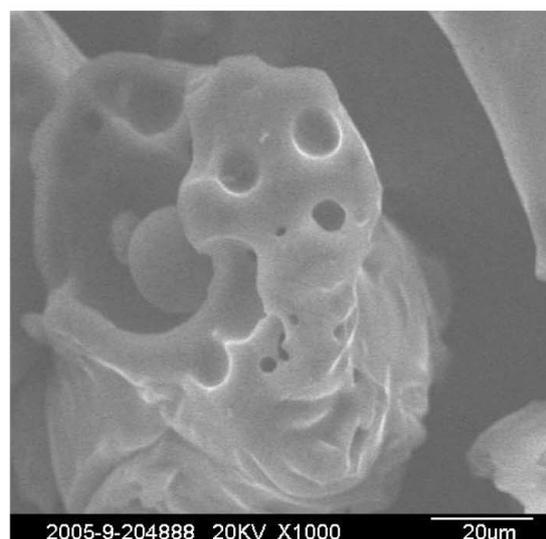


Fig. 8 – FTIR spectra of (a) PCL350 and (b) L800

9a



9b

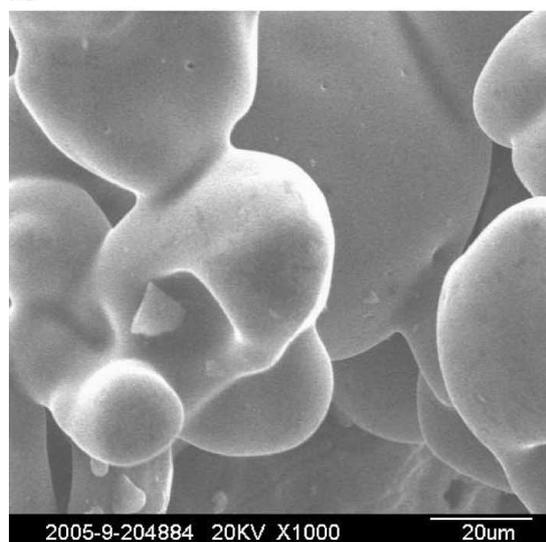


Fig. 9 – Scanning electron micrographs of (a) L800 and (b) PCL350

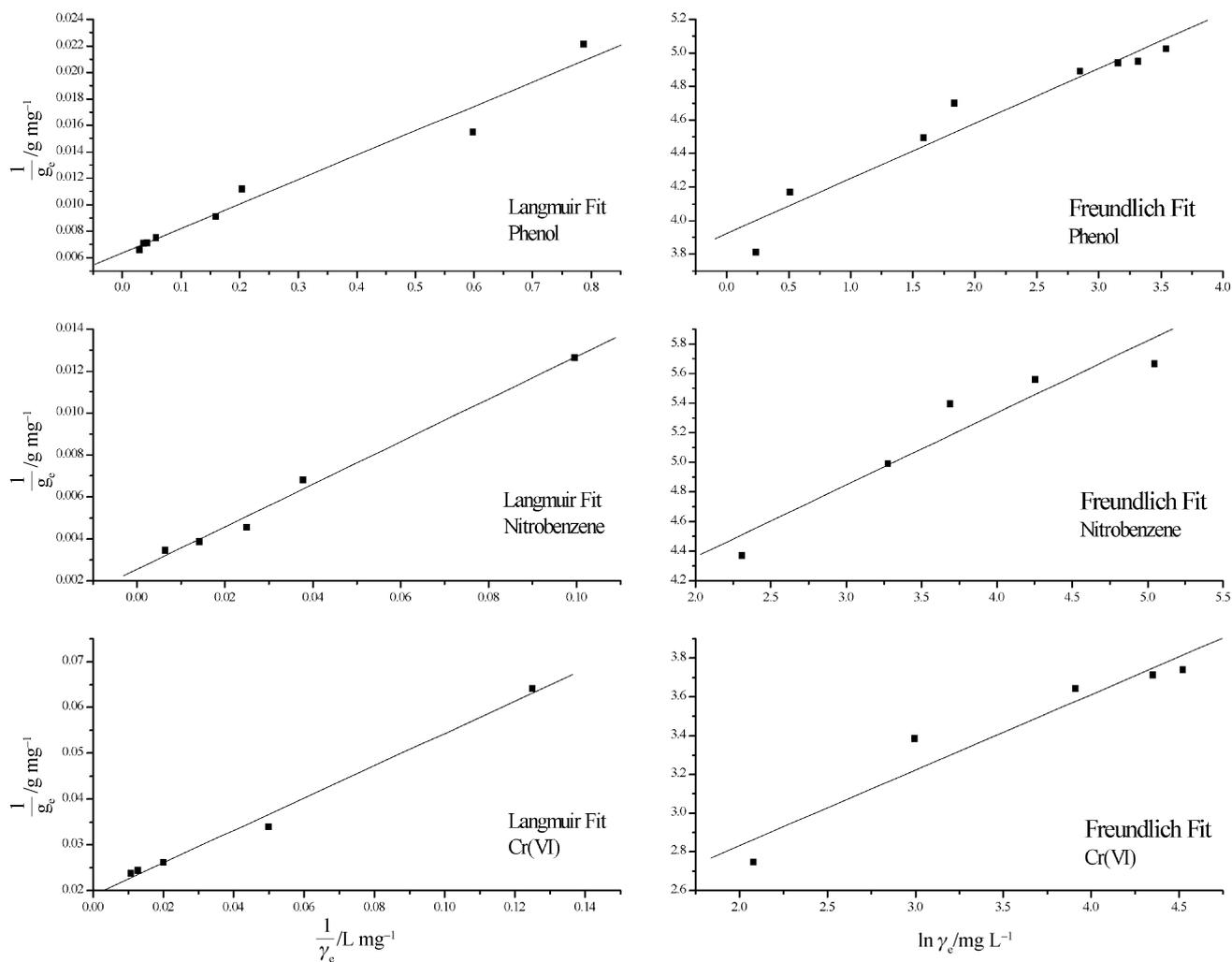


Fig. 10 – The Langmuir and Freundlich plot for the phenol, nitrobenzene and Cr(VI) adsorbed on L800

carbon surface of the hydroquinone type.¹⁵ The maximum adsorption capacity absorbing Cr(VI) of L800 is 52.60 (mg g⁻¹), which is comparable to the literature reports.¹⁶ In Freundlich equations, the values $1/n$ are all below 1, which indicates a favorable adsorption isotherm. All these results show that L800 has good adsorption capacity.

Table 3 – Isotherm fitting parameters of L800 adsorbing phenol, nitrobenzene and Cr(VI)

Adsorbate	Langmuir			Freundlich		
	q_m , mg g ⁻¹	K_L , L mg ⁻¹	R^2	$1/n$	K_F	R^2
Phenol	136.2	0.520	0.9969	0.33	50.57	0.9677
Nitrobenzene	393.7	0.025	0.9951	0.48	29.26	0.9513
Cr(VI)	52.6	0.054	0.9956	0.39	7.78	0.9618

K_F in mg g⁻¹(L mg⁻¹)^{1/n}

Conclusion

(1) The large specific surface area of activated carbon from reed black liquor can be made by precarbonized lignin at 350 °C for 5 min followed by the 800 °C activation, which the BET specific surface area and specific pore volume can reach $s = 1217$ m² g⁻¹ and $v = 0.65$ ml g⁻¹ respectively.

(2) The adsorption/desorption isotherm of L800 exhibits the type I isotherm. The carbon has essentially microporous character with some character of wider pores (mesopores and macropores). FTIR shows the existence of silica in the carbon.

(3) The Langmuir model gives the better fit than the Freundlich model in fitting the adsorption model of water pollutants. The adsorption capacity of L800 for three different target compounds (phenol, nitrobenzene, and Cr(VI)) can reach 136.2, 393.7 and 52.6 mg g⁻¹, respectively, and compares well with the literature reported.

ACKNOWLEDGEMENTS

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List of symbols

K_L	– constant, L mg ⁻¹
m	– mass, mg, g
n	– constant
p	– pressure, MPa
Q	– volume flow rate, L min ⁻¹
q_m	– absorption capacity, mg g ⁻¹
s	– specific surface area, m ² g ⁻¹
T	– temperature, °C
ΔT	– rate of temperature change, °C min ⁻¹
t	– time, min
V	– specific pore volume, mL g ⁻¹
w	– mass fraction, %
Y	– yield, %
γ	– mass concentration, mg L ⁻¹
ζ	– mass ratio

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