



# Chemical activation of bituminous coal for hampering oligomerization of organic contaminants

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## ABSTRACT

Activated carbons prepared by KOH activation of bituminous coal were studied for hampering oligomerization of phenolic compounds on its surface. A total of 24 activated carbons with different microporosity and BET surface area were created. The effect of the different variables of the activation process (KOH/bituminous coal ratio, heating temperature, activation time, and flow rate of nitrogen gas) on critical carbon parameters was analyzed. The impact of activated carbon on oligomerization was examined by conducting isotherm experiments at a neutral pH on Carbon<sub>exp</sub> produced with optimal characteristics and granular activated carbon (GAC) F400 for phenol, 2-methylphenol and 2-ethylphenol. These isotherms were collected under anoxic (absence of molecular oxygen) and oxic (presence of molecular oxygen) conditions. The single solute adsorption of phenol, 2-methylphenol and 2-ethylphenol on Carbon<sub>exp</sub> showed no obvious differences between oxic and anoxic environment, which indicated that the Carbon<sub>exp</sub> sample is very effective in hampering the oligomerization of phenolic compounds under oxic conditions. On the other hand, F400, which have lower micropore percentage and BET surface area, significant increases in the adsorptive capacity had been observed when molecular oxygen was present.

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## 1. Introduction

Phenol and its derivatives have been regarded as one major environmental concern around the world because they exist widely in industrial effluents. Phenolic compounds potentially cause long-term contamination of both surface water and groundwater bodies [1]. Among all treatment processes, activated carbon adsorption has been designated as the most widely effective technique in phenolic compounds removal because of its good adsorption capacity and flexibility [2–7]. However, economic use has been a major concern in granular activated carbon (GAC) usage due to poor regeneration efficiency of activated carbon [8,9]. The main reason for the drawback is that the presence of molecular oxygen in the aqueous phase promotes chemical transformation, such as oligomerization of the organic compounds adsorbed onto the carbon surface. Meanwhile, dimers, trimers and tetramers of phenolic compounds in the solvent extracts have been identified [10–14]. Majority of commercial carbons have been developed primarily to remove organic molecular without considering the possibility of

oligomerization of these compounds on the surface of the adsorbent.

Although many researchers have investigated phenolic compounds adsorption by GAC, only few studies have systematically examined the factors controlling oligomerization phenomenon. Some studies have investigated the impact of surface chemistry of activated carbon on oligomerization of phenolic compounds [8,10,13]. In particular, the chemical characteristics, including acidic and basic surface functional groups and metals and metal oxide complexes, that are commonly present on activated carbon surface were investigated. Based on the study of Vidic et al. [8,13], only basic surface functional groups was postulated to have little influence on the extent of oligomerization. Studies by Uranowski et al. [10] also found that acid-washable metals and metal oxides are not a key factor in promoting oligomerization of adsorbates on the surface of activated carbons. On the other hand, pore size distribution (PSD) of activated carbons has been shown to play a very important role in the adsorption process. Some studies have already figured out that narrow PSD and relative smaller pore diameter were more effective for phenolic compounds oligomerization control [15–18]. Meanwhile, studies on adsorption of phenolic compounds revealed that adsorbents with small pore diameters like activated carbon fiber (ACF) were very effective for single solute adsorption oligomerization control. Lu and Sorial [15] studied the impact of PSD of ACF on oligomerization of phenolic compounds. After studying the effects of PSD on the phenolic compounds oligomerization, they concluded that the oligomerization

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phenomenon of phenolic compounds can be effectively controlled by ACFs with narrow PSD (microporosity above 90% ACC-10). At the same time, ACC-10 showed higher adsorptive capacity than F400 (common adsorbent used in water treatment) for all the phenolic compounds under anoxic conditions [17,18]. Therefore, activated carbon with similar pore structure as ACC-10 (having their pore volume mostly distributed in micropores and low critical pore diameter) needs to be developed and used for hampering oligomerization in order to make activated carbon more cost effective.

Activated carbons can be prepared by chemical or physical activation technique. Physical activation involves carbonization of the precursor under inert atmosphere, followed by gasification of the char under oxidizing agents such as water or carbon dioxide. The chemical route consists of impregnating the carbonaceous precursor with a chemical reagent and heating [19–21]. Chemical activation has intrinsic advantages over physical activation, which includes lower temperature, single step, higher product yields, higher surface areas and better microporosity distribution control [22]. Studies have shown that the micropore of carbon is developed by removal of the carbon atoms during the activation process. However, after the optimum activation, microporosity evolution will be accompanied with mesopore and macropore development with further activation [23]. Hence, very high surface area carbons with high phenolic compounds adsorption per unit mass may not be effective for controlling oligomerization. Thus, the ideal carbon would be a carbon with the optimum combination of microporosity and surface area. Efforts have to be focused towards getting the optimum degree of activation that will produce an activated carbon with best combination between microporosity and surface area. Many studies have reported that activated carbon developed by KOH chemical activation from carbonaceous materials, such as charcoal and coal, can provide not only high BET surface area but also narrow PSD and well-developed porosity [24–27]. Because of the merits of KOH chemical activation, we will carry out the research works on production of activated carbons by KOH chemical activation. Furthermore, the studies of activated carbon precursors have shown that bituminous coal is a very good raw material for the preparation of activated carbons by chemical activation due to hardness, abrasion resistance, and relatively high density. Studies have shown that activated carbon from bituminous coals allows very high adsorption capacities to be reached with porosity that is mostly micropores [28,29]. These activated carbons can be interesting for oligomerization control applications.

Numerous studies were conducted on carbon activation [30–33]. However, no systematic effort has been made to produce activated carbons similar to ACFs pore structure for hampering oligomerization of phenolic compounds and to examine the practical consequences of such modifications. Thus, the objective of this study has two principal objectives: (1) to prepare a chemically activated carbon that provides the proper combination of microporosity and BET surface area, (2) to analyze its use for adsorption of phenolic compounds and hampering oligomerization of these compounds on its surface.

## 2. Experimental

### 2.1. Preparation and activation of GAC

A series of activated carbon was developed from a Colorado bituminous coal (American Educational Products), using KOH as the activation agent. The proximate and ultimate analyses of the raw coal are shown in Table 1. A progressive study of four important variables (KOH/coal ratio, activation temperature, activation time and flow rate of nitrogen gas) was used to determine the best activation condition for developing carbon with optimum pore structure

**Table 1**

Proximate and ultimate analyses of Colorado bituminous coal.

Proximate (wt%, as received)		Ultimate (wt%, dry basis)	
Moisture	2.4	Carbon	82.8
Volatile matter	26.4	Hydrogen	5.0
Fixed carbon	63	Nitrogen	2.4
Ash	8.2	Oxygen	8.8
		Sulfur	1.0

[23]. The coal was ground and sieved to a particle size range of 400–600  $\mu\text{m}$ . The corresponding amount of lentic KOH was then crushed into powder and mixed with 3 g of bituminous coal powder at different ratios of 1:1, 2:1, 3:1, 4:1 and 5:1. 3 ml DI water per 3 g activating agent was added to the mixture in order to prepare a paste. The resulting mixture was dried at 110 °C overnight in a horizontal quartz reactor tube with a conventional horizontal furnace under nitrogen atmosphere. The samples were heated at a present final heating temperature in a set of nitrogen flow rate (100, 200, 400 or 600 ml/min). Samples were kept at the final temperature for different heating times of 0.5, 1, 2, 3 or 4 h before cooling down under nitrogen gas atmosphere. According to the study of Fan et al. [34], the effect of  $\text{Cl}^-$  on the removal of phenolic compounds with activated carbon was very limited. Therefore, the obtained activated carbon was first washed with hydrochloric acid (5 M) to remove the activation agent and then with distilled water until the pH of the rinse water is the same as the pH of distilled water [35–39]. The nomenclature of each carbon sample consists of bituminous coal's name (BC), KOH/coal ratio (i.e. 3/1 would be 31), the heating temperature in centigrade, the heating time in hours, and the flow rate in ml/min. Thus, for an activated carbon prepared with a KOH/bituminous coal ratio of 3/1 and which was heated at 700 °C for 3 h, and with flow rate 100 ml/min, the nomenclature would be BC-31-700-3-100.

### 2.2. Physical characterizations of adsorbents

Surface area and PSD of samples were quantified using physical adsorption isotherms of nitrogen with a micromeritics analyzer (TRI3000) at 77 K. All samples were degassed at 423 K for 2 h prior to analysis. Surface area of samples was calculated from BET equation. PSD of activated carbon samples was determined by combining two widely accepted models: the *T*-plot method for micropore size distribution (<20 Å) and the BJH theory for meso- and macropore size distribution [40]. The total pore volume was determined from the total adsorbed nitrogen volume near the saturation point ( $P/P_0 = 0.99$ ). Micropore volumes have been calculated from the adsorption isotherm of nitrogen by applying the *T*-plot equation. By subtracting the micropore volume from the total volume, the total meso- and macropore volume was determined. To determine optimum pore structures of activated carbon samples, conventional bituminous GAC Filtrasorb 400 (Calgon, Pittsburgh, PA), was used as reference.

### 2.3. Chemical characterizations of adsorbents

#### 2.3.1. Total acidity and basicity

The determination of total acidic and basic groups on carbon surfaces was performed for the selected Carbon<sub>exp</sub> and F400 using NaOH or HCl uptake methods. 20 ml 0.05 N NaOH or 0.05 N HCl was added to 100 mg of carbon in several 25 ml vials. The bottles were sealed with a Teflon-lined cap and parafilm and allowed to equilibrate for 2 days in a tumbler at room temperature. Four Vials without carbon were also prepared and served as blanks. At the end of the equilibration period, ten milliliter of the solution was titrated with 0.05 N of either NaOH or HCl solution. The total acidity was

**Table 2**  
Physical property of adsorbates.

Adsorbates	Molecular dimensions (Å) <sup>a</sup>	Critical oxidation potential (COP) (V)	Water solubility (g/L <sub>H<sub>2</sub>O</sub> )	pK <sub>a</sub>
Phenol	5.76 × 4.17	1.089	93	9.9
2-Methylphenol	5.69 × 5.32 × 1.63	1.040	25	10.29
2-Ethylphenol	6.90 × 5.70 × 1.63	1.080	5.3	10.14

<sup>a</sup> Advanced Chemistry Development – ACD Labs 5.0 software, Toronto, Canada.

calculated as the difference in the amount of acid required to titrate the blank to pH 4.5 and the amount of acid required to titrate the sample to the same end point. Also the total basicity was calculated as the difference in the amount of acid required to titrate the blank to pH 11.5 and the amount of acid required to titrate the sample to the same end point.

### 2.3.2. pH of point of zero charge (pH<sub>pzc</sub>)

Batch equilibrium method was used for determining pH<sub>pzc</sub> of Carbon<sub>exp</sub> selected and F400. Carbon sample (100 mg) was contacted with 20 ml autoclaved de-ionized water with different initial pH values (2–11) in 25 ml vials. Initial pH values adjustment was accomplished by adding 0.5 N HCl or NaOH. Two Blanks with no carbon were also prepared for each set. Sealed vials were put into tumbler for 2 days at the room temperature, and then the final pH of the solution was measured. The pH<sub>pzc</sub> was determined as the pH of the water sample that did not change after contact with the samples.

## 2.4. Adsorption isotherms

### 2.4.1. Adsorbates

Three commercially available phenolic compounds, phenol (99%), 2-methylphenol (98%) and 2-ethylphenol (99%) (Aldrich Chemical Co., Inc., Milwaukee, WI) were used as adsorbates in this study. They were selected for this study because they represent commonly encountered phenolic pollutants in water and wastewater treatment. Meanwhile, the three phenolic compounds have various molecular structures. Phenol is two dimensional while 2-methylphenol and 2-ethylphenol are three dimensional. Table 2 provides the molecular dimensions, COP, water solubility and acid-ity constant for these adsorbates.

### 2.4.2. Adsorbents

The activated carbon sample with best porous characteristics developed from activation experiments was used to conduct isotherm adsorption. Furthermore, F400 (Filtrisorb 400) was chosen as a typical commercial GAC (Calgon Carbon Corporation, Pittsburgh, PA) for comparison. This bituminous base activated carbon is selected because it represents commonly used commercial GAC for organic compounds removal in water treatment. Prior to use in the study, the GAC was rinsed several times with de-ionized water to remove the fines, dried in an oven at 105 °C for 2 days, and then stored in a desiccator until use.

### 2.4.3. Isotherm procedure

Constant-dose bottle point isotherms adsorption experiments with two different initial concentrations of adsorbate (200 and 1000 mg/L) were performed. Accurately weighed (±0.1 mg) masses of activated carbon were placed in each 125 ml glass-amber bottle. Two adsorption conditions were considered, anoxic (absence of molecular oxygen) isotherms and oxic (presence of molecular oxygen) isotherms. The anoxic condition was attained by purging the adsorbents with nitrogen for about 1 min, twice a day for 3 days; moreover, the isotherm solution prior to the addition of the adsorbate was also purged with nitrogen to expel any dissolved oxygen and finally each isotherm bottle was completely filled with

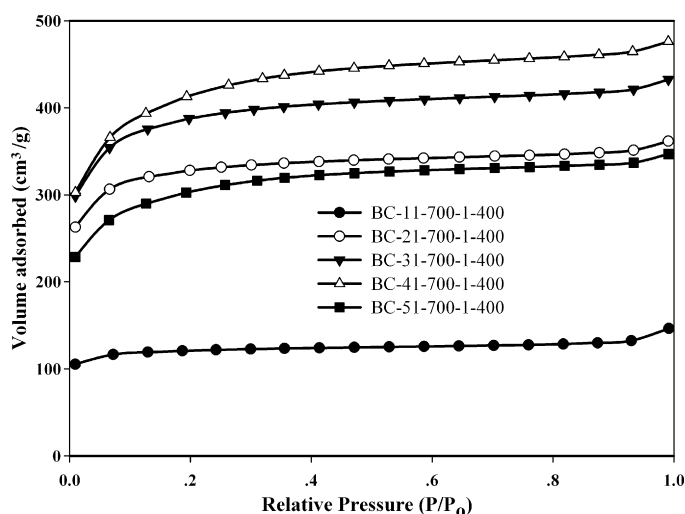
the adsorbate solution. For the oxic isotherms 100 ml of adsorbate solution was added in each 125 ml bottle and the head space purged by oxygen gas for a minute in order to ensure no oxygen limitation is attained during the adsorption isotherm equilibration time. Two blanks per set bottles served as controls during the isotherm experiments. The sealed bottles were then placed in a rotary tumbler for 2 weeks at 23 ± 1 °C [41]. After equilibration, all samples were filtered using 0.45 μm nylon filters (Micron Separation, Inc.) and analyzed for adsorbate concentration using a UV–vis spectrophotometer (UV mini 1240, Shimadzu, Japan) at a wavelength of 270.5 nm.

## 3. Results and discussion

### 3.1. Effect of KOH/coal ratio

Some studies have shown that this factor has a significant effect on the micropore volume as well as the micropore size distribution [24,25,27,42–44]. In order to investigate the optimum KOH/coal ratio, the ratio was varied in the range 1/1 to 5/1 while keeping the other factors constant (activation temperature 700 °C, activation time 1 h and nitrogen flow rate 400 ml, respectively). Fig. 1 presents nitrogen adsorption isotherms of activated carbons prepared with different KOH/coal ratios. All samples exhibit type I isotherms according to the IUPAC classification, characteristic of microporous solids. It is clear that the nitrogen adsorption capacity increased with increasing KOH/coal ratio from 1/1 to 4/1 ratio. However, nitrogen adsorption capacity for 5/1 ratio decreased significantly due to over activation. The pore structures of activated carbon samples are shown in Table 3. The BET surface area was, in some cases, larger than GAC F400.

It is known that one of the most important values for controlling oligomerization for activated carbon is the PSD [15]. This parameter was calculated from the nitrogen adsorption isotherms. Table 3



**Fig. 1.** Nitrogen adsorption isotherms (77 K) of the activated carbons prepared using different KOH/coal ratio (activation temperature = 700 °C, activation time = 1 h and nitrogen flow rate = 400 ml/min).

**Table 3**  
Pore structure of F400 and activated carbons prepared with different KOH/ coal ratio.

Sample	KOH/coal ratio	$S_{\text{BET}}^{\text{a}}$ ( $\text{m}^2/\text{g}$ )	$V_{\text{micro}}^{\text{b}}$ ( $\text{cm}^3/\text{g}$ )	$V_{\text{meso}} + V_{\text{macro}}^{\text{c}}$ ( $\text{cm}^3/\text{g}$ )	$V_{\text{Total}}^{\text{d}}$ ( $\text{cm}^3/\text{g}$ )	Micropore percentage <sup>e</sup> (%)
BC-11-700-1-400	1:1	354	0.162	0.064	0.226	71.6
BC-21-700-1-400	2:1	971	0.405	0.154	0.559	72.4
BC-31-700-1-400	3:1	1158	0.434	0.235	0.669	64.9
BC-41-700-1-400	4:1	1247	0.389	0.348	0.737	52.8
BC-51-700-1-400	5:1	920	0.295	0.242	0.537	55.0
F400	–	993	0.373	0.242	0.615	60.7

<sup>a</sup>  $S_{\text{BET}}$  is BET surface area.

<sup>b</sup>  $V_{\text{micro}}$  is the volume of micropore.

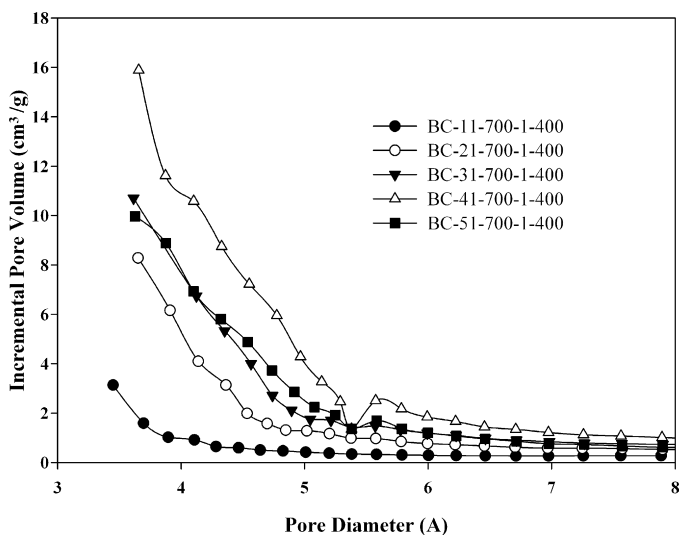
<sup>c</sup>  $V_{\text{meso}} + V_{\text{macro}} = V_{\text{Total}} - V_{\text{micro}}$ .

<sup>d</sup>  $V_{\text{Total}}$  is the total pore volume.

<sup>e</sup> Micropore percentage =  $V_{\text{micro}}/V_{\text{Total}} \times 100\%$ .

contains the micropore volume, total pore volume and micropore percentage values corresponding to the activated carbons prepared using different KOH/coal ratios. It is remarkable to note that the lower the KOH/coal ratio the higher the micropore volume percentage, up to a KOH/coal ratio 2/1 (see Table 3), reflecting a decrease in the pore size. This result is further confirmed by the values of PSD (Fig. 2). Fig. 2 presents the pore size distributions obtained for these samples by applying the  $T$ -plot equation to the  $\text{N}_2$  data. Clear differences can be seen between samples using different KOH/coal ratio. It can be observed that the higher the KOH/coal ratio the wider the PSD and the higher the critical pore diameter. In addition, it is shown that the sample with the narrowest PSD is the sample prepared with KOH/coal ratio 1/1 and 2/1, which agrees with the micropore volumes percentage calculated from the micropore volume and the total pore volume. However, as shown in Table 3, the BET surface area ( $354 \text{ m}^2/\text{g}$ ) and micropore volume ( $0.162 \text{ cm}^3/\text{g}$ ) of the sample using KOH/coal ratio 1/1 are significantly lower than F400. On the other hand, the BET surface area ( $971 \text{ m}^2/\text{g}$ ) and micropore pore volume ( $0.405 \text{ cm}^3/\text{g}$ ) of the sample with a 2/1 ratio are similar or better than F400.

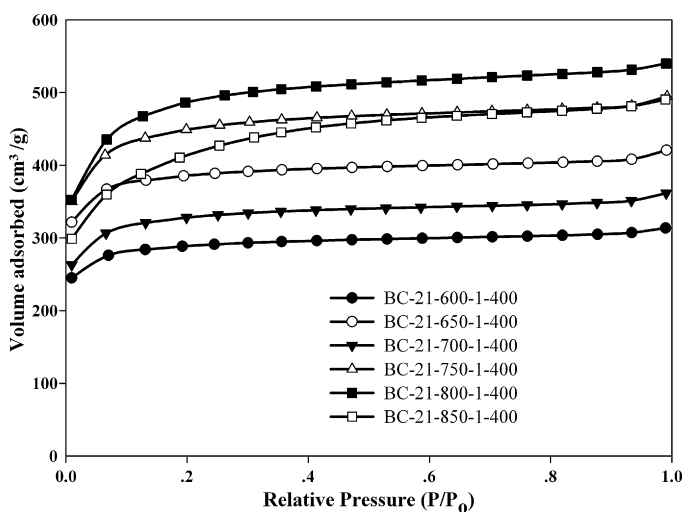
Consistent with the findings of previous studies [21–25], it is evident that the KOH/coal ratio used in the activation process controls the PSD of the resulting activated carbon. In addition, the sample with the most ideal BET surface area and microporosity is the sample with a 2/1 ratio (see Table 3).



**Fig. 2.** Pore size distribution of the activated carbons prepared using different KOH/coal ratio (activation temperature =  $700^\circ\text{C}$ , activation time = 1 h and nitrogen flow rate =  $400 \text{ ml}/\text{min}$ ).

### 3.2. Effect of activation temperature

The activation temperature was varied from  $600$  to  $850^\circ\text{C}$  while keeping the rest of the parameters constant (KOH/coal (2/1), activation time (1 h) and nitrogen flow rate ( $400 \text{ ml}/\text{min}$ )). Nitrogen adsorption isotherms measured at  $77 \text{ K}$  on samples activated at different activation temperatures are shown in Fig. 3. It can be seen again that all isotherm corespond to Type I. The steep slopes of the isotherm lines in the area of low relative pressure indicate that plenty of micropores were developed and all samples are microporous. BC-21-850-1-400 sample shows a special behavior. It can be seen that the shape of the isotherm for this sample changes drastically, indicating the presence of mesopores and a much lower amount of micropores. It can also be observed in Fig. 3 that higher activation temperature produces wider PSD (the slope of the nitrogen adsorption isotherms becomes lower with the temperature). Table 4 shows the pore structure parameters of samples prepared using different activation temperatures. It can be seen that for activation temperatures from  $650$  to  $850^\circ\text{C}$ , the BET surface area of all the samples were larger than F400. However, as the temperature was decreased below  $650^\circ\text{C}$  the BET surface area decreased significantly as a consequence of lack of proper activation of the resulting material. It can be observed from Table 4 that the higher the activation temperature the lower is the percent of micropore volume. This is due to the presence of more mesopores and macropores which is expected from the wider PSD. It seen from Table 4 that the samples prepared at  $650^\circ\text{C}$  (BC-21-650-1-400) had higher microporosity than other samples prepared at other activating



**Fig. 3.** Nitrogen adsorption isotherms ( $77 \text{ K}$ ) of the activated carbons prepared using different activation temperature (KOH/coal = 2/1, activation time = 1 h and nitrogen flow rate =  $400 \text{ ml}/\text{min}$ ).



**Table 4**  
Pore structure of activated carbons prepared with different activation temperature.

Sample	Temperature (°C)	$S_{\text{BET}}$ (m <sup>2</sup> /g)	$V_{\text{micro}}$ (cm <sup>3</sup> /g)	$V_{\text{meso}} + V_{\text{macro}}$ (cm <sup>3</sup> /g)	$V_{\text{Total}}$ (cm <sup>3</sup> /g)	Micropore percentage (%)
BC-21-600-1-400	600	845	0.381	0.104	0.485	78.4
BC-21-650-1-400	650	1128	0.507	0.144	0.651	77.9
BC-21-700-1-400	700	971	0.405	0.154	0.559	72.4
BC-21-750-1-400	750	1335	0.529	0.236	0.765	69.2
BC-21-800-1-400	800	1451	0.516	0.319	0.835	61.8
BC-21-850-1-400	850	1285	0.329	0.430	0.759	43.4

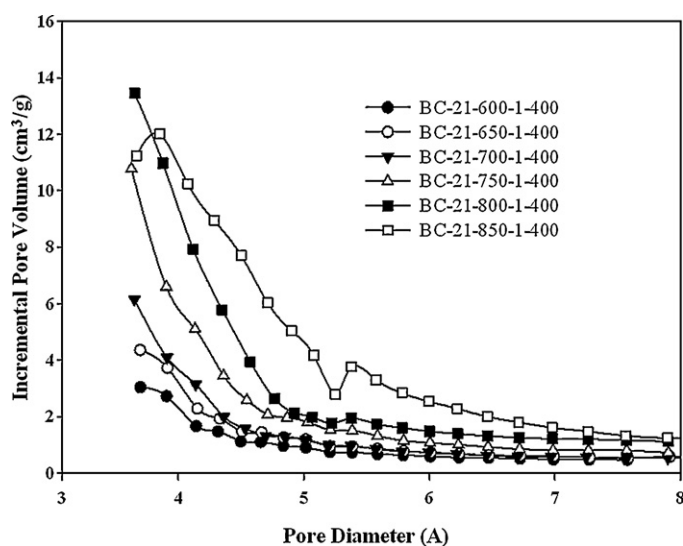
temperatures. These results can be confirmed from the PSD calculated by the  $T$ -plot method (Fig. 4).

Fig. 4 shows the PSD of samples prepared at different activation temperatures. As expected considering the micropore volume percentage, the samples prepared from 600 to 850 °C show a decrease in the critical pore size diameter with the activation temperature. This decrease is progressive for the all six temperatures.

In summary, the activating temperature is a very significant factor in controlling the porosity of carbon samples. As has been previously indicated, the optimal sample for controlling oligomerization depends on having high micropore percentage, narrow critical pore size and large BET surface area. Therefore, BC-21-650-1-400 presents a more suitable structure required for controlling oligomerization. The result shows that the optimum activating temperature should be 650 °C. A higher activating temperature gives a lower micropore percentage as well as wide PSD. Furthermore, a lower activation temperature provides a lower BET surface area than the conventional GAC F400.

### 3.3. Effect of activation time

In order to determine the optimum activation time for carbon samples, the activation time was varied from 0.5 to 4 h while keeping the rest of the parameters constant (KOH/coal (2/1), activation temperature (650 °C) and nitrogen flow rate (400 ml/min)).  $N_2$  adsorption isotherms and pore structure characteristics for the samples prepared at different activation times are shown in Fig. 5 and Table 5, respectively. As can be seen in Fig. 5,  $N_2$  adsorption increases with increase of activation time (from 0.5 to 2 h). However,  $N_2$  adsorption decreases with increase of activation time (from 2 to 4 h). On the other hand, Fig. 5 shows that nitrogen adsorption for the three samples prepared with 0.5, 1 and 3 h are



**Fig. 4.** Pore size distribution of the activated carbons prepared using different activation temperature (KOH/Coal=2/1, activation time=1 h and nitrogen flow rate = 400 ml/min).

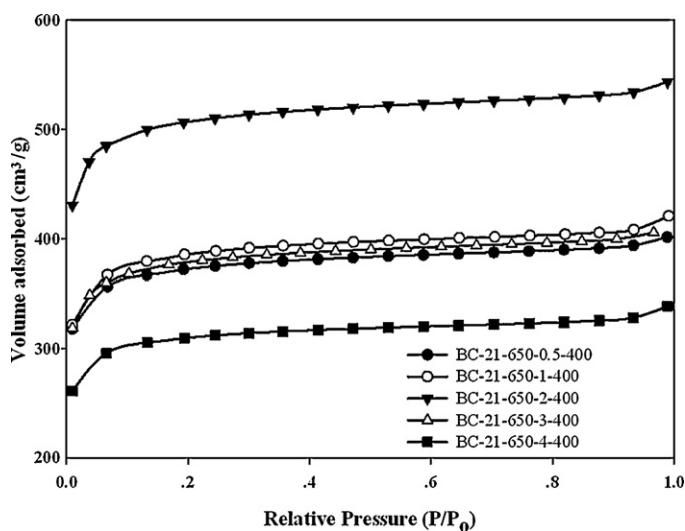
very similar. It can be seen in Table 5 that, the differences in the micropore percentages for all samples are very small. Basis on that, it means the effect of the activation time at this activation temperature (650 °C) on the micropore percentage is not particularly significant. However, sample developed with activation time of 2 h has the largest micropore volume, biggest micropore percentage and biggest BET surface area. Therefore, the activation time of 2 h could be considered to be optimum for the preparation of a good activated carbon with high micropore percentage as well as high BET surface area.

### 3.4. Effect of nitrogen flow rate

Samples were prepared using a KOH/coal ratio of 2:1, activation temperature at 650 °C for 2 h under nitrogen flow rate varying from 100 to 600 ml/min, studying the influence of gas flow rate on porosity of activated samples. Fig. 6 shows nitrogen adsorption isotherms for carbon samples prepared using different nitrogen flow rate. It is evident that the nitrogen adsorption increased with increase of flow rate (from 100 to 400 ml/min) and then decreased for flowrate of 600 ml/min. Table 6 displays the porous structure values of activated samples developed under four different  $N_2$  flow rates. As can be observed, the sample with highest BET surface area and highest micropore percentage is obtained using nitrogen flow rate of 400 ml/min.

### 3.5. Additional consideration

The above results indicate that BC-21-650-2-400 sample, which is prepared with activation condition (KOH/coal = 2/1, activation temperature = 650 °C, activation time = 2 h and nitrogen flow rate = 400 ml/min), has the best potential for controlling



**Fig. 5.** Nitrogen adsorption isotherms (77 K) of the activated carbons prepared using different activation time (KOH/coal = 2/1, activation temperature = 650 °C and nitrogen flow rate = 400 ml/min).

**Table 5**  
Pore structure of activated carbons prepared with different activation time.

Sample	Time (h)	$S_{\text{BET}}$ (m <sup>2</sup> /g)	$V_{\text{micro}}$ (cm <sup>3</sup> /g)	$V_{\text{meso}} + V_{\text{macro}}$ (cm <sup>3</sup> /g)	$V_{\text{Total}}$ (cm <sup>3</sup> /g)	Micropore percentage (%)
BC-21-650-0.5-400	0.5	1085	0.499	0.122	0.621	80.3
BC-21-650-1-400	1	1128	0.507	0.144	0.651	77.9
BC-21-650-2-400	2	1476	0.684	0.157	0.841	81.3
BC-21-650-3-400	3	1107	0.499	0.139	0.638	78.3
BC-21-650-4-400	4	903	0.415	0.109	0.524	79.2

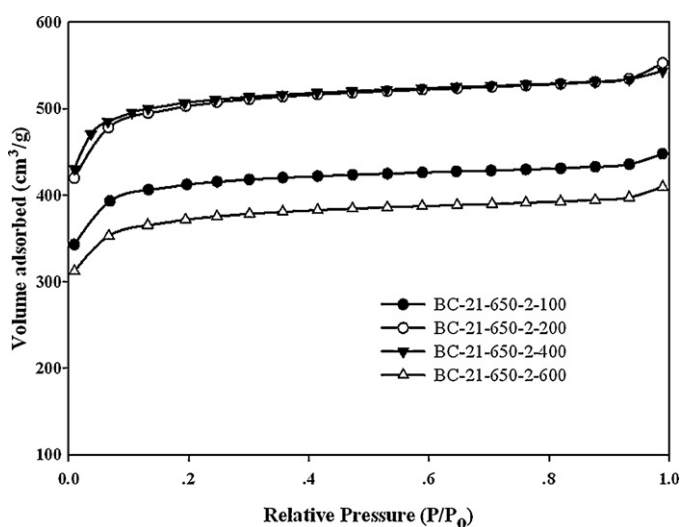
**Table 6**  
Pore structure of activated carbons prepared with different nitrogen flow rate.

Sample	Flow rate (ml/min)	$S_{\text{BET}}$ (m <sup>2</sup> /g)	$V_{\text{micro}}$ (cm <sup>3</sup> /g)	$V_{\text{meso}} + V_{\text{macro}}$ (cm <sup>3</sup> /g)	$V_{\text{Total}}$ (cm <sup>3</sup> /g)	Micropore percentage (%)
BC-21-650-2-100	100	1203	0.534	0.158	0.692	77.1
BC-21-650-2-200	200	1472	0.676	0.179	0.855	79.0
BC-21-650-2-400	400	1476	0.683	0.158	0.841	81.3
BC-21-650-2-600	600	1091	0.480	0.153	0.633	75.8

**Table 7**  
Pore structure of activated carbons prepared with extra conditions.

Sample	KOH/coal ratio	Temperature (°C)	$S_{\text{BET}}$ (m <sup>2</sup> /g)	$V_{\text{micro}}$ (cm <sup>3</sup> /g)	$V_{\text{Total}}$ (cm <sup>3</sup> /g)	Micropore percentage (%)
BC-31-650-2-400	3/1	650	786	0.293	0.460	63.7
BC-31-700-2-400	3/1	700	1158	0.434	0.669	64.9
BC-31-750-2-400	3/1	750	1426	0.387	0.846	45.8
BC-31-800-2-400	3/1	800	1462	0.359	0.874	41.1
BC-41-650-2-400	4/1	650	954	0.332	0.555	59.9
BC-41-700-2-400	4/1	700	1247	0.389	0.736	52.8
BC-41-750-2-400	4/1	750	1416	0.447	0.841	53.1
BC-41-800-2-400	4/1	800	1862	0.353	1.106	31.9

oligomerization of phenolic compounds. And the yields of this carbon sample can reach up to 78%. Other samples provide low micropore percentage and/or low BET surface area. However, to make sure all possibilities have been already taken into account, the interaction between KOH/coal ratio, activation temperature, activation time and nitrogen flow rate should be considered. It can be seen from previous sections (Sections 3.3 and 3.4) that activation time and nitrogen flow rate do not have significant influence on the micropore percentage which is the most important parameter for controlling oligomerization. Therefore, these two parameters can be set at 2 h and 400 ml/min. Finally, a series of samples were prepared using KOH/coal ratios of 3/1 and 4/1 for activation temperatures ranging from 650 to 800 °C. Ratios 1/1 and 5/1 were not



**Fig. 6.** Nitrogen adsorption isotherms (77 K) of the activated carbons prepared using different nitrogen flow rate (KOH/coal=2/1, activation temperature=650 °C and activation time=2 h).

considered because these ratios produced either low BET surface area or low micropore percentage (see Table 3). The specific porous structures for the prepared samples are displayed in Table 7. It can be observed that although those samples present quite high BET surface areas, the micropore percentages of those samples are too low. Therefore, among all the samples prepared, the sample with the best micropore percentage and BET surface area is BC-21-650-2-400. Thus, the optimum activation condition is by using a KOH/coal ratio of 2/1, an activation temperature of 650 °C, an activation time of 2 h and a nitrogen flow rate of 400 ml/min. This carbon will be referred to as Carbon<sub>exp</sub>. Based on the titration test, the Carbon<sub>exp</sub> was found to be an acidic carbon with total acidity and total basicity are 0.54 and 0 meq/g, respectively. In contrast, the total acidity and total basicity for F400 is 0.15 and 0.475 meq/g. On the other hand, the values of pH<sub>pzc</sub> for Carbon<sub>exp</sub> and F400 are 3.4 and 7.1, respectively.

### 3.6. Adsorption isotherm of phenolic compounds

Anoxic and oxidic adsorption isotherms of phenol, 2-methylphenol and 2-ethylphenol on Carbon<sub>exp</sub> were investigated to examine the practical consequences of activation on hampering oligomerization. In order to provide a comparative study, these adsorption isotherms were conducted on Calgon F400. The isotherm data are modeled using the Myers isotherm equation,  $C_{e,i} = (q_{e,i}/H_i) \exp(K_i q_{e,i}^{P_i})$  ( $q_{e,i}$  is equilibrium surface concentration of solute  $i$ ;  $C_{e,i}$  is equilibrium liquid-phase concentration of solute  $i$ ;  $H_i$ ,  $K_i$ , and  $P_i$  are regression parameters of solute  $i$ ). Myers equation was chosen because it follows Henry's law equation at low coverage. This criterion is very important when predicting Multicomponent adsorption systems by the ideal adsorption theory (IAST) because of the integration limits in the Gibbs adsorption equation [16]. Furthermore, the Myers equation has three regression parameters that can ensure better data fit. The equilibrium surface concentration  $q_{e,i}$  is calculated from the mass balance equation around the isotherm bottle,  $q_{e,i} = ((C_{o,i} - C_{e,i})v)/m$  ( $C_{o,i}$  is

**Table 8**  
Myers isotherm equation parameters.

Adsorbate	Adsorbent	Conditions	$H$ (L/g)	$K$ (mmol/g)	$P$	SSRE	$R^2$
Phenol	F400	Oxic	16,878.9	4.75	0.653	0.24	0.982
	F400	Anoxic	16,878.9	5.88	0.633	0.52	0.943
	Carbon <sub>exp</sub>	Oxic	16,878.9	5.55	0.518	0.27	0.982
	Carbon <sub>exp</sub>	Anoxic	16,878.9	6.33	0.429	0.15	0.992
2-Methylphenol	F400	Oxic	24,337.0	5.13	0.501	0.224	0.977
	F400	Anoxic	24,337.0	7.11	0.389	0.15	0.984
	Carbon <sub>exp</sub>	Oxic	24,337.0	4.68	0.574	0.31	0.981
	Carbon <sub>exp</sub>	Anoxic	24,337.0	5.44	0.474	0.243	0.962
2-Ethylphenol	F400	Oxic	22,000	4.18	0.616	0.399	0.978
	F400	Anoxic	22,000	5.23	0.568	0.36	0.961
	Carbon <sub>exp</sub>	Oxic	22,000	1.59	1.5421	0.79	0.941
	Carbon <sub>exp</sub>	Anoxic	22,000	2.66	1.093	0.15	0.989

initial liquid-phase concentration of solute  $i$ ;  $C_{e,i}$  is the final liquid phase concentration of solute  $i$ ;  $m$  is the mass of adsorbent;  $V$  is the adsorbate volume). The adsorbate volume,  $V$ , was 0.125 L for the anoxic isotherms and 0.1 L for the oxic isotherms. Evaluation of the Myers equation was done by calculating the sum of squares of relative error (SSRE),  $SSRE = \sum ((q_{e,i,observed} - q_{e,i,predicted})/q_{e,i,observed})^2$ . The correlation parameters for the Myers equation are presented in Table 8.

The results of oxic and anoxic adsorption isotherm tests of phenol, 2-methylphenol and 2-ethylphenol on the F400 and Carbon<sub>exp</sub> are presented in Figs. 7–9, respectively. The data shown in Fig. 7 indicate that the adsorptive capacity of F400 for phenol under oxic

conditions increased significantly as compared to anoxic data due to the presence of molecular oxygen. However, the presence of molecular oxygen in the test environment did not have a tremendous impact on the adsorptive capacity of Carbon<sub>exp</sub> for phenol (see Fig. 7). A similar behavior is seen for 2-methylphenol and 2-ethylphenol (see Figs. 8 and 9). Furthermore, the difference in the 2-methylphenol adsorptive capacity obtained for F400 under oxic and anoxic conditions is more significant than that for phenol and 2-ethylphenol. However, for Carbon<sub>exp</sub>, the adsorption capacity under both oxic and anoxic conditions is nearly identical. The major differences only occurred at low  $C_e$  values, i.e., at high carbon dosage.

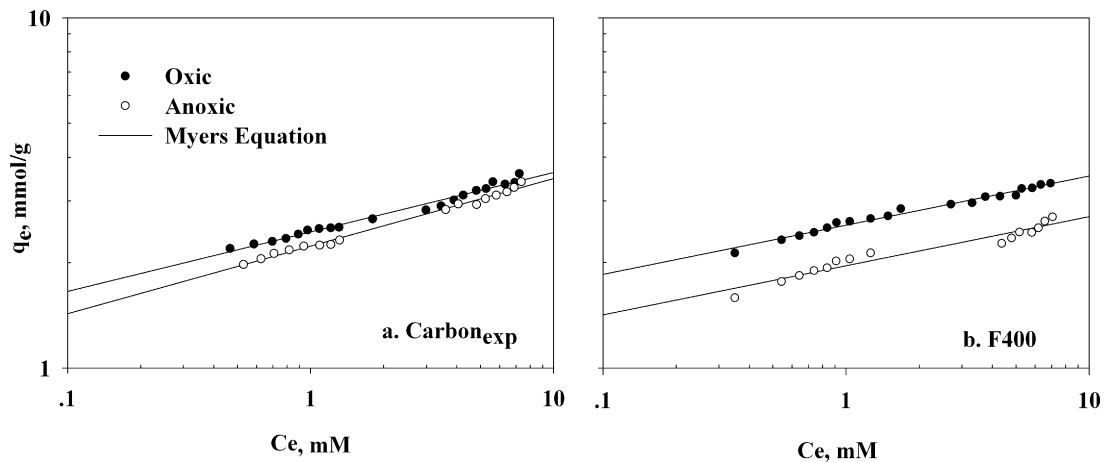


Fig. 7. Single solute adsorption isotherm of phenol.

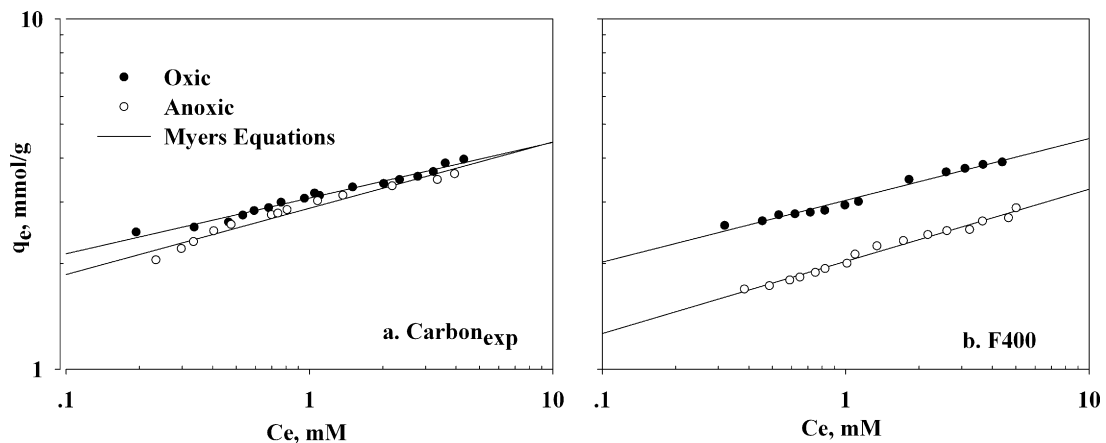


Fig. 8. Single solute adsorption isotherm of 2-methylphenol.

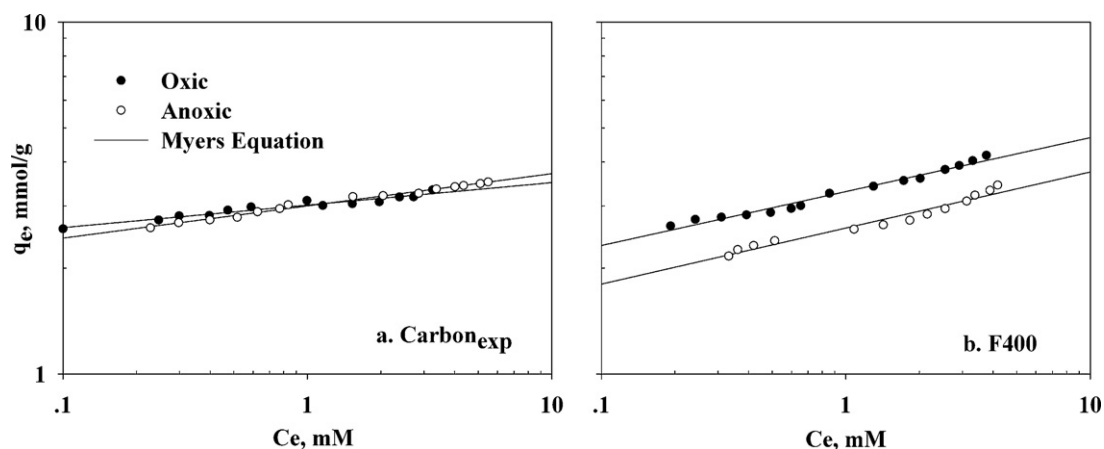


Fig. 9. Single solute adsorption isotherm of 2-ethylphenol.

A comparison of anoxic and oxic adsorptive capacity of phenol, 2-methylphenol and 2-ethylphenol on the two adsorbents studied at two equilibrium concentrations of 0.5 and 5 mM is shown in Table 9. These two limits were selected in order to represent the low and high carbon dosage. It can be seen that the difference between anoxic and oxic condition achieved with F400 is highly significant as compared to Carbon<sub>exp</sub>. Furthermore, it can be seen that higher difference at 0.5 mM can be observed than that at 5 mM and the difference for 2-methylphenol is larger than 2-ethylphenol and phenol. This suggests that 2-methylphenol is easier to have oligomerization phenomenon in comparison to phenol and 2-ethylphenol. The distinct performance can be attributed to the differences of critical oxidation potential (COP) of these phenolic compounds. The COP for 2-methylphenol is 1.040 V while that for phenol and 2-ethylphenol is 1.089 and 1.080 V (see Table 2). As shown in Table 9, the oxic adsorptive capacity of phenol on F400 compared to the anoxic capacity increased from 32.2% to 32.7% for an equilibrium concentration of 5 and 0.5 mM, respectively. Furthermore, in the case of 2-ethylphenol, for the equilibrium adsorbate concentrations of 5 and 0.5 mM, the adsorptive capacities of F400 exhibited under oxic condition are 25.1% and 33.5% higher than the anoxic adsorptive capacity, respectively. This difference in capacity is much more pronounced for 2-methylphenol. The oxic adsorption capacity for 2-methylphenol compared to the anoxic adsorptive capacity on F400 increases from 42.3% to 52.5% for an equilibrium concentration of 5 and 0.5 mM, respectively.

The Carbon<sub>exp</sub> exhibited very slight differences between the oxic and anoxic adsorption isotherms for the three phenolic compounds as compared to F400 (see Table 9). This indicates that there is no considerable change between both conditions. In other words, it is safely to assume that Carbon<sub>exp</sub> has a significant positive impact on hampering oligomerization of phenolic compounds on its surface. Especially, in case of 2-ethylphenol, the capacity difference on Carbon<sub>exp</sub> under both conditions (low and high carbon dosage) are less than 2.5%. The main reason for this distinct performance is that

Carbon<sub>exp</sub> had a significant higher micropore percentage than F400. In case of Carbon<sub>exp</sub>, forming larger stable oligomerized molecular products is much more difficult than F400. This could be attributed to the molecular dimensions of the adsorbates and the critical pore size of the adsorbent. For example, F400 has a broad PSD from 10 to 500 Å and oligomerization would not be constricted by its PSD. In contrast, Carbon<sub>exp</sub> has a critical pore diameter of 10 Å and a narrow PSD. The second widest dimensions of phenol, 2-methylphenol and 2-ethylphenol are 4.17, 5.32 and 5.70 Å, respectively. Therefore, it is just possible for phenol to form dimers, while formation of trimers is impossible. In case of 2-methylphenol and 2-ethylphenol, it is even impossible for them to get oligomerized. On the other hand, Vidic et al. [8] have postulated that oxygen-containing basic surface functional groups slightly promote oligomerization of phenolic compounds. Therefore, the behavior difference between Carbon<sub>exp</sub> and F400 may be partially due to the difference of the total basicity. The total basicity (0 meq/g) for Carbon<sub>exp</sub>, as determined by the titration method, was much lower than that of the GAC F400 (0.475 meq/g). This shows that GAC F400 has more basic surface functional groups than Carbon<sub>exp</sub> that could promote oligomerization of phenolic compounds.

It is worth to note that the equilibrium adsorptive capacity of Carbon<sub>exp</sub> for all three phenolic compounds was higher than F400 under anoxic adsorption condition (see Table 9). Some studies have shown that the effect of surface functional group content on phenolic compounds adsorptive capacity in the absence of molecular oxygen can be negligible [3,8]. Therefore, the results can be mainly attributed to the following physical reasons. Firstly, these results illustrate that higher BET surface area of Carbon<sub>exp</sub> can lead to higher adsorption than F400. Secondly, this phenomenon can also be elucidated by the comparison of the microporosity of the two adsorbents. The microporosity of F400 is only 60.7%, while for Carbon<sub>exp</sub> is 81.8%. Therefore, the adsorption capacity of Carbon<sub>exp</sub> is higher than F400 because micropores are primarily responsible for the adsorption.

Table 9  
Comparison of anoxic and oxic adsorption capacity.

	C <sub>e</sub> (mM)	Phenol			2-Methylphenol			2-Ethylphenol		
		Anoxic q <sub>e</sub> (mmol/g)	Oxic q <sub>e</sub> (mmol/g)	Δq <sub>e</sub> (%)	Anoxic q <sub>e</sub> (mmol/g)	Oxic q <sub>e</sub> (mmol/g)	Δq <sub>e</sub> (%)	Anoxic q <sub>e</sub> (mmol/g)	Oxic q <sub>e</sub> (mmol/g)	Δq <sub>e</sub> (%)
F400	0.5	1.854	2.461	32.7	1.760	2.683	52.5	2.146	2.865	33.5
	5	2.401	3.174	32.2	2.828	4.027	42.3	4.001	5.010	25.1
Carbon <sub>exp</sub>	0.5	1.943	2.182	12.3	2.552	2.796	9.54	2.844	2.877	1.16
	5	3.195	3.010	6.12	4.185	4.341	3.70	3.537	3.626	2.53



#### 4. Conclusion

This study has shown that chemical activation of bituminous coal by KOH provided a highly microporous and BET surface area  $\text{Carbon}_{\text{exp}}$  which could effectively hamper oligomerization of phenolic compounds.

It was also observed that over activation resulted in higher BET surface area but very poor microporosity. Thus, it was seen that the best activated carbon for oligomerization control is the one with which possesses the best BET surface area and microporosity. The best conditions for preparing a  $\text{Carbon}_{\text{exp}}$  seems to be a moderate KOH/coal ratio (2/1), a medium activation temperature (650 °C), a medium activation time (2 h) with a 400 ml/min nitrogen flow rate. Using these conditions in a single activation process, an activated carbon is developed that can effectively hamper oligomerization of phenolic compounds on its surface.

Finally, this work has displayed the improvement of the experimentally prepared activated carbon as compared to the conventional bituminous GAC Filtrasorb 400. It was seen that the single solute adsorption on  $\text{Carbon}_{\text{exp}}$  with a higher micropore percentage and more acidic surface characteristics presents an obvious smaller adsorptive capacity difference between oxic and anoxic isotherms than commercial GAC F400 which has a lower micropore percentage and higher basic surface content. Meanwhile, it was seen that the  $\text{Carbon}_{\text{exp}}$  has higher adsorptive capacity than F400 under anoxic conditions. These results has demonstrated that the  $\text{Carbon}_{\text{exp}}$  developed in this study is not only more effective in hampering oligomerization as compared to commercial GAC but also leads to better adsorptive capacity.

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