

The effect of functional groups on oligomerization of phenolics on activated carbon

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Abstract

Adsorption of seven phenolic compounds, namely phenol, 2-methylphenol, 2-ethylphenol, 2-chlorophenol, 2-nitrophenol, 4-chlorophenol, and 4-nitrophenol on granular activated carbon (GAC) F400 and two activated carbon fibers (ACFs), ACC-10 and ACC-15 were conducted to study the impact of functional groups on oligomerization. Single solute adsorption and binary solute adsorption were conducted under anoxic (absence of molecular oxygen) and oxic (presence of molecular oxygen) conditions at 23 ± 1 °C. For F400, the critical oxidation potential (COP), influenced by substitution of functional group, was found to be a limiting factor in oligomerization of adsorbates. For ACC-10, which has narrow pore size distribution (PSD) and small critical pore diameter (8.0 Å), only phenol and 2-methylphenol showed occurrence of oligomerization under oxic conditions. The degree of oligomerization under oxic conditions was related to the PSD of the adsorbent. The micro-pore diameter of the ACFs effectively reduced the oligomerization process. The oxic and anoxic binary adsorption isotherms of phenol/2-ethylphenol and 2-methylphenol/2-nitrophenol on ACC-10 overlapped indicating hampering of oligomerization by the limited micro-pore diameter of ACFs. The Ideal Adsorbed Solution Theory (IAST), using the Myers equation for correlating the single-solute anoxic isotherms, well predicted both anoxic and oxic binary isotherms.

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1. Introduction

Phenolic compounds are toxic to humans and aquatic life [1]. Some phenols, like chlorophenolic compounds, have been prescribed as priority pollutants by the US Environmental Protection Agency (EPA) [2]. Activated carbon adsorption has been used to remove phenolic compounds in the past decades [3–7]. The major advantage of activated carbon adsorption is that the solid adsorbent can easily be separated from the treated liquid or gas streams thus easy and flexible process operation as well as a reduction in process costs can be achieved, especially if the pollutants are to be recycled [8,9].

Adsorption on activated carbon adsorption is influenced by both the adsorbate and the adsorbent properties [10]. Carbons are essentially hydrophobic and display a strong affinity for organic molecules which have a limited solubility in water, like phenols [11]. Adsorption is a manifestation of complicated interactions

among the three components involved, i.e. the adsorbent, the adsorbate and the solvent. Normally, the affinity between the adsorbent and the adsorbate is the main interaction force controlling adsorption. However, the affinity between the adsorbate and the solvent (i.e. solubility) can also play a major role in adsorption. Hydrophobic compounds have low solubility and tend to be pushed to the adsorbent surface and hence are more adsorbable than hydrophilic compounds.

Phenolic compounds undergo oligomerization on the surface of activated carbon when molecular oxygen is present in the test environment. This has been confirmed by many researchers [12–15]. Phenolic radicals, formed from a phenol by the loss of a proton, form stable molecular products by coupling such as dimers. Dimers may couple with another phenolate radical to give a trimer and so forth [16]. Oligomerized phenols on the surface of the activated carbon are essentially irreversibly bound to the carbon surface [17]. As a consequence, the regeneration efficiency of activated carbon after oligomerization of phenolic compounds is low. Regeneration efficiency has been a major environmental concern in activated carbon usage. To enhance the efficiency of regeneration as well as to design

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the adsorption-desorption cycle in a fixed bed adsorber, the adsorption behavior of phenolic compounds with different functional groups has to be understood. Vidic et al. [18] studied the effect of functional groups on the adsorption of a wide variety of phenolic compounds on F400 granular activated carbon (GAC). In their study, molecular oxygen was found to promote the adsorptive capacity and they attributed this phenomenon to the oxidative coupling behavior that occurred on the surface of the adsorbents. They also found that the relative affinity of different adsorbates towards oxidative coupling on the GAC surface was related to their tendencies to undergo oxidative coupling, described by the critical oxidation potential (COP) [12]. Although the COP is not a precise redox potential, it was found that it agrees well with the ease of oxidation of these compounds.

Compared to the GAC traditionally used, activated carbon fibers (ACFs) have attracted increasing attention. ACFs had less than 5% surface oxides and contain very low amount of inorganic impurities. The low concentration of surface oxides results in limited surface chemistry effects and the low inorganic impurities results in minimal effects on pore development during the activation process, thus, ACFs always have narrow pore size distribution (PSD). Therefore, ACFs are more favorable than GAC for targeting the effects of PSD on oligomerization. According to our knowledge, no studies have been conducted to study the effect of functional groups on ACFs. The adsorbate structure relative to the pore diameter of ACFs is prominent in better understanding the adsorption on this kind of materials. For phenolic compounds, the methyl-, ethyl-, chloro- and nitro- are the most commonly encountered substitutional groups on parent phenol molecules. The existence of the functional groups offers parent phenol molecules different molecular dimensions and chemical properties.

The primary objective of this study is, therefore, to clarify the effect of functional groups of phenolic compounds on GAC and ACFs adsorption. The investigations were conducted under anoxic (absence of molecular oxygen) and oxic (presence of molecular oxygen) conditions. In order to achieve the goal of the primary objective, the following secondary objectives were evaluated: (1) impact of functional groups on adsorptive capacity under anoxic conditions; (2) impact of different functional groups on oligomerization; and (3) binary adsorption on ACC-10 and effectiveness of the Ideal Adsorbed Solution Theory (IAST) in prediction of the binary solute data.

2. Experimental materials and methods

2.1. Adsorbates

Seven commercially available phenolic compounds with different functional groups were studied. These compounds were phenol, 2-methylphenol ($-\text{CH}_3$), 2-ethylphenol ($-\text{CH}_2\text{CH}_3$), 2-chlorophenol ($-\text{Cl}$), 2-nitrophenol ($-\text{NO}_2$), 4-chlorophenol ($-\text{Cl}$), and 4-nitrophenol ($-\text{NO}_2$) (Aldrich Chemical Co. Inc., Milwaukee, WI). Table 1 provides the molecular dimensions, COP, water solubility and acidity constant for these adsorbates.

2.2. Adsorbents

F400 was chosen as a typical GAC (Calgon Carbon Corporation, Pittsburgh, PA). This bituminous base activated carbon is used primarily for the removal of taste and odor compounds and dissolved organic compounds in potable water treatment. Prior to use in the study, the GAC was rinsed several times with deionized (DI) water to remove the fines, dried in an oven at 105°C for 2 days to remove any moisture present, and then stored in a desiccator until use. Two microporous phenolic resin-based ACFs, designated as ACC-10 and ACC-15, were used in this study. They were received as twilled-weave fabrics. All the ACFs used in this study were dried in an oven at 105°C overnight, and then stored in a desiccator until use.

The pore volume, surface area and microporosity of F400, ACC-10 and ACC-15 and a detailed analysis of the PSD of the three adsorbents is provided by Lu and Sorial [19]. The critical pore diameter for ACC-10 is 8.0 \AA while that for ACC-15 is 12.8 \AA . On the other hand, F400 has a wide PSD which could be ranging from $4\text{--}800\text{ \AA}$.

2.3. Isotherm procedure

The bottle point method was used for conducting the adsorption isotherms at $23 \pm 1^\circ\text{C}$. Solutions of the adsorbates were prepared in autoclaved DI water buffered with $0.01\text{ M KH}_2\text{PO}_4$, and the pH was adjusted to 7.0 with a 10 M solution of NaOH. The total organic carbon concentration of the DI water used in this study was less than 0.2 mg L^{-1} . 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

Table 1
Physical properties of adsorbates

Adsorbates	Molecular dimensions (\AA) ^a	Critical oxidation potential (COP)	Water solubility ($\text{g L}_{\text{H}_2\text{O}}^{-1}$)	pK _a
Phenol	5.76×4.17	1.089	93	9.9
2-Methylphenol ($-\text{CH}_3$)	$5.68 \times 4.12 \times 1.63$	1.040	25	10.29
2-Ethylphenol ($-\text{CH}_2\text{CH}_3$)	$6.06 \times 5.62 \times 1.61$	1.080	5.3	10.14
2-Chlorophenol ($-\text{Cl}$)	5.76×4.82	1.095	28	8.56
2-Nitrophenol ($-\text{NO}_2$)	5.76×5.76	1.434	2.1	7.2
4-Chlorophenol ($-\text{Cl}$)	6.47×4.17	1.094	27	9.37
4-Nitrophenol ($-\text{NO}_2$)	6.84×4.17	1.433	17	7.15

^a Advanced Chemistry Development-ACDLabs 5.0 software, Toronto, Canada.

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 oxidic isotherms 100 mL of adsorbate solution was introduced in a 127.5 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. A detailed isotherm procedure is available elsewhere [20].

2.4. Adsorbate extraction

Adsorbents loaded with the phenolic compounds after adsorption isotherm experiments were extracted using the soxhlet apparatus. Carbon samples were extracted with methanol for 1 day followed by 3 days of extraction with dichloromethane (DCM). Extracts were then analyzed by using Agilent 6890 Series gas chromatography (GC) system equipped with DB-5 column and a flame ionization detector (FID). The extraction method used is described in other studies [21,22].

2.5. Analytical procedure

The Adsorbate concentrations at equilibrium for the single and binary solute system were measured by GC (Agilent 6890 Series; Agilent Technologies, Wilmington, DE). Chromatographic separation is conducted by using Agilent DB-5 column (30 m × 0.32 mm inside diameter with 0.25- μ m film thickness) and the eluted compounds were detected by FID. The injection port and detector temperature was set at 250 °C. The GC oven temperature was maintained at 35 °C for the first 2 min, then ramped to 100 °C at 8 °C min⁻¹ and kept at 100 °C for 2 min, and then ramped to 200 °C at 25 °C min⁻¹ and kept at 200 °C for 6 min. The flow rate of the carrier gas (N₂) was set at 2.0 mL min⁻¹. The detector makeup gas (N₂) flow rate was set at 52.5 mL min⁻¹. The flame gases hydrogen and air flow rates were set at 40 mL min⁻¹ and 450 mL min⁻¹, respectively. 4-Chlorophenol was used as an internal standard for 2-chlorophenol and 2-nitrophenol while 2-methylphenol was used as internal standard for 4-chlorophenol and 4-nitrophenol. At the conditions used, the retention time for phenol was 8.7 min, 2-chlorophenol 8.8 min, 2-methylphenol 10.2 min, 2-nitrophenol 11.8 min, 2-ethylphenol 12.1 min, 4-chlorophenol 13.2 min and 4-nitrophenol 16.2 min, respectively.

3. Results and discussions

Single solute adsorption of phenol, 2-methylphenol, 2-ethylphenol, 2-chlorophenol and 2-nitrophenol on F400, ACC-10 and ACC-15 was conducted under anoxic and oxidic conditions at 23 ± 1 °C. Adsorption of 4-chlorophenol and 4-nitrophenol was conducted on F400 and ACC-10. Two initial concentrations were conducted, namely, 200 mg L⁻¹ and 1000 mg L⁻¹. The use of two initial concentrations is mainly intended for confirming the reproducibility of the experimental results.

The Myers equation was used to simulate the single solute adsorption isotherms. Myers equation was chosen because it follows Henry's law equation at low coverage. This criterion is very important for accurately correlating the single solute system. The Myers equation is given by

$$C_{e,i} = \frac{q_{e,i}}{H_i} \times \exp(K_i q_{e,i}^{p_i}) \quad (1)$$

where $C_{e,i}$ is the liquid-phase concentrations at equilibrium (mM), $q_{e,i}$ is surface loading (mmol g⁻¹), H_i , K_i , and p_i are regression parameters.

The equilibrium surface loading, $q_{e,i}$, is calculated from the mass balance equation around the isotherm bottle

$$q_{e,i} = \frac{(C_{o,i} - C_{e,i}) \times V}{m} \quad (2)$$

where $C_{o,i}$ is initial liquid-phase concentration of solute i (mM), m is the mass of adsorbent (g), and V is the adsorbate volume (L). The adsorbate volume, V , was 0.1275 L for the anoxic isotherms and 0.1 L for the oxidic isotherms. Evaluation of the Myers equation was done by calculating the sum of squares of relative error (SSRE). Eq. (3) was used to estimate SSRE.

$$SSRE = \sum \left(\frac{q_{e,i}^{\text{observed}} - q_{e,i}^{\text{predicted}}}{q_{e,i}^{\text{observed}}} \right)^2 \quad (3)$$

Table 2 shows the Myers equation parameters for the single solute isotherms. The parameters for phenol, 2-methylphenol and 2-ethylphenol were published previously [19,20]. All the adsorption isotherms are found to be well described by Myers equation because of the low SSREs values. Anoxic and oxidic adsorption isotherms of nitrophenols (2- and 4-nitro) revealed that the presence of molecular oxygen had no significant influence on the adsorptive capacity and hence one set of Myers parameters are provided in Table 2. For the other adsorbates considered in this study, two sets of Myers equation parameters are given representing the anoxic and oxidic conditions.

3.1. Impact of functional groups on anoxic adsorptive capacity

The impact of functional groups on adsorptive capacity was examined through the adsorption isotherms of phenol, 2-methylphenol, 2-ethylphenol, 2-chlorophenol and 2-nitrophenol on F400, ACC-10 and ACC-15 under anoxic conditions. For easy comparison, all the experimental data for the five adsorbates is shown together in Fig. 1.

Under anoxic conditions, Fig. 1 indicates that for F400, the adsorptive capacity is in the order 2-nitrophenol > 2-chlorophenol > phenol > 2-ethylphenol > 2-methylphenol. It was believed that the main adsorption mechanism is the dispersion force between the activated carbon π -electrons of double bonds and π -electrons in phenols. For phenolic compounds, the existence of electron-withdrawing substitute, like -Cl and NO₂, favors adsorption onto activated carbon, while the existence of electron-donating substitute, like -CH₃ and CH₂CH₃, make adsorption unfavorable [2,23]. This is consistent with the results obtained in this study for 2-nitrophenol which showed highest

Table 2
Myers equation parameters for the different adsorbates

Adsorbate	Isotherm type	F400					ACC-10					ACC-15				
		H (L g ⁻¹)	K (mmol g ⁻¹) ^{-p}	P	SSRE	H (L g ⁻¹)	K (mmol g ⁻¹) ^{-p}	P	SSRE	H (L g ⁻¹)	K (mmol g ⁻¹) ^{-p}	P	SSRE			
Phenol [19]	Anoxic	8.49×10^9	19.3	0.207	0.005	1.36×10^{13}	24.9	0.207	0.083	1.03×10^{11}	20.9	0.159	0.016			
	Oxic	6.86×10^9	16.8	0.274	0.0084	9.57×10^7	11.9	0.375	0.075	1.43×10^{11}	19.4	0.193	0.006			
2-Methylphenol [20]	Anoxic	3.38×10^6	10.9	0.49	0.056	4.85×10^{11}	17.4	0.53	0.04	8.91×10^5	6.98	0.291	0.024			
	Oxic	3.06×10^{11}	15.5	0.529	0.026	4.36×10^9	10.6	0.797	0.013	4.48×10^{10}	10.6	0.65	0.047			
Ethylphenol [20]	Anoxic	2.95×10^8	14.5	0.42	0.0053	1.18×10^9	9.52	1.005	0.0041	1.86×10^{12}	16.8	0.426	0.017			
	Oxic	1.36×10^6	3.63	1.393	0.0054	1.49×10^6	7.07	0.914	0.0026	3.36×10^{12}	11.3	0.707	0.016			
Chlorophenol	Anoxic	2.65×10^9	16.1	0.296	0.075	4.93×10^{17}	30.8	0.29	0.099	3.54×10^{17}	28.5	0.193	0.012			
	Oxic	3.00×10^8	14.8	0.41	0.021	1.29×10^6	8.27	0.52	0.044	1.23×10^{36}	67.9	0.106	0.307			
4-Chlorophenol	Anoxic	5.45×10^6	5.08	1.03	0.077	7.91×10^{23}	41.8	0.25	0.098							
	Oxic	2.55×10^{13}	16.1	0.49	0.026	3.30×10^{12}	16.6	0.48	0.027							
2-Nitrophenol	Anoxic/oxic	3.52×10^{12}	21.1	0.25	0.083	3.50×10^{19}	32.4	0.33	0.084	1.17×10^{23}	39.8	0.141	0.012			
	Anoxic/oxic	3.37×10^{15}	30.4	0.144	0.044	8.83×10^{15}	27.0	0.26	0.037							

adsorptive capacity while 2-methylphenol and 2-ethylphenol showed the least.

Water solubility is another important factor in the adsorption process, it is generally expected that the lower the solubility of the compound, the easier it is pushed to the adsorbent surface and as a result, higher adsorptive capacity can be achieved. The water solubility for the phenolic compounds considered in this study is 2-nitrophenol < 2-ethylphenol < 2-methylphenol < 2-chlorophenol < phenol (see Table 1). Thus, 2-nitrophenol is again expected to have higher adsorptive capacity than the other adsorbates and that is manifested by the anoxic isotherms for F400. However, 2-ethylphenol did not show higher adsorptive capacity than 2-chlorophenol and 2-methylphenol was not higher than phenol. It is anticipated that the adsorbate molecular structure is another important factor that needs to be taken into account. 2-Methylphenol and 2-ethylphenol are three dimensional while 2-chlorophenol and phenol are two dimensional. However, the impact of the adsorbate dimensions on adsorption on F400 may be negligible since F400 has wide PSD, 4–800 Å. When considering adsorption of phenolics on ACFs, the adsorbate dimensions could be a limiting factor on adsorption.

For anoxic adsorption on ACC-10, Fig. 1 shows that the adsorptive capacity of 2-nitrophenol > 2-chlorophenol > 2-methylphenol > 2-ethylphenol. However, the differences were small as compared to F400. The trend was similar to F400 with exception of 2-methylphenol and 2-ethylphenol. Both of these adsorbates are three dimensional, however, 2-ethylphenol is larger than 2-methylphenol (see Table 1). The limited PSD of ACC-10 as compared to F400 restricted the adsorption of 2-ethylphenol due to its larger size as compared to 2-methylphenol. In case of phenol, it is interesting to note its distinct adsorption behavior on ACC-10. At liquid phase concentrations below 1 mM, the adsorptive capacity of phenol was equivalent to 2-methylphenol. At concentrations higher than 1 mM and less than 4 mM, phenol approached 2-chlorophenol and then approached 2-nitrophenol at concentrations greater than 4 mM. Phenol has the smallest molecular dimensions as compared to the other adsorbates. At low liquid phase concentrations (<1 mM), i.e., high carbon dosage, ACC-10 had enough sites for adsorption and thus the affinity of the adsorbates mainly depended on their solubility. At high liquid phase concentrations (>4 mM), i.e., low carbon dosage, there were less sites available on ACC-10, and hence the adsorption mainly depended on the molecular size of the adsorbate indicating that adsorbate water solubility is less important.

In case of ACC-15 under anoxic conditions, Fig. 1 shows that the adsorptive capacity of 2-nitrophenol > 2-chlorophenol > 2-ethylphenol > 2-methylphenol > phenol. However, at high carbon dosage, i.e., liquid concentrations greater than 1 mM, the adsorption capacities of 2-ethylphenol, 2-methylphenol, and phenol were similar. ACC-15 showed also the distinct adsorption behavior of phenol as outlined for ACC-10. However, the differences in adsorption capacities were more pronounced with ACC-15 as compared to ACC-10. This could be attributed to the larger critical pore diameter of ACC-15 as compared to ACC-10.

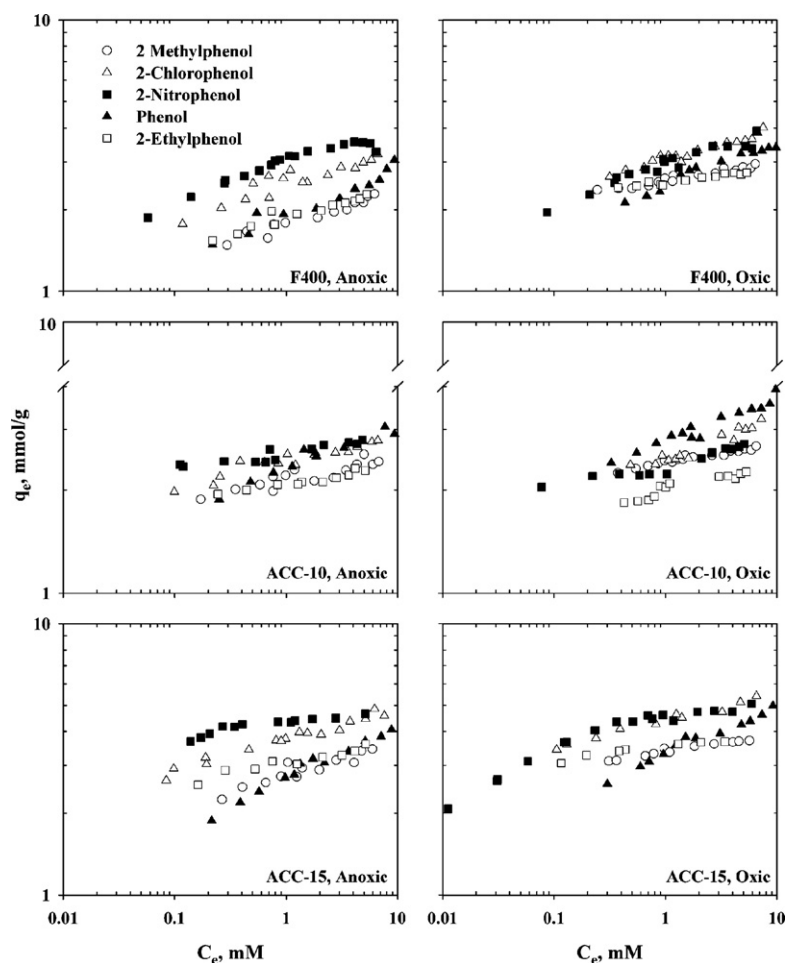


Fig. 1. Adsorption of phenolics on F400, ACC-10 and ACC-15.

On comparing F400 and ACC-10 under anoxic conditions, it is seen that the adsorption was steeper on F400 than ACC-10, especially for 2-nitrophenol. At concentration <1 mM, ACC-10 showed higher adsorptive capacity than F400, and the reverse when concentration >1 mM. The difference in surface chemistry between F400 and ACC-10 was excluded as the reason for this behavior because 2-nitrophenol did not show difference between anoxic and oxic on any adsorbent. The catalysis of F400 did not have impact for 2-nitrophenol. Actually, this could be attributed to the pore structure of these two adsorbent. In our previous study [19] we have shown that F400 and ACC-10 have similar BET surface area, micropore area and micropore volume. The major difference between F400 and ACC-10 was the fraction of microporosity. For F400, the microporosity is 60.7% with the micropores branching from the macropores; while for ACC-10, it is 95.9% and the micropores are directly on the surface [24,25]. The ACFs micropore structure makes them more favorable in adsorption. The total micropore volume or surface area are not determining factors for phenolic compounds adsorption because adsorption onto activated carbon surface is not coverage at the surface of adsorbents but filling of micropores [26]. The micropore volumes for ACFs could be 3–4 times higher than the pore volume required to accommodate the adsorbed molecules; only a portion of pores are actually occupied during adsorption [27,28].

ACC-15 has much higher micropore surface area and micropore volume than either F400 or ACC-10, thus the highest adsorptive capacity was achieved on ACC-15 under anoxic conditions for all the adsorbates, as manifested in Fig. 1.

In general, the adsorptive capacity was related to the electron-withdrawing or electron-donating functional groups, water solubility of the compound, the PSD of the adsorbent, and the molecular structure of the adsorbate under anoxic conditions. The less soluble compounds are easier to be adsorbed. The narrow PSD of ACFs make pore diameter a limiting factor for adsorption and oligomerization of phenolic compounds could be hampered by the small pore diameter of the adsorbent. Our previous study [20] on adsorption of 2-methylphenol and 2-ethylphenol on four ACFs with different average pore width also showed that the difference between anoxic and oxic isotherms was related to the adsorbent PSD. The larger the pore width, the more oligomerization was achieved; and with larger adsorbate molecular size, less oligomerization occurred.

3.2. Effect of functional groups on oligomerization

The effect of the different functional groups on oligomerization was studied by considering the adsorption of phenol, 2-methylphenol, 2-ethylphenol and 2-chlorophenol and 2-

nitrophenol on F400, ACC-10 and ACC-15 under oxic and anoxic conditions (see Fig. 1).

For all the adsorbates except 2-nitrophenol on F400, the oxic adsorptive capacity was higher than that of anoxic ones (as shown in Fig. 1). The increase in adsorptive capacity under oxic condition could be attributed to the oligomerization of the adsorbates on the adsorbent surface [15]. The first step in this oligomerization reaction is forming phenoxy radical by losing one proton; the phenoxy radical is highly reactive and can participate in oligomer formation through carbon-oxygen or carbon-carbon bonding [15]. The presence of an electron-attracting group, like the nitro and the chloro group, inhibited the parent phenol molecule to lose the proton, i.e., hydrogen, thus it increased the COP of the compound, and the first step of oligomerization was inhibited to some degree. On the contrary, the presence of an electron-donating group, like the methyl and the ethyl group decreased the COP thus aided the parent phenol molecule to form phenoxy radical. As for 2-nitrophenol, it did not show any differences between oxic and anoxic conditions for the three adsorbents, indicating no oligomerization taking place under oxic conditions. This is manifested by its high COP (see Table 1).

By comparing the anoxic and oxic adsorption on F400, it is seen that the sequence of the adsorbates oxic adsorptive capacity was in the same order as the anoxic isotherm; however, the relative difference under oxic conditions was less due to the different degrees of oligomerization of the adsorbates. The existence of electron withdrawing groups, like chloro and nitro groups, make 2-chlorophenol and 2-nitrophenol more adsorbable than other compounds under anoxic conditions, while at the same time, these existed chloro or nitro groups also make 2-chlorophenol and 2-nitrophenol less oligomerized than the others, which diminished the differences between these compounds.

In case of oxic adsorption on ACC-10, it is seen that the adsorptive capacity of phenol > 2-chlorophenol > 2-

nitrophenol ~ 2-methylphenol > 2-ethylphenol which is different from the order shown previously under anoxic conditions. In case of ACC-10 which has a narrow PSD and a critical diameter of 8.0 Å, the restricted pore diameter could be a limiting factor in hampering oligomerization. Thus, the molecular dimensions of the adsorbates played an important role. Among the longest dimensions for the four adsorbates, 2-ethylphenol is the largest, 6.06 Å (see Table 1).

Fig. 2 shows the ratio of the difference between oxic and anoxic capacities to the anoxic capacities for the three adsorbents studied. Fig. 2 shows that 2-ethylphenol had the least ratio which indicates it was the least oligomerized compound. In case of phenol, 2-methylphenol and 2-chlorophenol, the longest dimensions are similar, but are different in the second longest dimension. 2-Chlorophenol has the largest second longest dimension as compared to phenol and 2-methylphenol. As indicated above by the trend of the ratio of the difference between oxic and anoxic to the anoxic capacities on ACC-10, 2-chlorophenol showed less oligomerization than phenol and 2-methylphenol. As for phenol and 2-methylphenol, phenol molecules are two dimensional while 2-methylphenol molecules are three dimensional. Obviously, the limited pore diameter is more accessible for the two dimensional molecules (phenol) than the three dimensional ones (2-methylphenol). This is in agreement with the trend of oligomerization obtained for ACC-10. In general for ACC-10, the narrow PSD and the limited pore diameter of ACC-10 reduced the extent of oligomerization. As reported by Karanfil et al. [29] in their study of influence of dissolved oxygen (DO) on adsorption of organic macromolecules by GAC, sensitivity of sorption to DO generally increased with decreasing molecular size, polydispersity, and aromaticity and with increasing acidity. Thus, the large molecular size of 2-methylphenol and 2-ethylphenol made them less oligomerized on ACC-10.

The trend of oligomerization on ACC-15 for the four adsorbates was similar to that on ACC-10 with exceptions of the

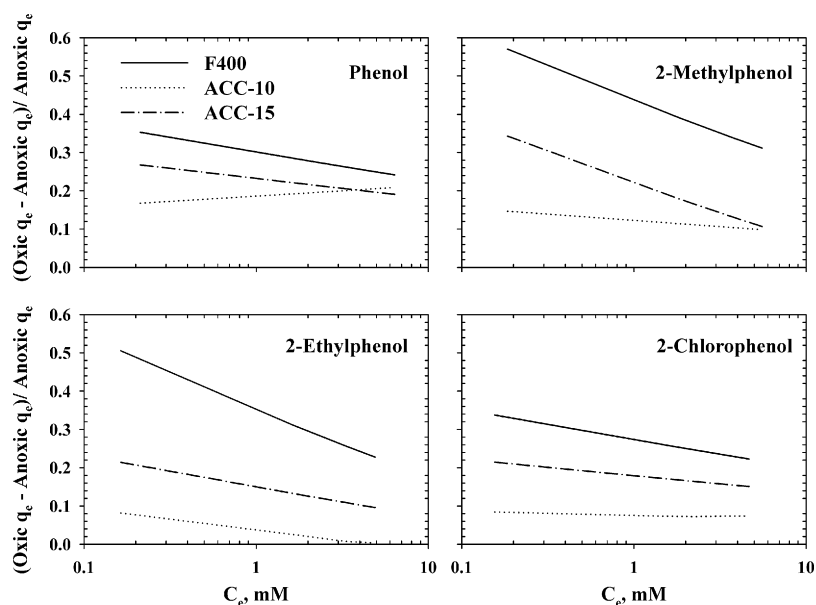


Fig. 2. Comparison of oxic and anoxic adsorption capacities of phenolics.

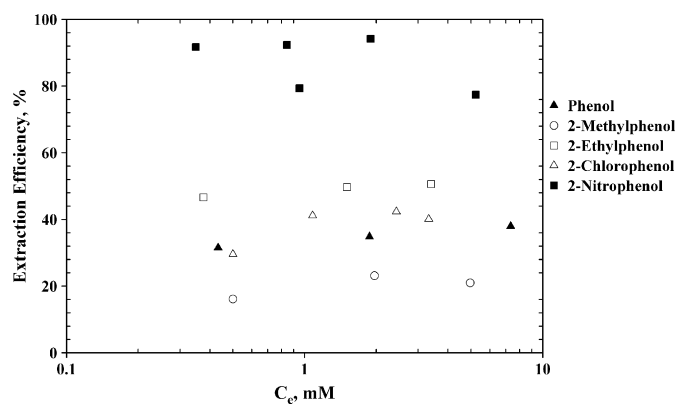


Fig. 3. Extraction efficiency of F400 used in oxic isotherms.

reversal between 2-methylphenol and phenol. Similar to ACC-10, ACC-15 has narrow PSD, but its critical pore diameter is 12.8 Å. It is speculated that the larger critical diameter played a role in reversing the order of oligomerization between phenol and 2-methylphenol.

It is seen from Fig. 2 that for the four adsorbates, F400 provided the largest ratio followed by ACC-15 and then ACC-10 indicating that the narrow PSD of the ACFs effectively reduced oligomerization. Furthermore, the sequence of the ratio differed among the three adsorbents. For ACC-10, the sequence of the ratio was phenol > 2-methylphenol > 2-chlorophenol > 2-ethylphenol; for ACC-15, 2-methylphenol > phenol > 2-chlorophenol > 2-ethylphenol; and for F400, 2-methylphenol > 2-ethylphenol > phenol > 2-chlorophenol. The degree of oligomerization on F400 under oxic conditions was in accordance with the COP of these compounds, i.e., 2-methylphenol < 2-ethylphenol < phenol < 2-chlorophenol (see Table 1).

The oligomerization of the adsorbates was further confirmed by the extraction efficiency of F400 after the oxic isotherms (see Fig. 3). Oligomerization is a chemisorption process which renders lower regeneration efficiency after being exhausted by the contaminants. It is seen from Fig. 3, more than 80% of 2-nitrophenol was recovered after oxic isotherms but for other compounds, the recovery was lower than 50%. 2-methylphenol showed the least extraction efficiency, lower than 23%.

3.3. Impact of position of functional groups on adsorption behavior

The impact of the position of the functional groups was examined by considering the adsorption isotherms of 2-chlorophenol/4-chlorophenol, 2-nitrophenol/4-nitrophenol on F400 and ACC-10. Previous studies have shown that the meta-substituted phenols are energetically more stable and less reactive when compared to ortho- and para- substituted phenols [15], thus the meta-substituted phenols are not considered in the study.

A comparison in adsorptive capacity between 2-chlorophenol and 4-chlorophenol, and between 2-nitrophenol and 4-nitrophenol is shown in Table 3. For 4-chlorophenol on ACC-10, negligible difference was seen between anoxic and oxic isotherms, thus only one set of data is shown in Table 3. It can be clearly seen from Table 3 that 4-chlorophenol and 2-chlorophenol had similar adsorptive capacity on F400, but 4-chlorophenol showed higher adsorptive capacity than 2-chlorophenol on ACC-10. 2-Chlorophenol and 4-chlorophenol have similar water solubility (see Table 1). Hence for F400, it is reasonable to expect similar adsorptive capacities. In case of ACC-10, it is anticipated that the adsorbate structure relative to the PSD and the pore diameter of the adsorbent played a major role. The second widest molecular dimension for 2-chlorophenol is 4.87 Å and 4-chlorophenol is 4.17 Å (see Table 1). The critical pore diameter for ACC-10 is 8.0 Å and the total pore volume is 0.395 cm³ g⁻¹ [19]. Since adsorption on ACC-10 is pore filling, therefore, it is feasible to have more 4-chlorophenol molecules adsorbed than 2-chlorophenol molecules.

In case of the nitrophenols, conflicting results were obtained on the two adsorbents studied. For F400, 2-nitrophenol showed higher adsorptive capacity than 4-nitrophenol and the reverse was true on ACC-10 (see Table 3). The main difference between 2-nitrophenol and 4-nitrophenol is water solubility (see Table 1). 4-Nitrophenol is more soluble than 2-nitrophenol, thus it is expected to be less absorbable on the activated carbon which is true for F400. In case of ACC-10, 4-nitrophenol showed higher adsorptive capacity than 2-nitrophenol which could be explained in a similar fashion as for 4- and 2-chlorophenol on ACC-10. Hence, again it is seen for ACC-10 the adsorbate molecular structure played an important role in adsorption.

Table 3
Comparison of 2-/4- Chlorophenol and 2-/4-Nitrophenol on F400 and ACC-10

	C _e (mM)	2-Chlorophenol q _e (mmol/g)		4-Chlorophenol q _e (mmol/g)		2-Nitrophenol q _e (mmol/g)	4-Nitrophenol q _e (mmol/g)
		Anoxic	Oxic	Anoxic	Oxic	Anoxic/oxic	Anoxic/oxic
F400	0.50	2.18	2.82	2.49	2.78	2.79	2.33
	2.00	2.64	3.30	2.75	3.22	3.22	2.90
	4.00	2.91	3.57	2.89	3.46	3.46	3.23
	6.00	3.08	3.74	2.97	3.61	3.61	3.45
ACC-10	0.50	2.31	2.25	2.74	2.53	2.53	2.82
	2.00	2.55	2.67	2.97	2.78	2.78	3.18
	4.00	2.67	2.91	3.10	2.91	2.91	3.38
	6.00	2.75	3.05	3.17	2.99	2.99	3.50

Table 4
Summary of the binary adsorption system

Adsorbates	Run no.	Conditions	Initial concentration (mM)		SSREs	
			Component 1	Component 2	Component 1	Component 2
2-Methylphenol (component 1) + phenol (component 2)	1	Anoxic	0.53	1.67	0.327	0.172
		Oxic	0.56	1.87	0.272	0.045
	2	Anoxic	2.12	1.71	0.122	0.040
		Oxic	2.14	1.83	0.130	0.096
	3	Anoxic	4.25	1.74	0.266	0.376
		Oxic	4.16	1.83	0.129	0.043
4	Anoxic	2.05	3.33	0.194	0.145	
	Oxic	2.06	3.44	0.184	0.243	
2-Methylphenol (component 1) + 2-chlorophenol (component 2)	1	Anoxic	0.51	1.72	0.182	0.156
		Oxic	0.64	1.41	0.202	0.098
	2	Anoxic	3.87	1.66	0.073	0.092
		Oxic	3.88	1.81	0.257	0.067
2-Methylphenol (component 1) + 2-nitrophenol (component 2)	1	Anoxic	0.48	1.45	0.175	0.044
		Oxic	0.67	1.34	0.204	0.029
	2	Anoxic	1.88	1.42	0.105	0.083
		Oxic	2.01	1.43	0.116	0.025

It is worthwhile to note that for both 4-chlorophenol and 4-nitrophenol, ACC-10 provided higher adsorptive capacity than F400. This behavior might be attributed to the high percentage of the microporosity of ACC-10 as compared to F400. However, in case of 2-chlorophenol and 2-nitrophenol, the large molecular dimensions caused them to be less adsorbable on ACC-10 which has limited PSD as compared to F400. Therefore, for F400, the impact of the position of the chloro and nitro group in the parent phenol on adsorptive capacity was mainly dependent on their solubility. In case of ACC-10, their molecular dimensions were the main factors.

3.4. Binary adsorption on ACC-10

Fixed beds of activated carbon are usually used to adsorb mixtures of pollutants. In this case, considering the impact of functional groups on a binary solute system would be advantageous. Binary adsorption isotherms of phenol/2-ethylphenol, 2-methylphenol/2-chlorophenol, and 2-methylphenol/2-nitrophenol were conducted on ACC-10 under anoxic and oxic conditions. In these chosen combinations, phenol and 2-methylphenol in the single solute system showed significant oligomerization on ACC-10 when molecular oxygen was present in the test environment, while for the other compounds, 2-ethylphenol, 2-chlorophenol or 2-nitrophenol, no significant oligomerization was detected. ACC-10 was chosen as a model adsorbent because it would help to understand the competitive effect between two adsorbates where one was affected by the presence of molecular oxygen and the other was slightly or not affected. Four initial concentration combinations were chosen for phenol/2-ethylphenol, and two for the other combinations. The initial concentration combinations used for the anoxic and oxic adsorption isotherms are shown in Table 4. These initial concentrations were chosen in order to determine if any adsorbate/adsorbate interaction would occur that would lead to deviations from ideal adsorbed solution behav-

ior and also to assess the reproducibility of the experimental results.

Fixed-bed adsorber models are based on parameters obtained from the single solute systems. Therefore, for multicomponent adsorption isotherms, it is necessary to accurately predict the adsorption equilibrium by using the single solute adsorption isotherms. Literature contains many adsorption isotherm models. A brief summary of these models was provided by the authors [19]. The model with the most thermodynamically accepted foundation is the IAST, originally proposed by Myers and Prausnitz [30] for gas mixtures and later developed by Radke and Prausnitz [31] for dilute liquid solutions. A brief listing of the necessary equations and prediction procedure was provided elsewhere by the authors [20]. It is worthwhile to note that the IAST is based on physical adsorption and thus it will not predict the irreversibility of the oxic adsorption isotherms due to oligomerization on the surface of the activated carbon. Hence, one can use the IAST as a measure for examining the occurrence of oligomerization under oxic conditions for the multicomponent system.

Fig. 4 represents one combination for the binary adsorption of phenol/2-ethylphenol and 2-methylphenol/2-nitrophenol on ACC-10. The other combinations showed similar results. The IAST, using the Myers equation for correlating the single solute anoxic isotherms, was used to predict the competitive adsorption behavior of these phenolic mixtures. Evaluation of the predictability of IAST was also done by calculating the sum of SSREs (see Table 4). It is seen from Fig. 4 that the experimental data for both oxic and anoxic conditions overlapped, indicating that molecular oxygen has no effect on the binary adsorption systems on ACC-10. The similar adsorption behavior under anoxic and oxic conditions for the binary system on ACC-10 is further confirmed by using the anoxic parameters determined for the single solute system in the IAST predictions for both the oxic and anoxic binary system. It can be seen from Fig. 4 and/or Table 4 that IAST predicted reasonably well both oxic and anoxic

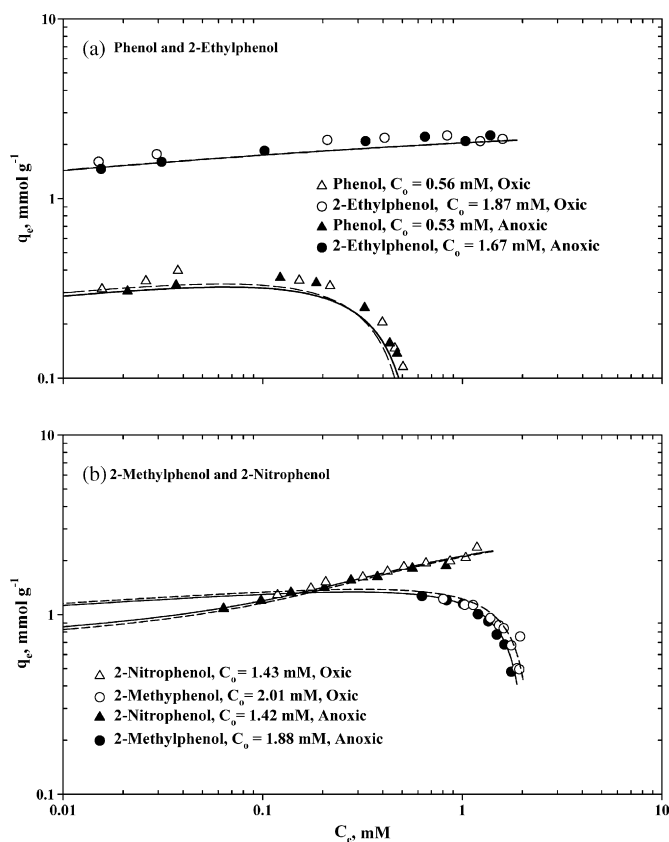


Fig. 4. Binary adsorption on ACC-10.

competitive adsorption on ACC-10. Similar results are obtained for the other binary systems.

In general, the anoxic and oxic binary adsorption isotherms on ACC-10 overlapped and oligomerization in these binary systems has been hampered by the small pore diameter of the adsorbent. Fundamental soundness of the IAST has been achieved for these systems.

4. Conclusions

The main adsorption mechanism is believed to be the dispersion force between the activated carbon π -electrons of double bonds and π -electrons in phenols; when electron-withdrawing substitute exists, the π -electrons of phenols decrease, thus the affinity to activated carbon π -electrons is stronger. As a result, the presence of the nitro and the chloro group, inhibited the parent phenol molecule to lose the proton, thus increased the COP of the compound, and the first step of oligomerization was inhibited to some degree. As for 2-nitrophenol, no oligomerization occurred. On the contrary, the presence of an electron-donating group, like the methyl and the ethyl group decreased the COP thus aided the parent phenol molecule to form phenoxy radical. As was shown in the adsorption on F400, the existence of electron withdrawing groups, $-\text{Cl}$ or $-\text{NO}_2$, made 2-chlorophenol and 2-nitrophenol more adsorbable on GAC F400 than phenol, 2-methylphenol and 2-ethylphenol. The difference between these adsorbates was more pronounced under anoxic conditions than under oxic conditions. The high COP of 2-chlorophenol

and 2-nitrophenol caused them to be less oligomerized than phenol, 2-methylphenol and 2-ethylphenol, thus the difference between these adsorbates decreased under oxic conditions.

ACC-10 had effectively hampered oligomerization of phenolic compounds. On ACC-10, only phenol and 2-methylphenol showed somewhat oligomerization. Phenol has the smallest molecule among all the adsorbates studied, while 2-methylphenol has lowest COP, which indicates the easiest to get oligomerized. Adsorptive capacity on ACC-15 is the highest among the three adsorbents while oligomerization was between ACC-10 and F400.

To further elucidate the impact of limited PSD on oligomerization, oxic and anoxic binary adsorption isotherms of phenol/2-ethylphenol, and 2-methylphenol/2-nitrophenol were conducted on ACC-10. The results indicated overlapping of both isotherms revealing that oligomerization was hampered by the limited micro-pore diameter of ACFs. The binary adsorption isotherms were well predicted by the Ideal Adsorbed Solution Theory (IAST), using the Myers equation for correlating the single-solute anoxic isotherms.

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