A comparative study of multicomponent adsorption of phenolic compounds on GAC and ACFs

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ABSTRACT

The impact of adsorbent pore size distribution (PSD) and adsorbate critical oxidation potential (COP) on competitive adsorption on activated carbon were investigated in this study. Three activated carbons with different pore size distribution were used as adsorbents—granular activated carbon (GAC) F400, and two activated carbon fibers (ACFs), namely ACC-10 and ACC-15. Binary adsorptions of 2-methylphenol/2-chlorophenol and 2-methylphenol/2-nitrophenol were conducted on all three adsorbents. Ternary adsorption of 2-methylphenol/2-nitrophenol/2-chlorophenol was conducted on ACC-15 and F400. 2-Nitrophenol was more physically adsorbable than the other two adsorbates, while 2-methylphenol was the easiest to get oligomerized due to its low COP.

ACC-10, which has the smallest critical pore size and narrow PSD, was shown to be effective in hampering oligomerization of phenolic compounds in all binary adsorption systems. ACC-15, which has larger critical pore size than ACC-10 and also narrow PSD, showed somewhat effectiveness in hampering oligomerization in binary adsorption systems and total effectiveness in ternary adsorptions. On the other hand, the wide pore size variations of F400 played a role in the oligomerization of the phenolic compounds. The Ideal Adsorbed Solution Theory (IAST) well predicted the multicomponent adsorption systems that did not undergo oligomerization.

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1. Introduction

Activated carbon has been a reliable technique used increasingly in water and wastewater treatment for the removal of relatively low-molecular-weight organic compounds, such as phenols [1–3]. Phenol and its derivatives are the basic structural units of a wide variety of synthetic organic pollutants including many pesticides [4]. Studies of the adsorptive properties of granular activated carbon (GAC) have shown that molecular oxygen plays an important role in the adsorption of phenolic compounds [5–8]. It was found that molecular oxygen in the aqueous phase promotes chemical transformation, such as oligomerization of the organic compounds adsorbed onto the carbon surface [9], thus improving the adsorptive capacity. Higher extraction efficiencies of the carbons used in the oxic isotherms (presence of molecular oxygen) were obtained for the carbons that exhibited lower increases in capacities when compared to anoxic isotherms—absence of molecular oxygen [10]. Economic use has been a major concern in activated carbon usage. To get higher regeneration efficiency of activated carbon

after adsorption of phenols, the oligomerization must be minimized.

The impact of surface functional groups has been studied extensively on activated carbon adsorption in order to provide an explanation of the oligomerization of phenolic compounds on activated carbon surface when molecular oxygen is present [7,9–11]. In particular, acidic and basic surface functional groups, metals, and metal oxide complexes that are commonly present on activated carbon surface were investigated for their role in catalyzing oligomerization of phenolic compounds under oxic conditions. Despite of all the studies, none of them provided a conclusive result. It is postulated that the heterogeneity of GAC is not very suitable for elucidating the impact of the surface properties on the adsorption behavior. Compared with GAC, activated carbon fibers (ACFs) have low concentration of surface oxides which results in limited surface chemistry effects [3]. Besides, ACFs have unique pore size distribution (PSD) and all the micropores are directly on the carbon surface [12–14]. The perfect surface properties of ACFs make them ideal for elucidating the impact of PSD on oligomerization. Adsorbent PSD is one of the most important properties that influence the adsorption process.

Adsorbate property is another factor that influences activated carbon adsorption. Adsorbate properties include physical properties (molecular size, and structure, and water solubility) and

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chemical properties (pKa and the critical oxidation potential). The critical oxidation potential (COP) was the most important features when considering oligomerization [15–19].

The model with the most thermodynamically accepted foundation is the Ideal Adsorbed Solution Theory (IAST), which was originally proposed by Myers and Prausnitz [20] for gas mixtures and later developed by Radke and Prausnitz [21] for dilute liquid solutions. The IAST is based on the assumption that the adsorbed mixture forms an ideal solution at a constant spreading pressure. For better prediction of real multicomponent adsorption, many researchers modified the IAST for including heterogeneity of the adsorbent [22–24] or non-ideality by including adsorbate interactions [25,26]. Despite all the efforts made by many researchers, including heterogeneity or non-ideality renders the model a correlating one rather than a predictive. A multicomponent adsorption model should be based on fundamental soundness, speed and simplicity of calculation. Based on our previous studies [18,19,27], the IAST was chosen for the multicomponent adsorption systems in this study. The Myers equation was used for describing single solute adsorption in IAST.

Phenolic compounds are usually present in various form [28], therefore, it is important to understand the competitive effects that can take place in such systems. Unfortunately, few researchers have studied the competitive adsorption of ternary mixtures [26] and even fewer were on phenolic compounds oligomerization in these systems. A good understanding of the impact of pore size distribution on competitive adsorption is required as a basis for selecting the best activated carbon and applying it in an optimal way. Thus, the objective of this study is to elucidate the importance of adsorbent PSD and adsorbate COP on oligomerization in terms of binary and ternary adsorptions.

2. Materials and methods

2.1. Adsorbates

Three phenolic compounds, 2-methylphenol, 2-chlorophenol, and 2-nitrophenol (Aldrich Chemical Co. Inc, Milwaukee, WI), were used as adsorbates in this study. 2-Methylphenol molecules are three-dimensional ($5.68 \text{ Å} \times 4.12 \text{ Å} \times 1.63 \text{ Å}$) while 2-nitrophenol ($5.76 \text{ Å} \times 5.76 \text{ Å}$) and 2-chlorophenol ($5.76 \text{ Å} \times 4.82 \text{ Å}$) are two-dimensional (Advanced Chemistry Development-ACDLabs 5.0 software, Toronto, Canada). It is worthwhile to note that the molecular structure plays an important role in adsorption on ACFs since ACFs have uniform micropores. The COP for the three adsorbates are 2-methylphenol (1.040 V) < 2-chlorophenol (1.095 V) < 2-nitrophenol (1.434 V) [27].

2.2. Adsorbent

F400 (Filtrasorb 400) was chosen as a typical GAC (Calgon Carbon Corporation, Pittsburgh, PA). Two microporous phenolic resin-based ACFs (Nippon Kynol, Japan), designated as ACC-10 and ACC-15, were used in this study. Prior to use in the study, activated carbon was dried in an oven at $105 \,^{\circ}\text{C}$ for 2 days to remove any moisture present, and then stored in a desiccator until use. ACC-10 and ACC-15 have very narrow pore size range with BET surface area of 900 and $1137 \text{ m}^2 \text{ g}^{-1}$ respectively. The microporosity for both adsorbents is higher than 93%. The critical pore diameter for ACC-10 is 8.0 Å. Beyond a pore diameter of 8.0 Å, the incremental pore volume approaches zero in N_2 adsorption isotherm at 77.2 K. The critical pore diameter for ACC-15 is 12.8 Å. F400 has wide pore size distribution, ranging from 4 to 800 Å. A detailed analysis of the PSD of the three adsorbents is provided by Lu and Sorial [19].

2.3. Isotherm procedure and analytical procedures

Binary adsorption of 2-methylphenol/2-chlorophenol and 2-methylphenol/2-nitrophenol were conducted on F400, ACC-10, and ACC-15. Based on binary adsorption results, ternary adsorption of 2-methylphenol/2-nitrophenol/2-chlorophenol was conducted on ACC-15 and F400. Two experimental conditions were considered—anoxic (absence of molecular oxygen) and oxic (presence of molecular oxygen) at $23 \pm 1 \,^{\circ}\text{C}$.

The bottle point method was used for conducting the adsorption isotherms. Solutions of the adsorbates were prepared in autoclaved deionized water buffered with 0.01 M KH_2PO_4, and the pH was adjusted to 7.0 with a 10 M solution of NaOH. For the anoxic isotherms, molecular oxygen was excluded from the isotherm bottles and adsorbents. The dissolved oxygen (DO) for the anoxic isotherms was maintained under 1 mg L^{-1}, while for the oxic isotherms, DO was not lower than 15 mg L^{-1}. Detailed procedure is provided elsewhere [18,19].

Concentration determinations were made by gas chromatography (GC) (Agilent 6890 Series; Agilent Technologies, Wilmington, DE) separation equipped with Agilent DB-5 column ($30 \text{ m} \times 0.32 \text{ mm}$ inside diameter with 0.25-μm film thickness) and flame ionization detector (FID). The temperature ramp was set the same as our previous studies [18,19]. 4-Chlorophenol was used as an internal standard. The retention time for 2-metylphenol was 10.2 min, 2-chlorophenol was 8.8 min, and 2-nitrophenol was 11.8 min.

3. Results and discussions

3.1. Review of single solute adsorption

Prior to this study, single solute adsorption of 2-methylphenol, 2-chlorophenol, and 2-nitrophenol were conducted on F400, ACC-10, and ACC-15 [27]. In single solute adsorption, the COP, influenced by substitution of functional groups, was found to be a limiting factor in oligomerization of adsorbates. The first step of oligomerization is to form phenolic radicals 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 [29]. The presence of the nitro or 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. On the contrary, the presence of an electron-donating group, like the methyl or the ethyl group decreased the COP thus aided the parent phenol molecule to form phenoxy radical. As a result under anoxic conditions, the adsorptive capacity was in the order of 2-nitrophenol > 2-chlorophenol > 2-methylphenol on F400, ACC-10, and ACC-15. Under oxic conditions, the extent of oligomerization which is defined as the difference between oxic and anoxic adsorptive capacity, was in the order 2-methylphenol > 2-chlorophenol > 2-nitrophenol on all three adsorbents. Under oxic conditions, 2-Nitrophenol did not show any oligomerization on the three adsorbents. At the same time, the adsorbent PSD was another factor that influenced oligomerization. For 2-methylphenol and 2-chlorophenol, the oligomerization extent was in the order F400 > ACC-15 > ACC-10, which was in the same sequence as the decrease of the pore size of the adsorbents. For ACC-10, which has narrow PSD and smallest critical pore diameter (8.0 Å), oligomerization was hampered.

3.2. Binary adsorption

Based on single solute adsorption results, binary adsorptions of 2-methylphenol/2-chlorophenol and 2-methylphenol/2-

Table 1
Summary of binary adsorption of 2-methylphenol and 2-chlorophenol.

Adsorbent	Run No.	Conditions	Binary adsorption			
			Initial concentration (mM)		SSRE	
			2-Methylphenol	2-Chlorophenol	2-Methylphenol	2-Chlorophenol
ACC-10	Run No. 1	Anoxic	3.87	1.66	0.073	0.092
		Oxic	3.88	1.81	0.257	0.067
	Run No. 2	Anoxic	0.51	1.72	0.182	0.156
		Oxic	0.64	1.41	0.202	0.098
ACC-15	Run No. 1	Anoxic	3.77	1.53	0.076	0.178
		Oxic	3.62	1.53	0.301	0.139
	Run No. 2	Anoxic	0.48	1.60	0.102	0.0068
		Oxic	0.41	1.57	0.366	0.0643
F400	Run No. 1	Anoxic	3.77	1.53	0.098	0.039
		Oxic	3.64	1.53	1.028	0.103
	Run No. 2	Anoxic	0.48	1.60	0.052	0.113
		Oxic	0.42	1.57	0.542	0.773

nitrophenol were conducted on F400, ACC-10 and ACC-15 under anoxic and oxic conditions. 2-Methylphenol was shown to be the easiest one to get oligomerizaed in single solute adsorption, thus these combinations were chosen to observe the competitive behavior between 2-methylphenol and the other phenolic compounds.

3.3. Binary adsorption of 2-methylphenol/2-chlorphenol

Binary adsorption isotherms of 2-methylphenol/2-chlorophenol were conducted on F400, ACC-10 and ACC-15 under anoxic and oxic conditions in this section. Two initial concentration combinations were chosen for the binary systems on all three adsorbents. These initial concentrations are summarized in Table 1. The IAST was used to predict the multicomponent adsorption isotherms. Predictions were conducted by using the single solute anoxic parameters based on correlations by the Myer's equation which were reported in our previous publication [27].

As stated previously in the single solute adsorption, 2-chlorophenol showed higher adsorptive capacity than 2-methylphenol under anoxic conditions on the three adsorbents studied. The higher adsorptive capacity was attributed to the electron withdrawing substitute, –Cl group, and its two-dimensional structures. At the same time, it was found that the extent of oligomerization for 2-methylphenol on all three adsorbents was higher than 2-chlorophenol under oxic conditions. The lower COP of 2-methylphenol (1.048 V) made it easier to get oligomerized than 2-chlorophenol (1.095 V). The competitive adsorption of 2-methylphenol and 2-chlorophenol could be interesting to note since the two adsorbates showed different adsorption behavior under anoxic and oxic conditions.

Fig. 1 shows two runs of binary adsorption of 2-methylphenol/2-chlorophenol on ACC-10. In the first combination, 2-methylphenol had higher concentration than 2-chlorophenol. 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. It can be seen from Fig. 1 that the experimental data for both the oxic and anoxic conditions overlapped, no obvious difference was observed. In single solute adsorption, both 2-methylphenol and 2-chlorophenol showed somewhat oligomerization under oxic conditions [27], yet in the binary system, there was no difference between oxic and anoxic isotherms. This is similar to our previous study for binary adsorption of 2-methylphenol/2-ethylphenol and phenol/2-methylphenol on ACC-10 [18,19].

In the second combination studied, 2-methylphenol had lower initial concentration than 2-chlorophenol. The slight difference seen in Fig. 1 between anoxic and oxic experimental data was due

to the different initial concentrations under oxic and anoxic conditions.

The IAST, using anoxic Myers parameters, well predicted both anoxic and oxic binary adsorption isotherms 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 [27]. Evaluation of the predictability of IAST was also done by calculating the sum of squares of relative error (SSRE). Eq. (1) was used to estimate SSRE:

$$\text{SSRE} = \Sigma \left(\frac{q_{e,i}\text{obeserved} - q_{e,i}\text{predicted}}{q_{e,i}\text{observed}} \right)^2 \tag{1}$$
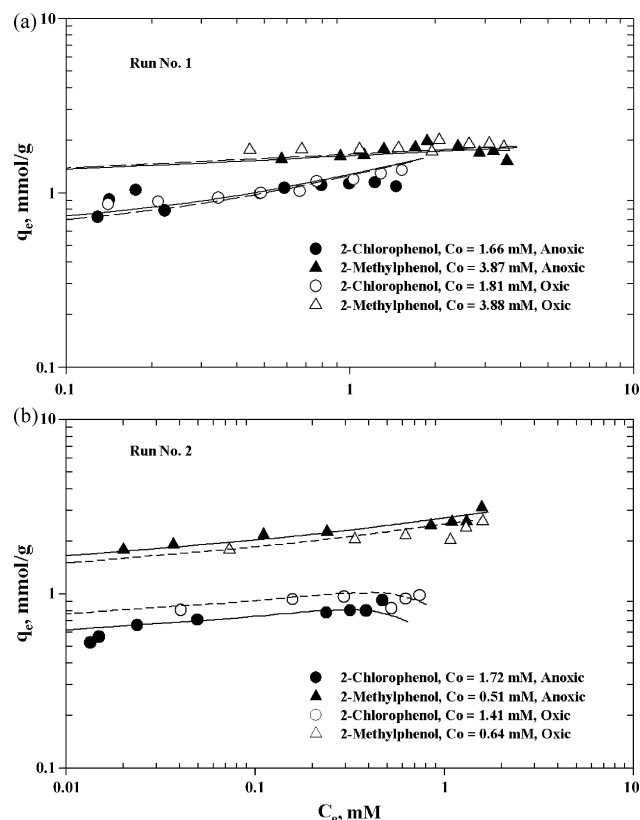

Fig. 1. Binary adsorption of 2-methylphenol/2-chlorophenol on ACC-10 (solid lines represent anoxic IAST prediction and dashed lines represent oxic IAST predictions).

The SSREs together with the initial concentrations of 2-methylphenol/2-chlorophenol are summarized in Table 1. It can be seen from Fig. 1 and Table 1 that IAST predicted reasonably well both oxic and anoxic competitive adsorption on ACC-10 when using anoxic Myers parameters. It is worthwhile to note further that the model predicted the data with different trend lines for the oxic and anoxic isotherms due to the difference in the initial concentration. Therefore, no possibility of oligomerization at low coverage could have occurred. It is further seen in Table 1, all the SSREs are very small, showing a good prediction for the binary adsorption isotherm sets studied. Thus, ACC-10, which has narrow PSD and small critical pore diameter (8.0 Å) was shown to be effective in hampering oligomerization.

For the binary adsorption of 2-methylphenol/2-chlorophenol on ACC-15, slight difference was noticed between oxic and anoxic binary adsorption isotherms (see Fig. 2). The oxic adsorptive capacity was higher than anoxic ones for 2-methylphenol. The SSREs values are shown in Table 1. It can be seen from Fig. 2 that the anoxic adsorption isotherms were well predicted by IAST. On the other hand, the IAST under predicted 2-methylphenol oxic isotherms (represented by the dashed line) which could be attributed to the oligomerization that took place at the surface of the carbon. As shown in Table 1, the oxic SSREs for 2-methylphenol was greater than the anoxic SSREs, indicating that the anoxic isotherms were better predicted by IAST.

Obvious difference was noticed between the experimental oxic and anoxic binary adsorption isotherms of the binary adsorption of 2-methylphenol/2-chlorophenol on F400 (see Fig. 3). The oxic adsorptive capacity was much higher than the anoxic ones. Similar results were seen for both runs. The SSRE values are shown in Table 1. Fig. 3 indicated that the anoxic adsorption isotherms were well predicted by IAST. On the other hand, the IAST under predicted the oxic isotherms for either adsorbates. It is further seen in Fig. 3,
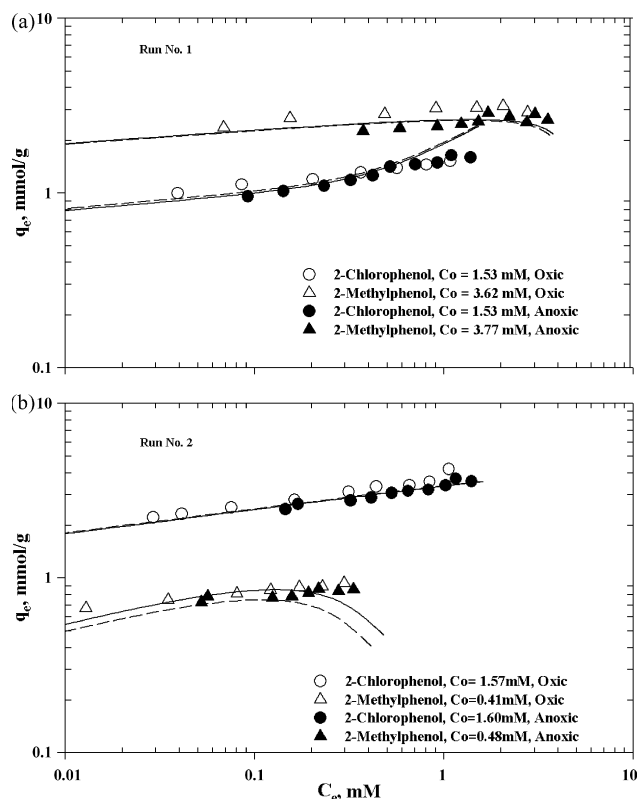

Fig. 2. Binary adsorption of 2-methylphenol/2-chlorophenol on ACC-15 (solid lines represent anoxic IAST prediction and dashed lines represent oxic IAST predictions).
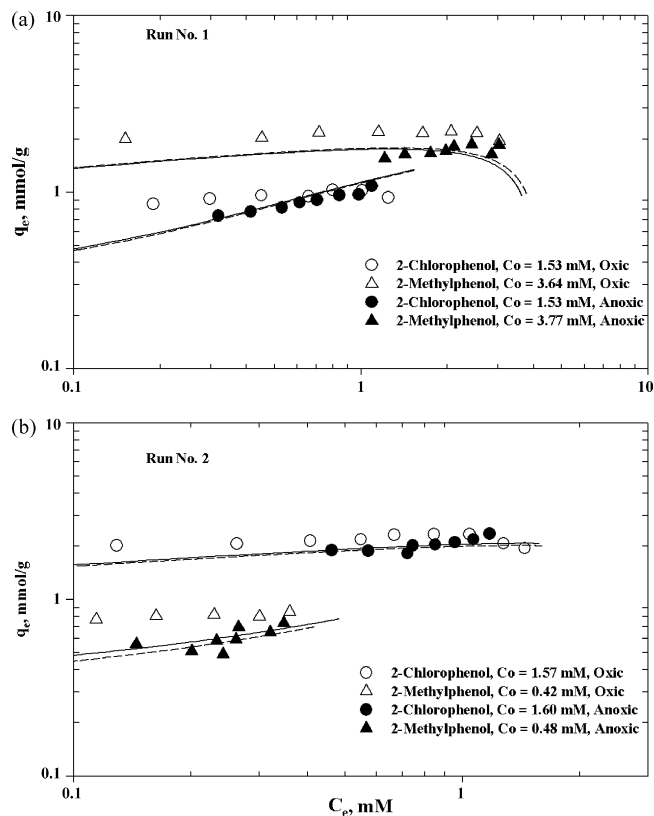

Fig. 3. Binary adsorption of 2-methylphenol/2-chlorophenol on F400 (solid lines represent anoxic IAST prediction and dashed lines represent oxic IAST predictions).

that the under prediction was greater in the low concentration (i.e., higher carbon dosage) range. This seems to indicate that lower surface loading allows oligomerization readily. As shown in Table 1, the higher oxic SSREs also confirmed the poor prediction of IAST.

The binary adsorption of 2-methylphenol/2-chlorophenol on ACC-15 and F400 showed that the deviation of the experimental adsorption isotherms from IAST predictions for F400 was larger than that of ACC-15. Thus, it is postulated that the effectiveness of PSD in hampering oligomerization is in the order ACC-10 > ACC-15 > F400 which is in the same order as the increase of the pore diameter of the adsorbent. F400 has a wide PSD, and the extent of oligomerization in binary systems under oxic condition for F400 is expected to be larger than ACC-15. For ACC-10, which has the smallest critical pore diameter, oligomerization was hampered. Thus, it can be postulated that the larger the pore width of the adsorbent, the greater is the tendency for oligomerization to occur on the surface in the presence of molecular oxygen. The extent of the oligomerization will depend on the molecular dimensions of the adsorbate relative to the pore diameter of the adsorbent and the COP of the adsorbate.

A further comparison between 2-methylphenol and 2-chlorophenol showed the same trend for the competitive behavior of the adsorbates (see Figs. 1–3). 2-Chlorphenol in the binary system shows an increasing trend of the adsorbed phase capacity with increase of the equilibrium liquid phase concentration. Whereas for 2-methylphenol, a decrease in adsorbed phase concentration is obtained with increase of equilibrium liquid concentration. This behavior indicates that 2-chlorophenol has more affinity than 2-methylphenol on the adsorbents studied. The decreasing trend in adsorbed phase concentration for 2-methylphenol is due to the less availability of sites on the activated carbon at the low carbon dosage due to the competitive effect of 2-cholrphenol. This is consistent with what has been found in single solute adsorption. In

Table 2
Summary of binary adsorption of 2-methylphenol and 2-nitrophenol.

Adsorbent	Run No.	Conditions	Binary adsorption			
			Initial concentration (mM)		SSRE	
			2-Methylphenol	2-Nitrophenol	2-Methylphenol	2-Nitrophenol
ACC-10	Run No. 1	Anoxic	1.88	1.42	0.055	0.03
		Oxic	2.01	1.43	0.17	0.024
	Run No. 2	Anoxic	0.48	1.45	0.23	0.18
		Oxic	0.67	1.37	0.16	0.028
ACC-15	Run No. 1	Anoxic	1.93	1.46	0.083	0.040
		Oxic	1.90	1.45	0.15	0.097
	Run No. 2	Anoxic	0.47	1.47	0.057	0.15
		Oxic	0.46	1.45	0.072	0.024
F400	Run No. 1	Anoxic	1.93	1.46	0.154	0.023
		Oxic	2.19	1.50	2.20	0.046
	Run No. 2	Anoxic	0.47	1.47	0.162	0.016
		Oxic	0.75	1.42	2.18	0.46

single solute adsorption, 2-chlorophenol showed higher adsorptive capacity than 2-methylphenol [27].

3.4. Binary adsorption of 2-methylphenol/2-nitrophenol

Binary adsorption isotherms of 2-methylphenol/2-nitrophenol were conducted on F400, ACC-10 and ACC-15 under anoxic and oxic conditions in this section. It was known from the single solute adsorption, 2-nitrophenol did not show any oligomerization on either adsorbent under oxic conditions, while 2-methylphenol was the easiest to get oligomerized [27]. This combination would help to understand the competitive effect between the two adsorbates where one was affected by the presence of molecular oxygen and the other was not. Two initial concentration combinations were chosen for the binary systems on all the adsorbents. The initial concentration of 2-nitrophenol was kept constant while the initial concentration of 2-methylphenol was either similar to or lower than that of 2-nitrophenol. The IAST was used to simulate the multicomponent adsorption isotherms. The Initial concentration combinations are shown in Table 2.

Fig. 4 shows the two runs of binary adsorption on ACC-10. It is seen from Fig. 4 that the experimental data for both oxic and anoxic conditions overlapped in the first run and no obvious difference was observed. For the second run on ACC-10, the differences between anoxic and oxic isotherms for 2-methylphenol is due to the different initial concentrations used; for anoxic 2-methylphenol, the initial concentration was 0.48 mM (see Table 2), while for oxic isotherms, it was 0.67 mM. The good prediction of IAST indicates that 2-Methylphenol did not show oligomerization for either combination. Evaluation of the predictability of IAST was done by calculating the sum of SSREs which is shown in Table 2. The SSREs of 2-methylphenol were ranging between 0.055 and 0.16 and for 2-nitrophenol were between 0.024 and 0.18. The low SSREs indicate good IAST predictions. Thus, although ACC-10 showed difference between oxic and anoxic isotherms for the single solute system for 2-methylphenol indicating occurrence of oligomerization while for the binary system oligomerization was hampered.

Fig. 5 shows two combinations of the binary adsorption of 2-methylphenol/2-nitrophenol on ACC-15. Differently from the 2-methylphenol/2-chlorophenol adsorption on ACC-15, the binary adsorption of 2-methylphenol and 2-nitrophenol on ACC-15 did not show any difference between anoxic and oxic isotherms. ACC-15 has shown similar results as ACC-10, that is, the oxic and anoxic adsorption isotherms overlapped. The IAST well predicted both the anoxic and oxic binary systems using the anoxic parameters. This indicates that the oligomerization of 2-methylphenol on ACC-15 has been hampered. However, previously it has been shown that

the binary adsorption of 2-methylphenol/2-chlorophenol on ACC-15 showed obvious difference between oxic and anoxic isotherms and IAST only well predicted the anoxic isotherms, but failed to predict the oxic ones. The poor model predictions for ACC-15 under oxic conditions were attributed to oligomerization of the adsorbates on the surface of activated carbon. Differently from 2-chlorophenol, 2-nitrophenol didn't show any oligomerization under oxic conditions in single solute adsorption [27]. It can be, therefore, assumed that 2-nitrophenol is going to occupy similar sites under oxic conditions as compared to anoxic conditions. As for 2-methylphenol, although it got oligomerized in single solute adsorption on ACC-15, there will not be enough sites for it to get oligomerized in the binary systems under oxic conditions.

Fig. 6 shows two runs of 2-methylphenol/2-nitrophenol on F400. Evaluation of the predictability of IAST was done by calculating
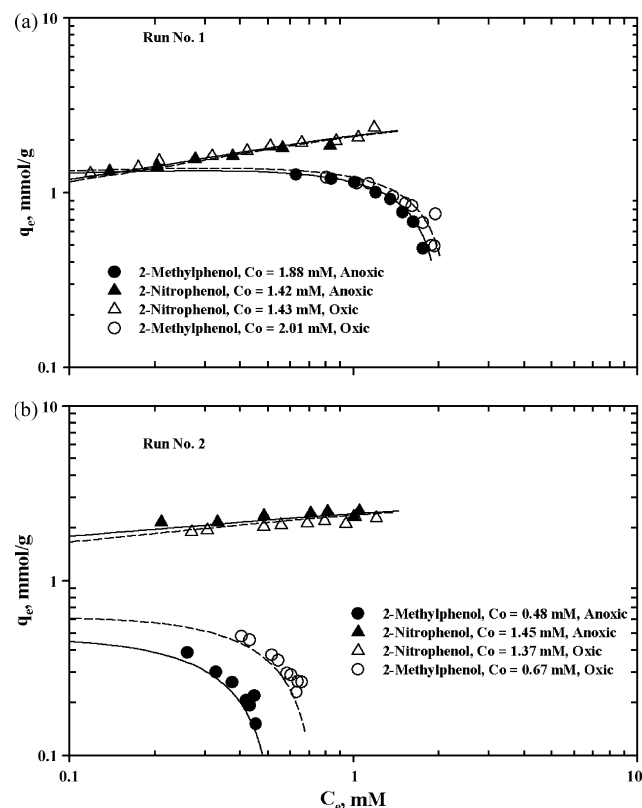

Fig. 4. Binary adsorption of 2-methylphenol/2-nitroophenol on ACC-10 (solid lines represent anoxic IAST prediction and dashed lines represent oxic IAST predictions).
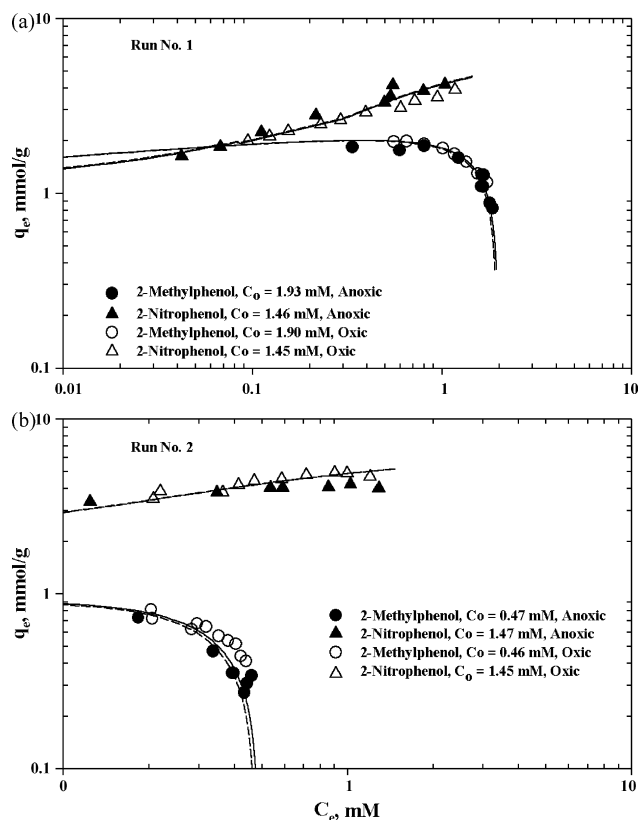
Fig. 5. Binary adsorption of 2-methylphenol/2-nitrophenol on ACC-15 (solid lines represent anoxic IAST prediction and dashed lines represent oxic IAST predictions).
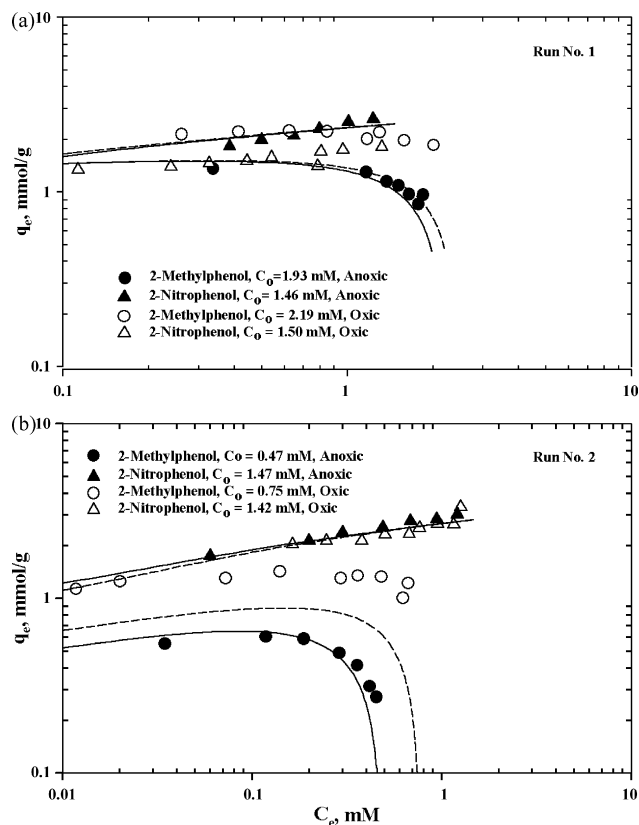

Fig. 6. Binary adsorption of 2-methylphenol/2-nitrophenol on F400 (solid lines represent anoxic IAST prediction and dashed lines represent oxic IAST predictions).

the sum of SSREs (shown in Table 2). For 2-methylphenol, IAST well predicted only the anoxic isotherms, but under predicted the oxic ones. This is similar to the combination of 2-methylphenol/2-chlorophenol. However, the result for 2-nitrophenol is very interesting. In run No. 2, there is no difference between anoxic and oxic experimental isotherms for 2-nitrophenol, but for run No. 1, the anoxic 2-nitrophenol is much higher than the oxic ones and IAST over predicted the 2-nitrophenol adsorption under oxic conditions. In run No. 2, 2-methylphenol had much lower concentration than 2-nitrophenol. Therefore, although 2-methylphenol occupied more adsorption sites under oxic conditions than under anoxic conditions, this change did not influence 2-nitrophenol much. But in run No. 1, 2-methylphenol had similar initial concentrations as 2-nitrophenol. Under oxic conditions, 2-methylphenol occupied more adsorption sites due to oligomerization, hence, there will be fewer sites available for 2-nitrophenol. This explains why the oxic adsorptive capacity for 2-nitrophenol in run No. 1 was lower than anoxic ones.

3.5. Ternary adsorption

ACC-10 was shown to be effective in hampering oligomerization of the adsorbates in the binary adsorption of 2-methylphenol/2-chlorophenol and 2-methylphenol/2-nitrophenol. This was confirmed by different combinations of these adsorbates. Oligomerization was shown to occur on ACC-15 for 2-methylphenol/2-chlorophenol system and on F400 for both binary systems. To further elucidate the impact of adsorbent PSD and adsorbate COP on oligomerization in competitive adsorptions, ternary adsorption of 2-methylphenol/2-chlorophenol/2-nitrophenol was conducted on ACC-15 and F400 in this study.

3.6. Ternary adsorption on ACC-15

Ternary adsorption of 2-methylphenol/2-chlorophenol/2-nitrophenol were conducted on ACC-15 and F400 under anoxic and oxic conditions. The molecular dimensions for the three adsorbates are three-dimensional (D)/2-D/2-D. Two initial concentration combinations were studied, as shown in Table 3. These combinations would be helpful in understanding the impact of different molecular structure on multicomponent adsorption.

Fig. 7 shows two runs of the 2-methylphenol/2-chlorophenol/2-nitrophenol ternary system on ACC-15. Evaluation of the predictability of IAST was also done by calculating the sum of SSREs. The SSREs are summarized in Table 3.

It can be seen from Fig. 7 that the experimental data for both oxic and anoxic conditions overlapped, no obvious difference was observed. As can be recalled, the binary adsorption of 2-methylphenol/2-chlorophenol on ACC-15 indicated slight difference between oxic and anoxic binary adsorption isotherms. The oxic adsorptive capacity was higher than the anoxic for both 2-methylphenol and 2-chlorophenol. For the binary adsorption of 2-methylphenol/2-nitrophenol on ACC-15, oxic and anoxic adsorption isotherms overlapped, showing no difference between oxic and anoxic isotherms. Thus, when considering ternary adsorption of 2-methylphenol/2-chlorophenol/2-nitrophenol on ACC-15, it is supposed that oligomerization would be hampered since there are less available sites for the ternary system as compared to the binary system due to competitive adsorption. The experimental results agreed well with this hypothesis. It is thus postulated that oligomerization was hampered for all adsorbates due to narrow PSD and small pore diameter. This result also agreed well with our previous studies in ternary adsorption of phenol/2-methylphenol/2-ethylphenol on ACC-15 [19].

The similar adsorption behavior under anoxic and oxic conditions for the ternary system on ACC-15 is further confirmed by using

Table 3
Summary of ternary adsorption of 2-methylphenol, 2-chlorophenol and 2-nitrophenol.

Adsorbent	Run No.	Conditions	Initial concentrations (mM)			SSREs		
			2-Methylphenol	2-Chlorophenol	2-Nitrophenol	2-Methylphenol	2-Chlorophenol	2-Nitro phenol
ACC-15	Run No. 1	Anoxic	0.46	0.78	2.93	0.21	0.29	0.10
		Oxic	0.52	0.79	2.98	0.046	0.078	0.081
	Run No. 2	Anoxic	3.55	1.56	0.34	0.081	0.064	0.12
		Oxic	3.75	1.54	0.35	0.031	0.046	0.13
F400	Run No. 1	Anoxic	0.46	0.78	2.93	0.18	0.30	0.48
		Oxic	0.50	0.81	2.87	1.85	0.32	0.072
	Run No. 2	Anoxic	3.49	1.54	0.68	0.13	0.15	0.68
		Oxic	3.65	1.50	0.68	1.59	0.69	1.42

the anoxic parameters determined for the single solute system in the IAST predictions for both the oxic and anoxic ternary system. It can be seen from Fig. 7 that IAST predicted reasonably well both oxic and anoxic ternary adsorption on ACC-15 when using anoxic Myers parameters.

3.7. Ternary adsorption on F400

Fig. 8 shows two runs of the adsorption of 2-methylphenol/2-chlorophenol/2-nitrophenol ternary system on F400. In the first run, the initial concentration was in the order 2-nitrophenol > 2-chlorophenol > 2-methylphenol. As shown in Fig. 8, both 2-chlorophenol and 2-methylphenol showed oligomerization under oxic conditions since the oxic adsorptive capacities were higher than the anoxic isotherms. However, for 2-nitrophenol, the anoxic adsorptive capacities were higher than the oxic isotherms. This is consistent with the results in binary adsorption systems described previously. In the binary adsorption of 2-methylphenol/2-nitrophenol on F400, 2-nitrophenol showed higher adsorptive

capacities under anoxic conditions than oxic conditions; this behavior was attributed to the occupation of more sites by 2-methylphenol under oxic conditions than that under anoxic conditions. Similar explanation can be given to the ternary adsorption on F400. When oligomerization occurred for 2-chlorophenol and 2-methylphenol under oxic condition more adsorption sites were occupied. Accordingly, there are fewer sites for 2-nitrophenol which does not exhibit any oligomerization under oxic conditions based on the single solute isotherms [27]. Therefore, this behavior led to the oxic adsorptive capacity for 2-nitrophenol to be lower than anoxic isotherms.

In the second run of ternary adsorption of 2-methylphenol/2-chlorophenol/2-nitrophenol on F400, the initial concentration was in the order of 2-nitrophenol < 2-chlorophenol < 2-methylphenol. As shown in Fig. 8, 2-methylphenol showed oligomerization under oxic conditions while for 2-chlorophenol, the oxic and anoxic adsorption isotherms overlapped. 2-Nitrophenol showed higher adsorptive capacities under anoxic conditions. Considering the anoxic single solute adsorption for these compounds, 2-nitrophenol
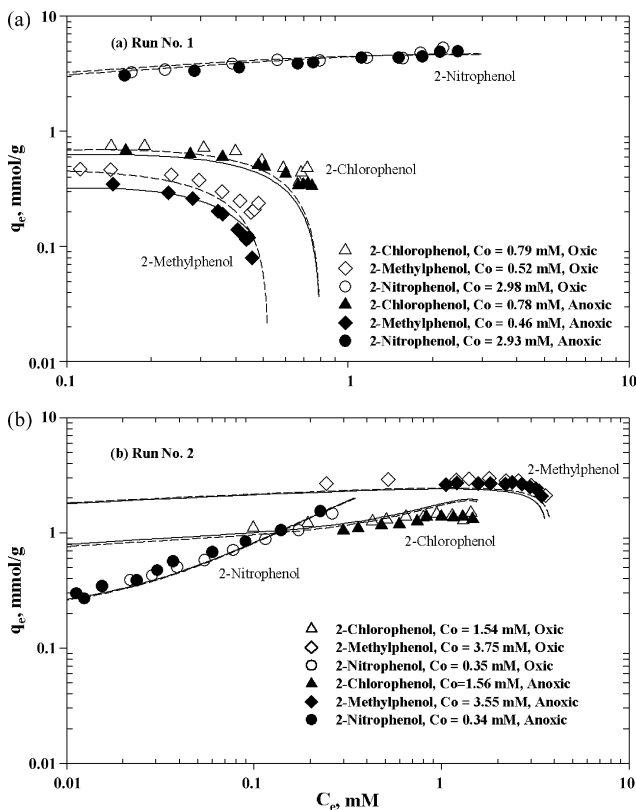

Fig. 7. Ternary adsorption of 2-methylphenol/2-chlorophenol/2-nitrophenol on ACC-15 (solid lines represent anoxic IAST prediction and dashed lines represent oxic IAST predictions).
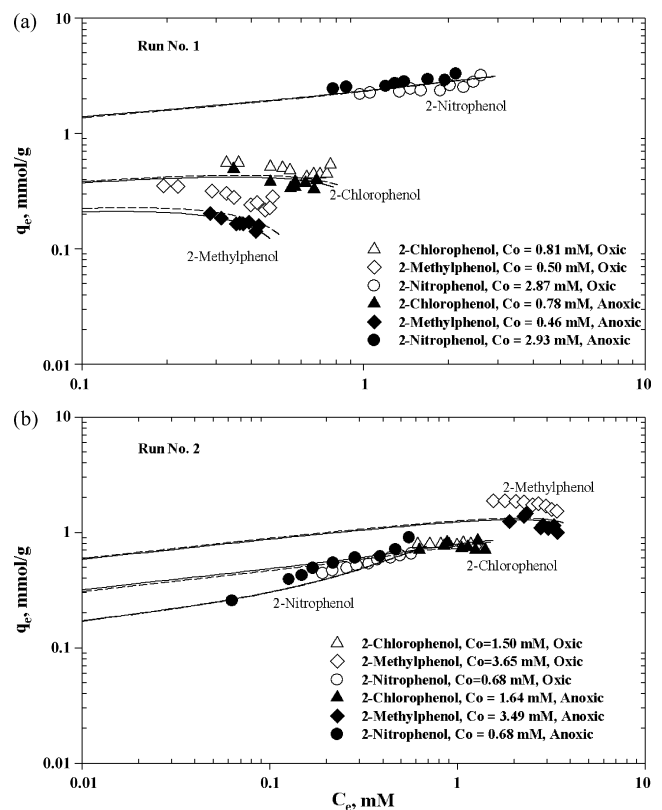

Fig. 8. Ternary adsorption of 2-methylphenol/2-chlorophenol/2-nitrophenol on F400 (solid lines represent anoxic IAST prediction and dashed lines represent oxic IAST predictions).

was more adsorbable than 2-chlorophenol, while 2-methylphenol was the least adsorbable among the three [27]. Under oxic condition, 2-methylphenol is the easiest to get oligomerized due to its low COP (1.04 V); while 2-chlorophenol (1.095 V) and 2-nitrophenol (1.434 V) have much higher COP values. Due to the overall competitive effects of 2-methylphenol and 2-nitrophenol, 2-chlorophenol happened to not show any difference between the oxic and anoxic isotherms. The fact that 2-nitrophenol showed higher adsorptive capacities under anoxic conditions than oxic ones can be explained as stated previously for run No. 1.

Fig. 8 and Table 3 indicate clearly the poor prediction of IAST for this ternary system on F400. In all cases considered, the IAST predicted reasonably well the anoxic data and under predicted the oxic data confirming our previous postulation that oligomerization occurred under oxic conditions.

4. Conclusions

Binary and Ternary adsorption of phenolic compounds were conducted on ACC-10, ACC-15, and F400 in this study. For all the binary isotherms on ACC-10, anoxic and oxic isotherms overlapped and IAST well predicted these isotherms. The small pore diameter and narrow PSD of ACC-10 made it effective in hampering oligomerization of phenolic compounds in the binary system. For binary adsorption of 2-methylphenol/2-chlorophenol on ACC-15, oxic adsorption isotherms showed somewhat oligomerization and IAST predicted only the anoxic isotherms. Deviations of IAST encountered in predicting the oxic isotherms were attributed to the oligomerization of the adsorbates on the adsorbent surface. There was no difference between oxic and anoxic isotherms for 2-nitrophenol/2-methylphenol on ACC-15. 2-nitrophenol occupied similar sites under oxic conditions as compared to anoxic conditions and it is speculated that the oligomerization of 2-methylphenol was hampered, consequently. Obvious difference between anoxic and oxic binary adsorption was noticed on F400. IAST well predicted only the anoxic adsorption but under-predicted the oxic ones. The deviation of the experimental adsorption isotherms on F400 from predictions was larger than that of ACC-15. The narrow PSD of ACC-15 reduced the oligomerization to some extent and the wide PSD of F400 favored the oligomerization.

In ternary adsorption, ACC-15 was effective in hampering oligomerization of phenolic compounds when molecular oxygen was present. IAST fairly predicted ternary adsorption on ACC-15 under anoxic and oxic conditions. In ternary adsorption of 2-methylphenol/2-chlorophenol/2-nitrophenol on F400, 2-methylphenol showed oligomerization under oxic condition. The oligomerization of 2-chlorophenol depends on the overall competitive effect of 2-methylphenol and 2-nitrophenol. 2-Nitrophenol showed higher adsorptive capacity under anoxic conditions than oxic ones due to more available adsorption sites under anoxic conditions. This behavior was consistent with the results of the binary adsorption of 2-methylphenol/2-nitrophenol on F400. The narrow PSD of ACFs was shown to be effective in hampering oligomerization of phenolic compounds in the adsorption systems.

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