Effect of molecular oxygen on adsorptive capacity and extraction efficiency of granulated activated carbon for three ortho-substituted phenols

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Abstract

Adsorptive capacity of activated carbon for several organic compounds was found to be strongly influenced by the presence of molecular oxygen. This influence is manifested by the polymerization of adsorbate on the surface of activated carbon. As a result, GAC exhibits much higher adsorptive capacities for these compounds under oxic rather than under anoxic conditions. Therefore, a new experimental procedure for conducting adsorption isotherm tests is investigated in this work. The results of kinetic experiments show that this polymerization of adsorbate proceeds at a very slow rate which extends the time required for equilibrium conditions to be established. Extraction efficiency obtained for GAC used in anoxic isotherm experiments were significantly higher than those obtained for GAC used in isotherm experiments conducted in the presence of molecular oxygen.

1. Introduction

Activated carbon has been successfully used in many of the processes encountered in both drinking water and wastewater treatment for the removal of a wide range of natural and synthetic organic compounds. However, the adsorption mechanisms and all the parameters that affect adsorptive properties of activated carbon are not yet clearly defined. The capacity of activated carbon for the retention of organic compounds is most commonly given by an adsorption isotherm that represents the constant temperature equilibrium between the quantity of adsorbate retained per unit mass of adsorbent, q_e, and the concentration of adsorbate in solution, C_e. Theoretically, equilibrium data are independent of the way they are obtained and

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activated carbon capacities must be in agreement irrespective of the experimental procedure adopted. The most commonly used experimental method is the bottle-point technique. Unfortunately, a unique procedure for conducting this test has not yet been established. As a result, many different isotherms for the same adsorbate–adsorbent pair are reported in the literature [1]. Some of the important issues related to the experimental determination of granular activated carbon (GAC) adsorptive capacity are discussed by Randtke and Snoeyink [2]. Peel and Benedek [1] reported that particle size, the presence or absence of a weak buffer, and the initial concentration of adsorbate, had no effect on the equilibrium relationship for phenol and o-chlorophenol. Several other investigators [1, 3] also found no influence of GAC particle size on the adsorptive capacity of activated carbon provided that sufficient equilibration time is allowed in the isotherm experiment. Contradictory findings regarding the effect of the initial adsorbate concentration on the capacity of GAC are reported in the literature. Some researchers [4, 5] found GAC capacities to be higher for lower initial adsorbate concentrations while others [1, 6, 7] reported no such effect.

Many researchers have found that the adsorptive capacities of activated carbon determined from isotherm tests and batch and column studies are often not in agreement [4–6, 8, 9]. This was attributed to continuously decreasing liquid phase adsorbate concentration during the equilibration period [6], irreversible adsorption [6], decline in intraparticle diffusion rate during the later part of breakthrough as saturation is approached [5], and the difference in diffusion processes into macropores and micropores [10–12].

A considerable number of studies have been conducted on the nature of oxygen-containing functional groups present on the surface of activated carbon and their influence on the adsorptive properties of that carbon [13–16]. Coughlin and Ezra [13] found that oxidation of the surface of activated carbon increases the quantity of acidic oxygen, which diminishes its capacity for the adsorption of phenol and nitrobenzene. Magne and Walker [15] showed that chemisorption of oxygen on activated carbon at 573 K reduces the initial capacity of that carbon for the retention of phenol.

No research has been done to evaluate the effect of the presence of molecular oxygen on the adsorption process. Prober et al. [17] showed that the adsorptive capacity of activated carbon for molecular oxygen ranges from 10 to 40 mg/g. This is manifested as an increased base sorption capacity, particularly in the pH ranges for the carboxylic acid groups (3–5.5). Earlier investigations by the authors [18] revealed that the presence of molecular oxygen in the test environment (oxic conditions) can cause an increase in the adsorptive capacity of GAC for several phenolic compounds by as much as 200%. This study was undertaken to provide further explanation for the observed phenomenon.

2. Experimental procedures

The adsorbent used in this study was Filtrasorb 400 GAC (Calgon Carbon, Pittsburgh, PA) supplied in 12 × 40 US mesh size. The fraction used for the experiments was 16 × 20 having a geometric mean particle diameter of 0.1 cm. Carbon was thor-

oughly washed with deionized water, dried at 110°C for 2 d and stored in a desiccator until used. All the experiments were performed using one batch of activated carbon.

Reagent grade 2-methylphenol, 2-chlorophenol, and 2-ethylphenol were used as adsorbates in this study. These compounds were chosen for the study to evaluate the influence of the type of functional group substituted on the parent phenol molecule on the same position on the adsorptive properties of activated carbon under oxic and anoxic conditions. All the adsorbates were obtained from the manufacturers in the highest purity form available and were not further purified prior to use in this study. Milli-Q water (tap water treated by reverse osmosis, ion exchange, and GAC adsorption) containing 0.01 M phosphate buffer and adjusted to pH 7.0 with 10 M NaOH solution was used for preparation of the sorbate solutions.

2.1. Adsorption isotherm tests

The bottle-point technique was used for all adsorption isotherm tests. However, two different procedures, denoted henceforth as 'oxic' and 'anoxic', were employed in this study. The oxic procedure is very similar to the traditionally used techniques and involves placing accurately weighed portions of GAC (± 0.1 mg) into a series of 160 ml bottles. After the addition of 100 ml of sorbate solution, bottles were sealed with rubber stoppers and aluminum caps. This procedure is denoted as oxic since it allows three different sources of molecular oxygen in the bottles: namely, air or oxygen in the headspace of isotherm bottles, air associated with carbon particles, and the dissolved oxygen (do) present in the water used in preparing the solutions.

The anoxic procedure, on the other hand, requires the absence of molecular oxygen from the isotherm bottles. This was achieved by displacing the air associated with carbon particles with nitrogen gas, stripping the oxygen from the water with nitrogen prior to addition of adsorbate, and purging the headspace, if any was used, in the bottle with nitrogen gas prior to sealing. To ensure maximum displacement of oxygen entrapped in carbon pores, GAC was purged with nitrogen gas twice a day for 3 d prior to the start of the experiment. It is possible that not all of the oxygen adsorbed on the surface of GAC particles during preparation will be removed just by purging with nitrogen gas. However, it was not the intention of this study to evaluate the effects of irreversibly adsorbed or chemisorbed oxygen, but rather the effects of molecular oxygen present in the air associated with carbon particles or headspace in the isotherm bottles and oxygen dissolved in the sorbate solution.

Isotherm bottles were placed on a rotary shaker and allowed to equilibrate for at least 2 weeks. Several bottles from each isotherm run were permitted to equilibrate an additional week. Each isotherm run include two bottles containing sorbate solution and no GAC that served as blanks to check for sorbate volatilization and/or adsorption onto the walls of the container during the equilibration period. All the isotherm tests were conducted at room temperature, which varied in a very narrow range of 21 $\pm$ 1°C.

Concentration measurements were performed on a 8452 A Hewlett Packard diode-array spectrophotometer using a 1 cm quartz cell. For more accurate measurements at low sorbate concentrations, a 5 cm quartz cell was employed. Wavelengths used were: 272 nm for 2-methylphenol, 274 nm for 2-chlorophenol, and 272 nm for 2-ethylphenol.

Periodic photometric scans in the range of 230 to 300 nm were also performed. These scans were determined to be always identical to the scans obtained for standard solutions prepared for the calibration of the instrument. It is important to note that the liquid samples from all isotherm tests were first filtered through 0.45 μm nylon filters (Micron Separation, Inc.) to eliminate the interference of carbon fines. Preliminary tests showed that none of the compounds used in this study adsorb on the filters. Dissolved organic carbon (DOC) and inorganic carbon analyses (Envirotech Dohrmann DOC Analyzer, model DC-80) were performed on liquid samples randomly selected from the isotherm bottles that were filled to the top with sorbate solution. DOC concentrations were compared with theoretical values that were calculated from concentration measurements of phenols obtained by ultraviolet (UV) spectroscopy. Inorganic carbon analyses were performed at the beginning and end of the isotherm run to check for possible biological activity in the isotherm bottles.

The activated carbon used in the isotherm tests was extracted in a soxhlet extraction apparatus. The GAC samples were extracted for 24 h with methanol followed by extraction with methylene-chloride for an additional 3 d. These extracts were first analyzed using a gas chromatograph (GC) equipped with a DB-1 30 m fused silica capillary column and a flame ionization detector (FID). Gas chromatographic/mass spectroscopic (GC–MS) analyses of the extracts were also performed to provide further explanations for the differences in the GAC adsorptive capacity observed in the presence and absence of molecular oxygen.

2.2. Kinetic experiments

All the rate experiments conducted in this study were performed in a completely mixed, closed-batch reactor. These experiments were carried out in a fermentor (New Brunswick Scientific Co., Edison, N.J.) chosen to provide excellent control of mixing conditions during the experiment. The adsorbate solutions were buffered at pH 7 to ensure that the adsorbates were in their molecular forms. Two types of batch experiments, oxic and anoxic, were conducted using the same initial sorbate concentration, the same mass of activated carbon, and the same mixing conditions. A batch experiment that allows the presence of oxygen, like most batch experiments described in the literature, is denoted as oxic. On the other hand, the anoxic batch experiment was ideally conducted in the air-tight fermentor vessel using a sampling procedure that prevented introduction of any air into the vessel. Once again, molecular oxygen was eliminated from the test environment using the same procedure as in the anoxic isotherm experiments. Samples of 15 ml volume were taken at predetermined time intervals for concentration analysis.

3. Results and discussion

A total of five oxic and eight anoxic adsorption isotherm tests were conducted at room temperature using 2-methylphenol as an adsorbate. Experimental conditions for these tests are given in Table 1. All the oxic adsorption isotherm tests were

conducted using 60 ml of headspace in the isotherm bottle filled with pure oxygen. Anoxic adsorption isotherm tests were conducted either in the absence of any headspace (completely filled bottles) or with the headspace filled with nitrogen gas.

All the experimental data on adsorptive capacity of activated carbon for 2-methylphenol are presented in Fig. 1. Both oxic and anoxic adsorption isotherms for 2-methylphenol are modeled using the Freundlich isotherm equation. Freundlich isotherm equation was used since it provided very good correlation with the experimental data over a wide range of equilibrium concentrations (coefficient of correlation was in all cases above 0.94). Parameters K and $1/n$ in the isotherm equation $q_e = KC_e^{1/n}$ together with standard asymptotic errors, obtained using nonlinear least square regression analysis, are listed in Table 2.

There is no detectable influence of initial adsorbate concentration on the adsorptive capacity of GAC for 2-methylphenol (Fig. 1). This is one indication that the equilibration period of 2 weeks was sufficient for true equilibrium to prevail [1, 2]. However, the equilibration period in several isotherm experiments was extended to 3 and 4 weeks. Since there was no additional removal of 2-methylphenol from the liquid phase during the third and fourth weeks of the experiment, all subsequent runs were conducted for the period of 2 weeks. Nevertheless, a few bottles from each run were allowed to equilibrate for an additional week.

Table 1
Experimental conditions for 2-methylphenol isotherm tests

Initial concentration (mg/l)	Headspace	Isotherm type
1000 (2 runs)	Pure oxygen	oxic
150	Pure oxygen	oxic
100 (2 runs)	Pure oxygen	oxic
1000	Absent	anoxic
1000 (2 runs)	Nitrogen	anoxic
200	Nitrogen	anoxic
150	Absent	anoxic
50 (3 runs)	Nitrogen	anoxic

Table 2
Freundlich isotherm equation parameters for 2-methylphenol

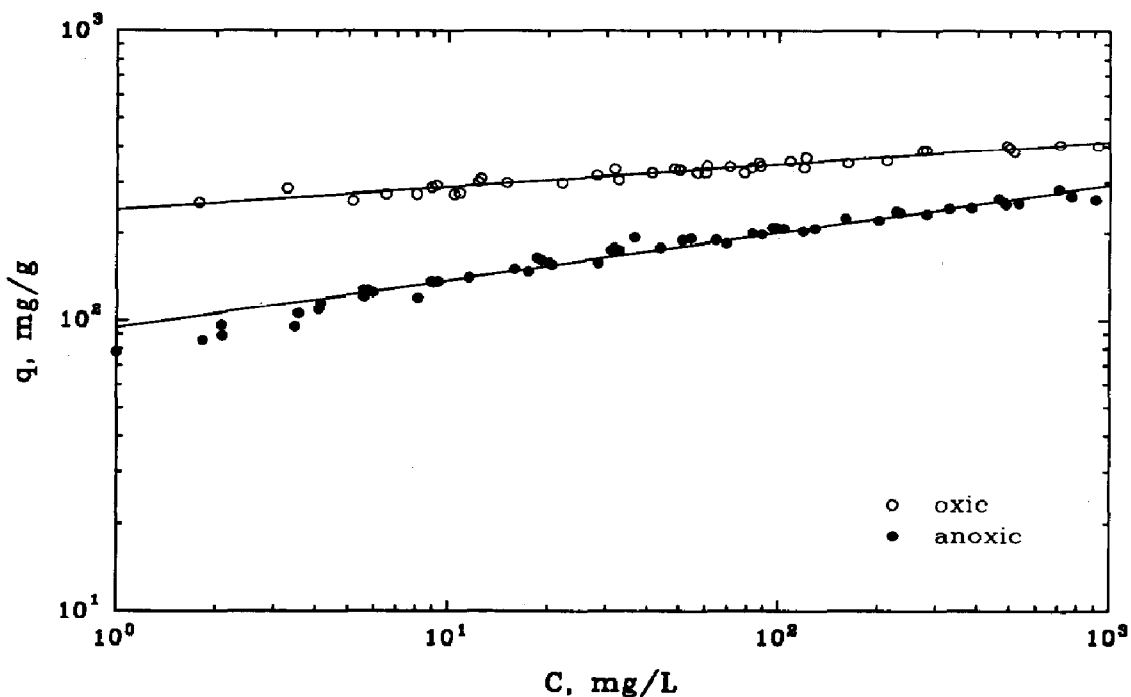| Isotherm type	K $(mg/g)/(mg/l)^{1/n}$	$1/n$
Oxic	241.3 ± 3.6	0.079 ± 0.003
Anoxic	94.14 ± 1.92	0.165 ± 0.004

Fig. 1. Adsorption isotherms for 2-methylphenol.

The headspace in the bottles used in the oxic adsorption isotherm experiments filled with pure oxygen provided a total of 86 mg of oxygen in each bottle. Additional sources of oxygen in these tests were oxygen dissolved in the water used in preparing the adsorbate solutions and from sorbed oxygen and air associated with the carbon pores. Therefore, almost all adsorption isotherms reported in the literature can be considered as oxic since they all facilitate interference of molecular oxygen from these two sources. As is apparent from Fig. 1, the presence of molecular oxygen has a significant impact on the adsorptive capacity of GAC for 2-methylphenol. For the equilibrium 2-methylphenol concentration in the liquid phase of 1000 mg/l, for example, the presence of molecular oxygen (oxic conditions) caused an increase in adsorptive capacity of 42% compared to the capacity that was attainable in the absence of oxygen (anoxic conditions). This difference is even more accentuated in the lower concentration range. For the equilibrium liquid phase 2-methylphenol concentration of 1 mg/l, the oxic adsorptive capacity is 2.56-fold the anoxic one.

Several tests were conducted to evaluate the possibility that biological degradation under oxic conditions in the test environment could be responsible for this higher removal of 2-methylphenol from the liquid phase. This assumption was discarded as a possible explanation for the observed phenomenon due to the reasons listed below:

(1) DOC measurements conducted on liquid samples agreed extremely well with theoretical values computed from concentration measurements for 2-methylphenol obtained by UV spectroscopy (DOC to 2-methylphenol concentration ratio, measured on 28 samples randomly selected from different isotherm runs was 0.772×0.032 while the theoretical value equals 0.779).

(2) An increase in inorganic carbon, which would normally be expected as a result of biological activity, was not observed during the equilibration period (inorganic carbon measured on these 28 samples after the equilibration period averaged 1.9 mg/l, while the inorganic carbon concentration in the stock solution was 1.8 mg/l).

(3) Companion plate count studies conducted by Calgon Carbon (Pittsburgh, PA) on samples of GAC equilibrated by the authors under oxic and anoxic conditions with 2-methylphenol revealed the absence of any microorganisms capable of degrading 2-methylphenol.

(4) Spectroscopic scans of liquid samples at the beginning and end of isotherm runs agreed extremely well with the ones obtained for solutions prepared for the calibration of the instrument.

Results of GC–MS analyses performed on the extracts of the carbon used in oxic and anoxic isotherm experiments indicated that polymerization reactions taking place on the surface of the carbon in the presence of molecular oxygen were responsible for the observed phenomenon. Extracts from the carbons used in the oxic isotherm tests contained significant amounts of dimers, trimers, and even tetramers of 2-methylphenol. The ability of phenolic compounds to form polymers in an oxidizing environment was previously demonstrated by several researchers. Chrostowski et al. [19] showed that catechol, resorcinol, cathecin, gallic acid, and tannic acid undergo oxidative coupling during ozone/oxygen treatment. The same study also concluded that the reactions of phenolics with ozone are accomplished in a shorter time frame than those with oxygen. Voudrias et al. [20] showed that chlorine reacts with phenolic compounds in dilute aqueous solutions to produce mono-, di-, or tri-chloro derivatives, but when it reacts with phenols adsorbed on granular activated carbon, oxidative coupling (dimer formation) of these compounds is also promoted. The study conducted by the authors supports the finding that the surface of activated carbon plays a key role in catalyzing these polymerization reactions since no polymerization was detected in the blanks that accompanied every set of isotherm bottles prepared according to the oxic procedure. Furthermore, molecular oxygen alone was found capable of oxidizing phenol to phenoxy radicals [21].

The tremendous difference in extraction efficiencies obtained from the carbons used in the oxic and anoxic adsorption isotherm tests is apparent in Fig. 2. Extraction efficiency in the anoxic adsorption isotherm tests averaged 89.7% and exhibited very little dependence on the surface loading of the carbon with 2-methylphenol. On the other hand, extraction efficiency obtained for the carbons used in the oxic adsorption isotherm experiments ranged from 12.15% to 32.76% and was strongly dependent on the amount of 2-methylphenol adsorbed per unit mass of GAC (Fig. 2). The lower extraction efficiency obtained for these carbons could be attributed to the fact that polymers of 2-methylphenol formed on the carbon surface in the presence of molecular oxygen are more difficult to extract due to their lower solubility as well as pore blockage caused by these high molecular weight compounds.

The initial phases of the closed-batch kinetic experiments conducted under oxic and anoxic experiments are compared in Fig. 3. It is apparent from this figure that the presence of molecular oxygen exerts almost no influence on the initial (the first 12 h only) rate of removal of 2-methylphenol from the liquid phase. However, after that
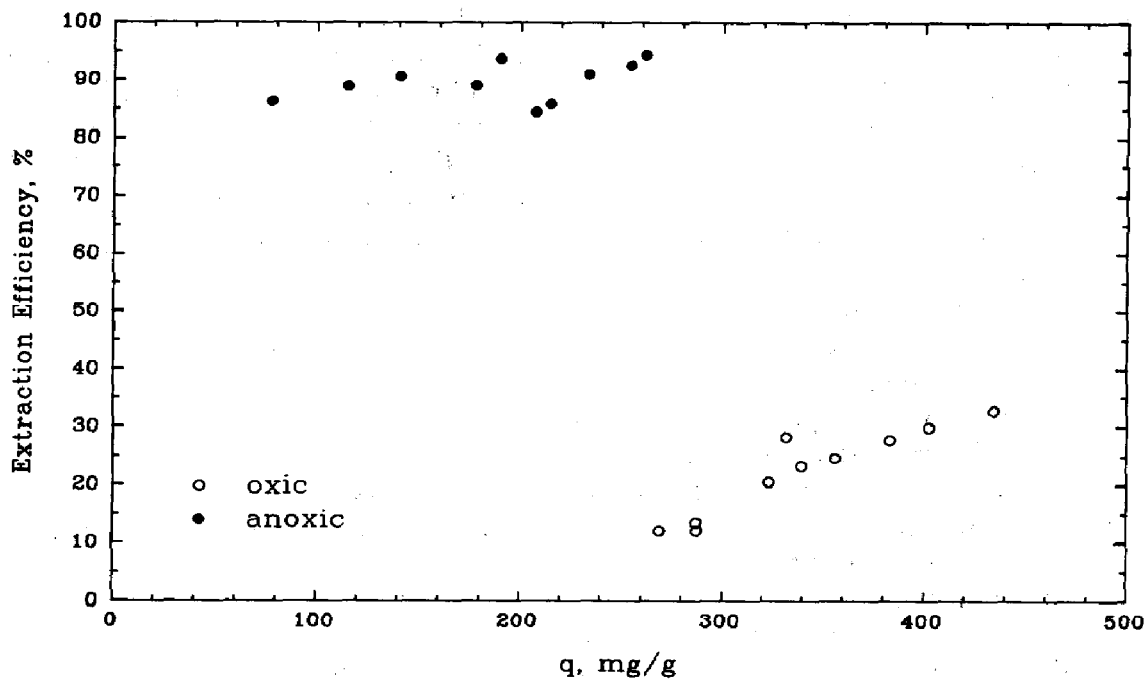
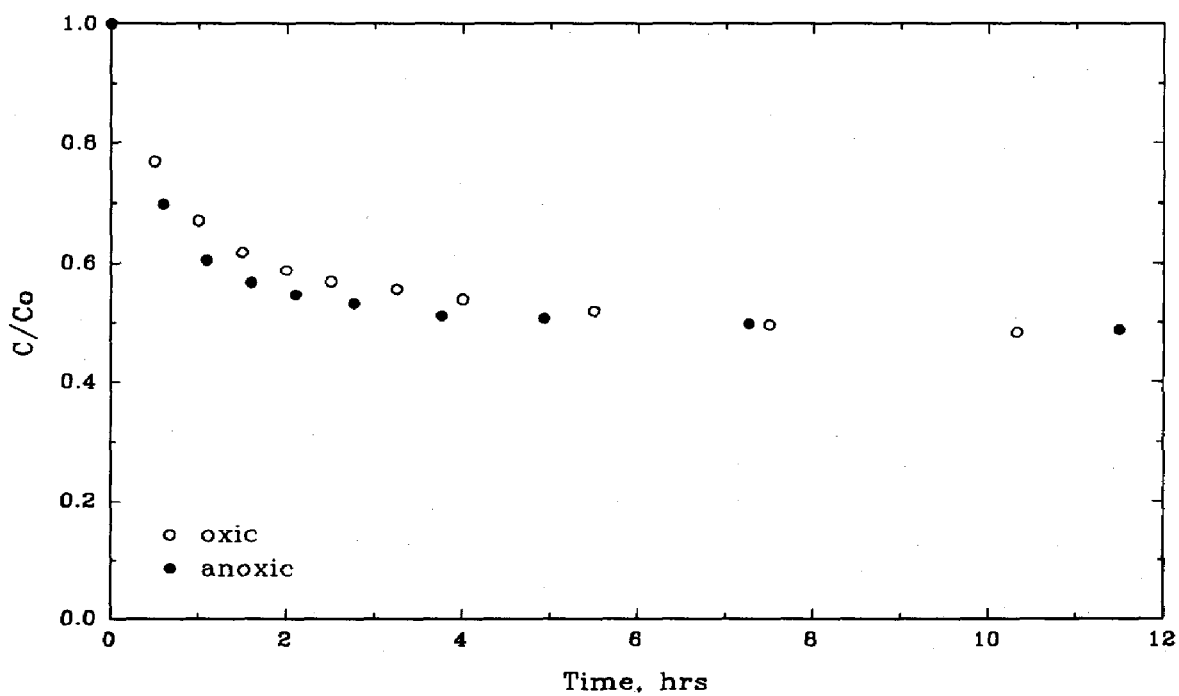Fig. 2. Extraction efficiency for GAC used in adsorption tests with 2-methylphenol.

Fig. 3. Initial phase of closed batch kinetic experiments with 2-methylphenol.

initial period, the liquid phase concentration of 2-methylphenol in the anoxic batch test reached equilibrium very quickly while in the presence of molecular oxygen (oxic test), the removal of 2-methylphenol from the liquid phase continued at a slower rate and took almost 10 d to reach stable levels (Fig. 4). Keeping in mind that the rate of polymerization decreases with an increase in the length of polymer chains formed, it is possible that the period of 12 d was still not sufficient for establishing the true equilibrium in the adsorption experiment conducted in the presence of oxygen. However, the oxic experiment was terminated after 12 d with the assumption of established equilibrium since measurable removal of 2-methylphenol from the liquid phase had ceased. It is reasonable to assume that the amount of 2-methylphenol removed from the liquid phase under anoxic conditions is solely due to the adsorption process, while the higher capacity of GAC for 2-methylphenol that occurs under oxic conditions could be partially attributed to chemical reactions that are taking place on the surface of activated carbon.

The apparent lack of interference from molecular oxygen during the initial portion of the adsorption process may explain why adsorption isotherms obtained using pulverized carbon and shorter periods of time, or from short column runs, tend to predict a much lower adsorptive capacity than adsorption isotherms conducted with intact GAC using equilibration periods of 2 or 3 weeks. Another important conclusion from these batch experiments is that polymerization of 2-methylphenol on the surface of carbon and in the presence of molecular oxygen is occurring at a much slower rate
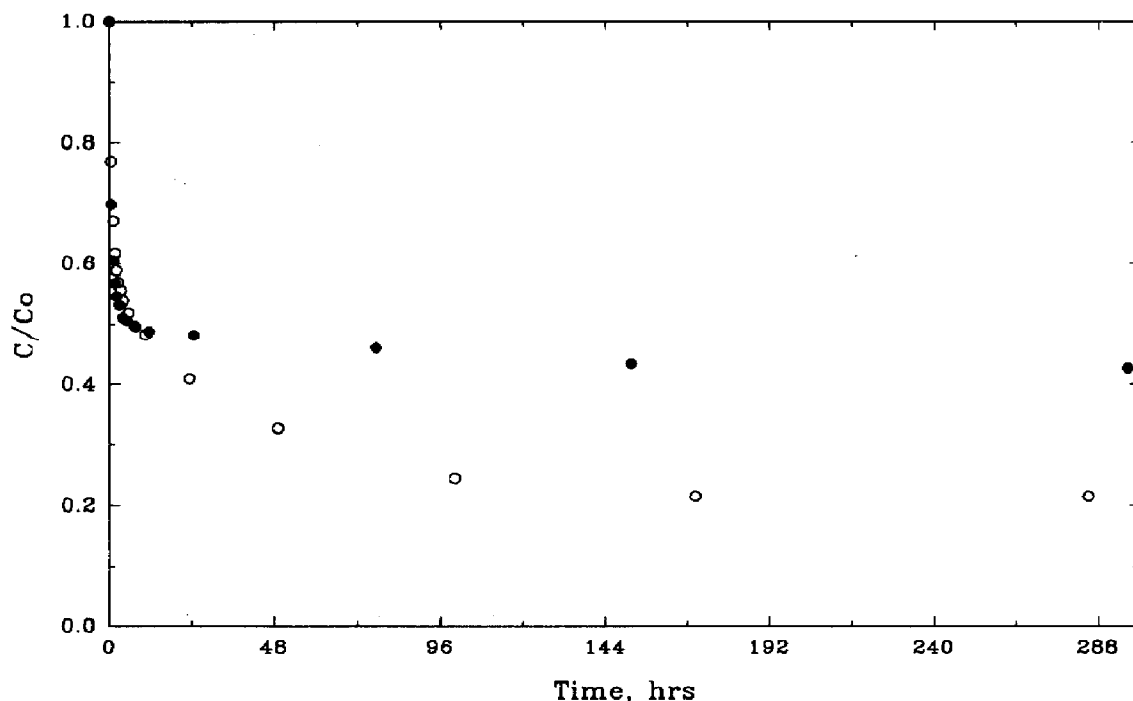

Fig. 4. Closed batch kinetic experiments with 2-methylphenol.

than physical adsorption which causes a slow approach to equilibrium under these conditions.

The adsorptive capacity of GAC in the presence and absence of molecular oxygen was also evaluated for 2-chlorophenol and 2-ethylphenol. Experimental conditions used for evaluating the adsorptive capacity of GAC for these two compounds are listed in Table 3. All the 2-chlorophenol isotherm data, collected from four oxic and two anoxic isotherm runs, are presented in Fig. 5. Adsorption isotherm data for

Table 3
Experimental conditions for 2-chlorophenol and 2-ethylphenol isotherm tests

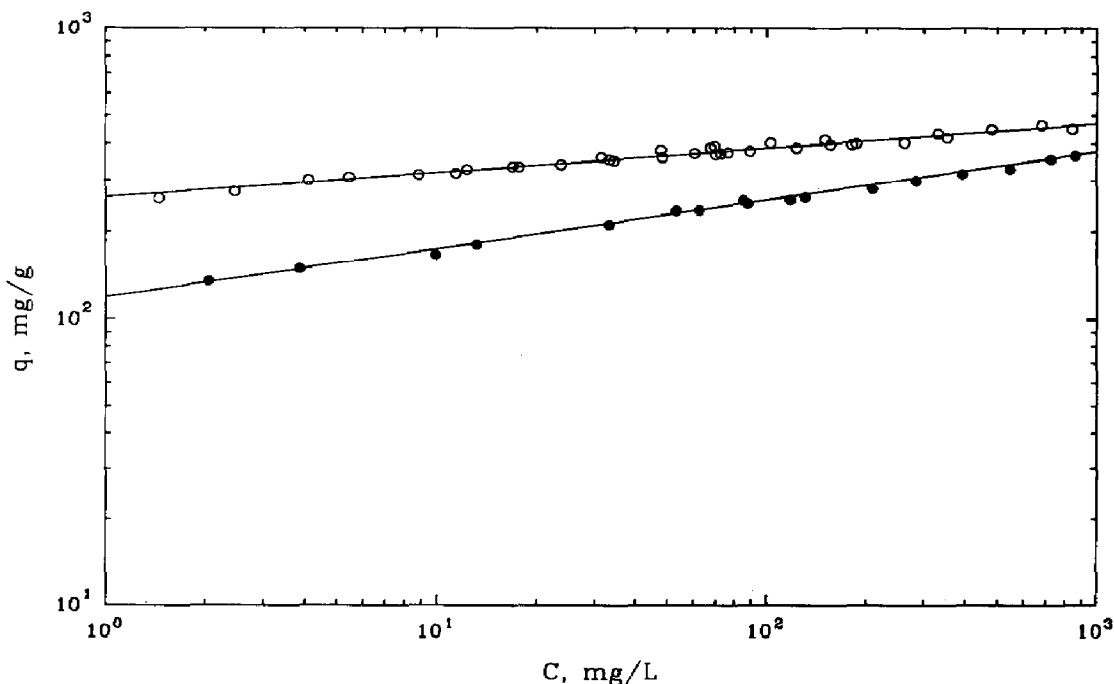| Compound	Initial concentration (mg/l)	Headspace	Isotherm type
2-Chlorophenol	1000 (2 runs)	Pure oxygen	Oxic
	200	Pure oxygen	Oxic
	100	Pure oxygen	Oxic
	1000	Absent	Anoxic
	150	Absent	Anoxic
2-Ethylphenol	1000 (2 runs)	Pure oxygen	Oxic
	150 (2 runs)	Pure oxygen	Oxic
	1000	Absent	Anoxic
	150	Absent	Anoxic

Fig. 5. Adsorption isotherms for 2-chlorophenol.

2-ethylphenol, obtained from two experiments conducted under oxic conditions and two experiments conducted under anoxic conditions are given in Fig. 6. The Freundlich isotherm equation was again found to fit the data for all four adsorption isotherms. Freundlich parameters K and $1/n$ together with standard asymptotic errors obtained for these four isotherms are listed in Table 4.

The presence of molecular oxygen in the test environment also had a tremendous impact on the adsorptive capacity of GAC for these two organic compounds. For example, for the equilibrium liquid phase concentration of 1000 mg/l, oxic conditions yielded an increase in GAC adsorptive capacity for 2-chlorophenol of 24% and for 2-ethylphenol of 25%. Because the anoxic adsorption isotherms obtained for all three compounds investigated in this study yielded significantly higher values for the
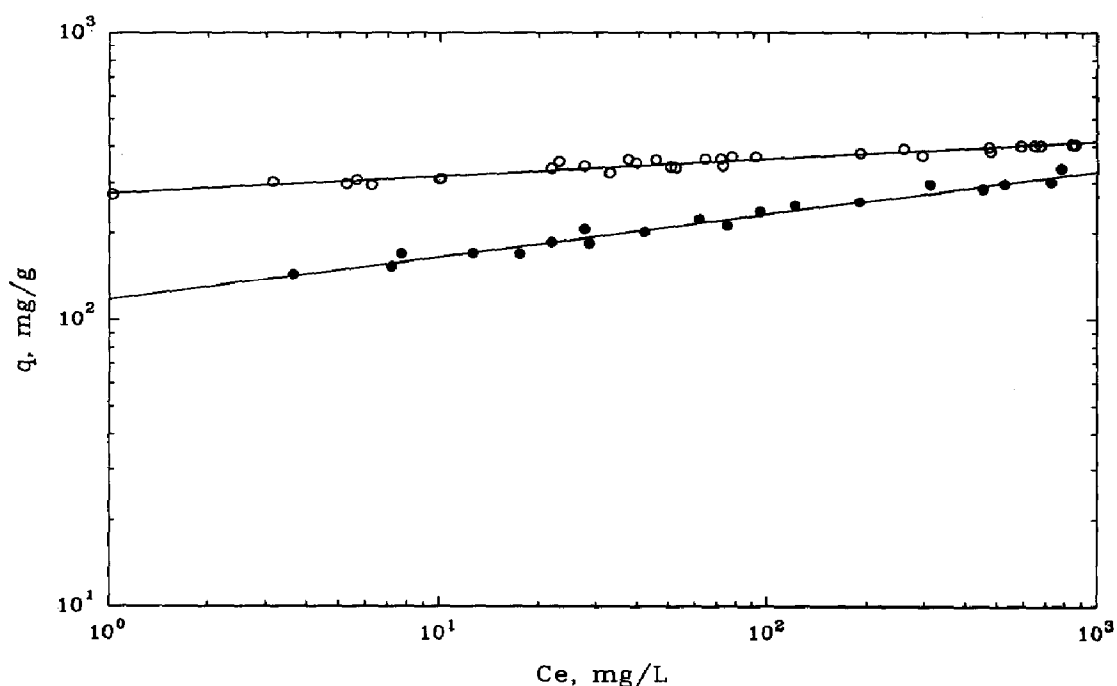

Fig. 6. Adsorption isotherms for 2-ethylphenol.

Table 4
Freundlich isotherm equation parameters for 2-chlorophenol and 2-ethylphenol

Compound	Isotherm type	K $(mg/g)/(mg/l)^{1/n}$	$1/n$
2-Chlorophenol	Oxic	262.5 ± 3.5	0.084 ± 0.003
	Anoxic	119.0 ± 1.96	0.167 ± 0.003
2-Ethylphenol	Oxic	275.6 ± 3.3	0.059 ± 0.003
	Anoxic	117.0 ± 3.9	0.151 ± 0.006

Freundlich parameter $1/n$ than did the oxic adsorption isotherms, this difference in capacities is much more pronounced in the lower concentration range. For the equilibrium liquid phase concentration of 1 mg/l, oxic GAC adsorptive capacity for 2-chlorophenol is 2.21-fold the anoxic capacity, while for the adsorption of 2-ethylphenol that ratio was 2.36. This difference in capacities is best summarized in Fig. 7 where the ratio of oxic to anoxic GAC adsorptive capacity for all three compounds is plotted as a function of the equilibrium liquid phase concentration of adsorbate. This figure clearly shows that the effect of molecular oxygen on the GAC adsorptive capacity depends on the equilibrium liquid phase adsorbate concentration and, consequently, on the amount of adsorbate removed from the solution. Another important conclusion from Fig. 7 is that the influence of molecular oxygen on the adsorptive capacity of GAC becomes more pronounced with an increase in the molecular weight of the substituted functional group. The comparison of oxic and anoxic adsorption isotherms obtained for the compounds investigated in this study, given in Fig. 8, reveals that the absolute values of both anoxic and oxic adsorptive capacity of GAC for these compounds also increased as the molecular weight of the functional group substituted on the ortho position increased.

Extraction efficiencies obtained for the carbons used in oxic and anoxic adsorption isotherm experiments with 2-chlorophenol and 2-ethylphenol are presented in Figs. 9 and 10, respectively. The extraction efficiencies obtained for carbons used in the anoxic isotherm tests are, once again, significantly higher than those obtained for the carbons used in the oxic adsorption isotherm experiments. It is reasonable to believe
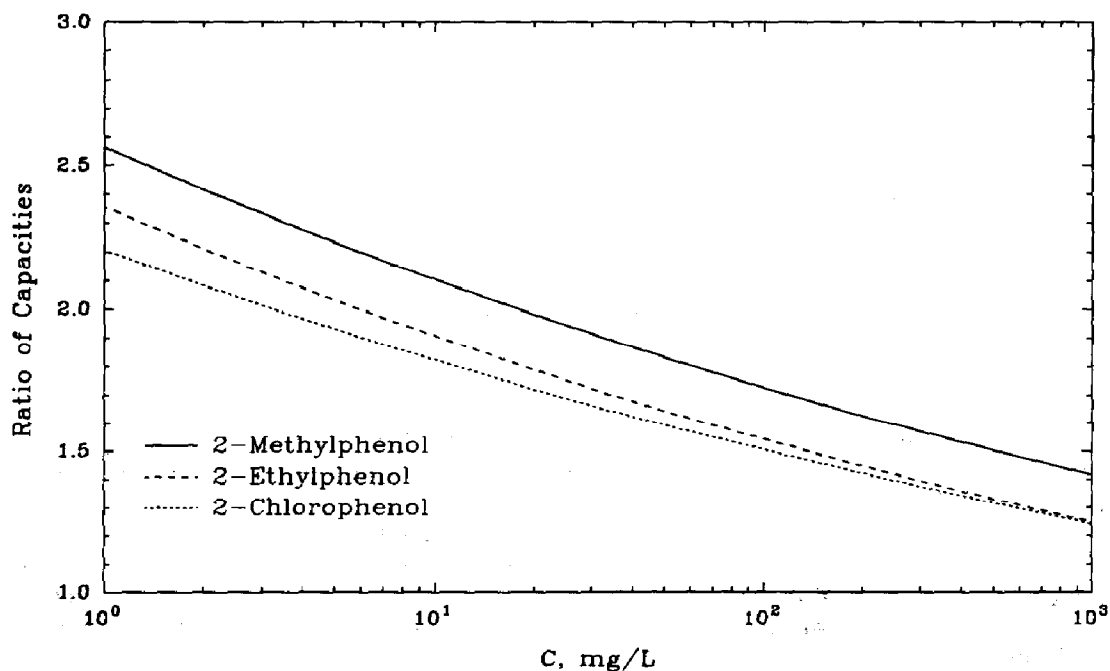

Fig. 7. Ratio of oxic and anoxic GAC adsorptive capacity for three substituted phenols.
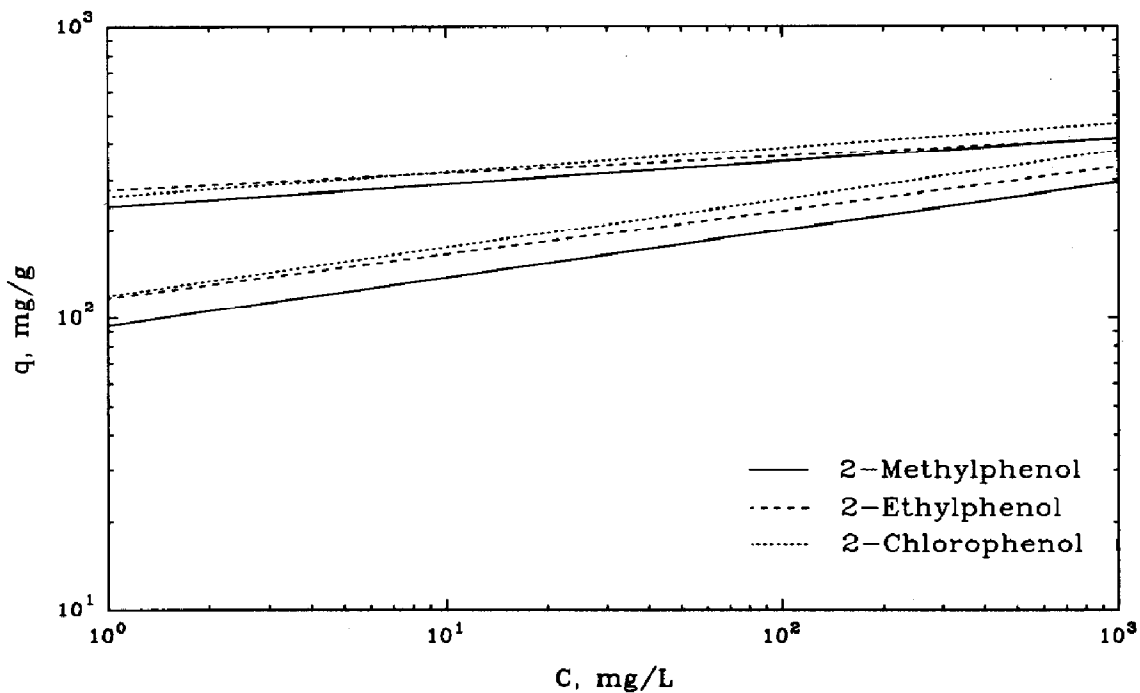
Fig. 8. Effect of different functional groups on GAC adsorptive capacity for phenolic compounds.
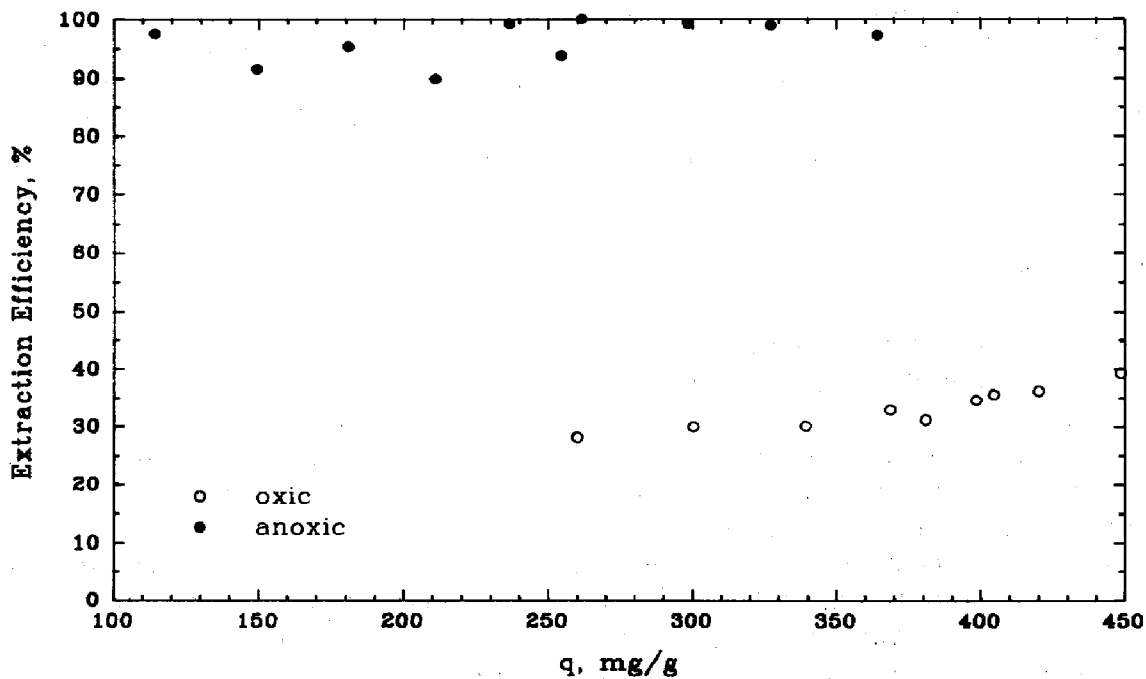

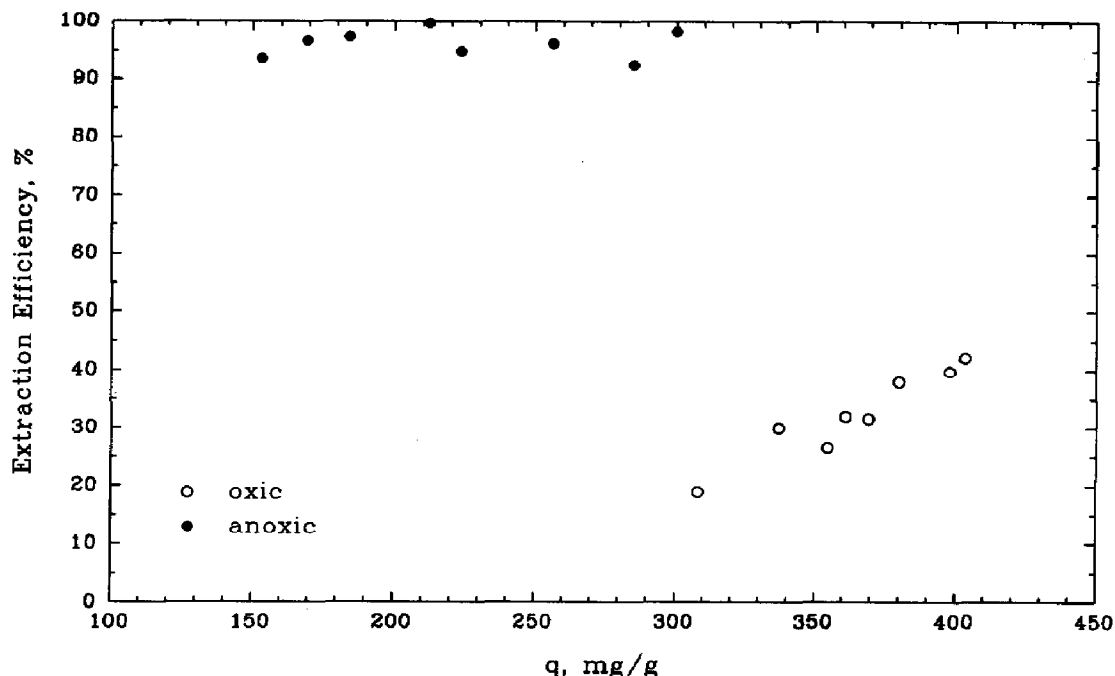Fig. 9. Extraction efficiency for GAC used in adsorption tests with 2-chlorophenol.

Fig. 10. Extraction efficiency for GAC used in adsorption tests with 2-ethylphenol.

that this behavior is, like in the case of 2-methylphenol adsorption, due to some polymerization of 2-chlorophenol and 2-ethylphenol on the GAC surface under oxic conditions. The extraction efficiencies obtained for GAC used in the oxic isotherm experiments with 2-methylphenol are significantly lower than those obtained for GAC used in the oxic isotherm tests with 2-chlorophenol and 2-ethylphenol. On the other hand, the average extraction efficiency obtained for GAC used in anoxic isotherm experiments with all three compounds is 90%, indicating that anoxic conditions promote a truly physical and reversible adsorption process.

4. Summary

The effect of molecular oxygen on the adsorptive capacity of activated carbon for phenolic compounds, previously reported by the authors [18], is investigated further in this study. The presence of molecular oxygen (oxic conditions) causes a significant increase in the adsorptive capacity of GAC for 2-methylphenol, 2-chlorophenol, and 2-ethylphenol. The ratios of oxic to anoxic GAC adsorptive capacity for 2-methylphenol, 2-chlorophenol, and 2-ethylphenol range from 1.42 to 2.56, 1.42 to 2.56, and 1.25 to 2.36, respectively. This increase in capacity is due to polymerization of phenolic compounds that takes place on the carbon surface in the presence of molecular oxygen. Appreciable quantities of dimers, trimers, and even tetramers of 2-methylphenol were detected in the extracts from the carbons used in the oxic adsorption isotherm experiments. The extraction efficiencies obtained for the carbons

used in the adsorption isotherm tests conducted under anoxic conditions averaged approximately 90% for all three compounds. Furthermore, no dependency of extraction efficiency on the loading of the carbon with adsorbate was observed. On the other hand, appreciably lower extraction efficiencies were obtained for the carbons used in the experiments conducted in the presence of molecular oxygen. Furthermore, the extraction efficiency for the carbons equilibrated under oxic conditions increased as the surface loading on the carbon increased.

Kinetic experiments conducted with the same mass of carbon, the same initial adsorbate concentration, and the same mixing conditions revealed very little influence of the presence of molecular oxygen on adsorption kinetics during the initial phase of the tests. Time required for equilibration in the anoxic test was significantly lower than that needed for the test conducted under oxic conditions. It is speculated that polymerization of adsorbate, which induces an increase in the removal of adsorbate from the liquid phase under oxic conditions, occurs at a very slow rate, thereby extending the equilibration time required for this test.

Acknowledgments

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