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**Oxidative Coupling of Phenolics on the
GAC Surface**

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OXIDATIVE COUPLING OF PHENOLICS ON THE GAC SURFACE

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ABSTRACT

Previously reported results by the authors revealed that the presence of molecular oxygen (oxic conditions) in the test environment can, in some instances, cause an almost threefold increase in the adsorptive capacity of granular activated carbon (GAC) for phenolic compounds. It was discovered that these compounds undergo oxidative coupling on the carbon surface under oxic conditions. The polymers formed as a result of these chemical reactions are very difficult to desorb from the surface of GAC. This led to significant irreversible adsorption in the presence of molecular oxygen. On the other hand, when the same compounds are adsorbed on the carbon surface under anoxic conditions, essentially all of the adsorbate can be recovered from the carbon surface by solvent extraction.

The ionized species of phenolic compounds showed even higher susceptibility towards polymerization on the surface of GAC than the parent neutral molecules. GAC particle size did not influence the extent of polymerization. Oxygen uptake measurements revealed significant consumption of molecular oxygen during the adsorption of phenolic compounds. The amount of molecular oxygen consumed in these experiments was found to be linearly proportional to the amount of irreversibly adsorbed compound. This study also showed that some phenolic compounds undergo oxidative coupling in the presence of molecular oxygen even in the absence of the catalytic GAC surface.

KEY WORDS

Adsorption, Activated Carbon, Phenols, Oxidative Coupling, Polymers

INTRODUCTION

Presence of low concentrations of various refractory compounds can be a major obstacle to the use and reuse of water streams. Phenolic compounds can cause objectionable taste and odor problems in drinking water and can exert adverse effects on various biological treatment processes. Some phenolic compounds originate from natural sources while others are manufactured. The urine of some animals and decay of vegetation release phenol to water bodies. Several industrial sources such as coal gasification sites, coke-ovens, oil refineries, town gas sites, and petrochemical units, generate large quantities of phenolic compounds that can, if improperly managed, cause long-term contamination of both surface and groundwater bodies.

Several treatment methods for the removal of phenolic compounds that have been

investigated in the past include both aerobic (Adams, 1974) and anaerobic biodegradation (Suidan, 1983), chemical oxidation with ozone (Gould and Weber, 1976; Chrostowski *et al.*, 1983), adsorption by ion exchange resin (Kim *et al.*, 1976; van Vliet *et al.*, 1981), and activated carbon (Weber and Morris, 1964; Coughlin and Ezra, 1968; Snoeyink *et al.*, 1969; Zogorski *et al.*, 1976; Crittenden and Weber, 1978; Peel and Benedek, 1980; Seidel *et al.*, 1985; Magne and Walker, 1986).

One of the key parameters in designing the activated carbon adsorption process for the removal of organic compounds is the capacity of carbon for the retention of the compounds of interest. This capacity is usually expressed in terms of adsorption isotherms, which represent a relationship between the concentration of the organic compound in the aqueous phase and the mass of that compound on the carbon surface that is in equilibrium with the aqueous phase concentration. The experimental protocol widely used for obtaining adsorption equilibrium data is the bottle point technique. Some of the parameters that affect the adsorption equilibrium determined from this test are discussed by Martin and Al-Bahrani (1978) and Randtke and Snoeyink (1983). Due to the lack of a unified procedure for conducting this test, many different adsorption isotherms for the same adsorbent-adsorbate pair can be found in the literature (Peel and Benedek, 1980).

Recent studies by Vidic *et al.* (1990) and Vidic and Suidan (1991) revealed that the adsorptive capacity of granular activated carbon (GAC) for several phenolic compounds is highly influenced by the presence of molecular oxygen (oxic conditions) in the test environment. The GAC adsorptive capacity for o-cresol that was attainable under oxic conditions was as much as 200% above that obtained in the absence of molecular oxygen (Figure 1). A similar phenomenon was demonstrated for the adsorption of phenol, 2-chlorophenol, and 3-ethylphenol as well as natural organic matter (Vidic and Suidan, 1991).

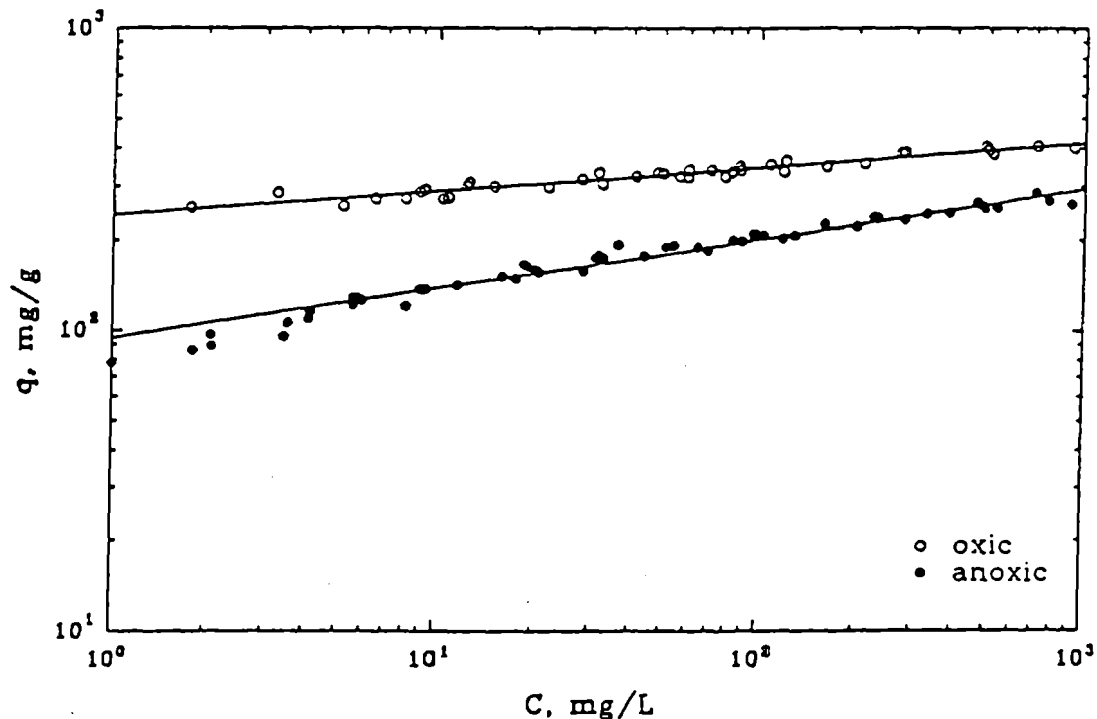


Figure 1. Adsorption Isotherms for o-Cresol

Extraction of the carbon preloaded with o-cresol revealed that almost 100% of the originally adsorbed compound can be recovered from the surface of GAC by solvent extraction if the adsorption was carried out in the absence of molecular oxygen (Figure 2). Conversely, only 10-30% of the adsorbed compound was recovered from GAC loaded under oxic conditions (Figure 2). Similar behavior was also documented for phenol and 3-ethylphenol (Vidic and Suidan, 1991).

This study was designed to further evaluate the role of molecular oxygen on the adsorption of phenolic compounds by activated carbon and to provide possible explanation for the observed phenomena.

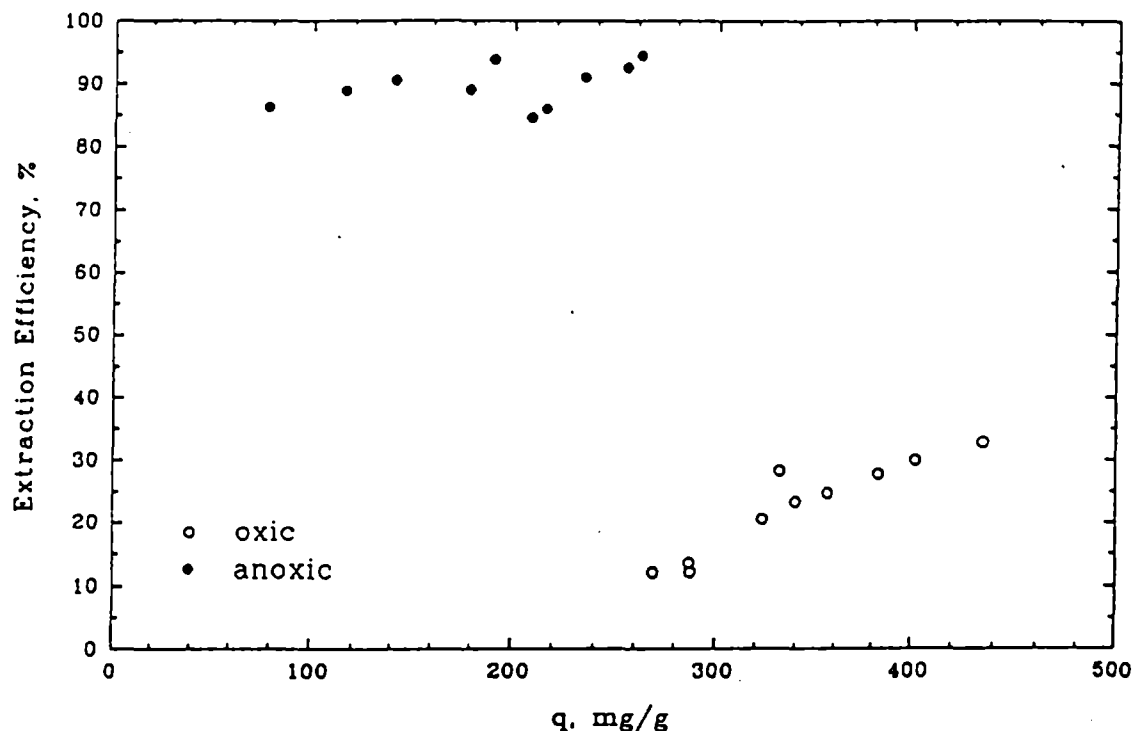


Figure 2. Extraction Efficiency for GAC Used in the Isotherm Tests with o-Cresol

METHODOLOGY

All adsorption experiments were performed at pH 7.0 using autoclaved Milli-Q water (deionized water passed through Millipore purification system, Millipore Corp., Bedford, MA) to prepare the adsorbate solutions. Water was buffered with 0.01M phosphate buffer, and the pH was adjusted with a 10M NaOH solution. The adsorbent used in this study was 16x20 U.S. Mesh Size Filtrasorb 400 (Calgon Carbon Corp., Pittsburgh, PA). Prior to use, carbon was thoroughly washed with Milli-Q water, dried at 105°C, and stored in a desiccator until use. All the experiments described in this study were performed using the same batch of GAC.

Adsorbates used in this study were phenol; 2-, 3-, and 4-methylphenol; 2-ethylphenol; 2- and 4-chlorophenol; 4-hydroxybenzoic acid; 2,4-dimethylphenol; 2,4,6-trichlorophenol; aniline; and

p-anisidine. All the adsorbates were reagent grade or better. Adsorbate concentration measurements were performed on a Hewlett Packard (HP) 8452 Diode-Array Spectrophotometer (Hewlett-Packard Co., Palo Alto, CA) using both 1-cm and 5-cm quartz cells. The extracts from the GAC used in the adsorption isotherm tests were analyzed using an HP 5890A Gas Chromatograph equipped with a DB-1 30-m fused silica capillary column (J&W Scientific, Folsom, CA) and a flame ionization detector (FID). Gas Chromatography/Mass Spectroscopy (GC/MS) analyses were performed on an HP 5985A GC/MS using the electron-impact positive ion mode. The gas chromatograph was equipped with a DB-1 30-m fused silica capillary column (J&W Scientific, Folsom, CA). The oven temperature was programmed from 40-280°C at 10°C/min with a 5 min hold at 40°C.

Adsorption Equilibrium: Detailed description of the experimental protocol used to evaluate GAC adsorptive capacity in the presence and absence of molecular oxygen is provided elsewhere (Vidic and Suidan, 1991) and will not be repeated here.

GAC Extraction: GAC samples from the adsorption isotherm bottles were first separated from the liquid phase by filtering through 0.45- μ m nylon filters (Micron Separations, Inc., Westboro, MA) and transferred into cellulose extraction thimbles (Whatman International, Ltd., Maidstone, England). The thimbles were then placed into a soxhlet extractor apparatus minimizing any contact with ambient air. The extraction was first carried out for one day using methanol (Fisher Scientific, Fair Lawn, NJ) as a solvent. Extraction was then continued for an additional three days with methylene chloride (Fisher Scientific, Fair Lawn, NJ) since it allows for the extraction to be performed at a lower temperature, thus minimizing alteration of the organics due to excessive heat. After the extraction phase, methylene chloride was allowed to evaporate from the round bottom flasks and the extract, dissolved in methanol, was transferred into a volumetric flask where the volume was complemented to 100 ml with fresh methanol.

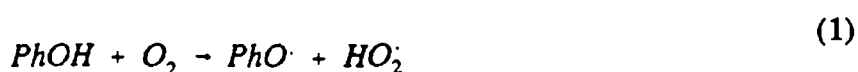
Oxygen Uptake Measurements: The amount of molecular oxygen consumed during the adsorption of organic compounds was measured using a computerized respirometer (N-CON Comput-OX, Model WB512, N-CON Systems Co., Inc., NY). GAC was first wetted in air saturated buffered water with DO concentration of 8.5 mg/L. GAC was then transferred together with the buffered water to a 500-mL respirometer bottle where it was complemented to a total volume of 400 mL with air saturated buffered water that contained known concentrations of the organic compound to be tested. The bottle was then connected to the oxygen supply system that maintains a constant partial pressure of oxygen in the bottle headspace. Data on the amount of oxygen supplied to the bottle were automatically collected and stored in the computer. These experiments were carried out for a period of at least two weeks, which was the equilibration period for most of the adsorption isotherm tests.

RESULTS AND DISCUSSION

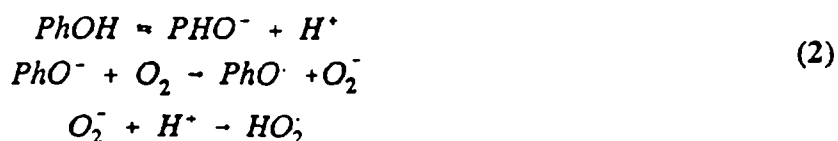
GC/MS analyses performed on the extracts from the GAC used in the oxic isotherm tests with o-cresol revealed the presence of appreciable amounts of dimers, trimers, and even tetramers of o-cresol. Therefore, a reasonable conclusion is that the increase in the GAC adsorptive capacity under oxic conditions is a result of adsorbate polymerization on the carbon surface. It is generally believed that the mechanism of phenolic compounds coupling involves

radicals of these compounds (Musso, 1967 and Nonhebel and Walton, 1974), although some researchers proposed that nonradical oxidative coupling of phenolics can also occur (McDonald and Hamilton, 1973). The first step in the oxidative coupling of phenolics is usually the formation of phenoxy radicals from the phenol molecule or phenolate ion. The radical formation is generally initiated by the removal of a hydrogen atom from each phenolic molecule to form phenoxy radicals. These radicals can then participate in direct coupling with other radicals, homolytic aromatic substitution with phenol molecules, or heterolytic coupling with phenolate ions to form dimers (McDonald and Hamilton, 1973). Electron localization in the radicals determines the coupling position (ortho or para position to hydroxyl group). Coupling is predominantly achieved through carbon-carbon bonding and less frequently through carbon-oxygen bonding (Musso, 1967).

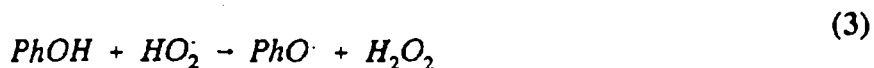
Several studies have shown that molecular oxygen can act as an initiator in oxidative coupling reactions of phenols (Denisov, 1980). Molecular oxygen can react directly with phenol according to the following reaction (Shibaeva *et al.*, 1969):



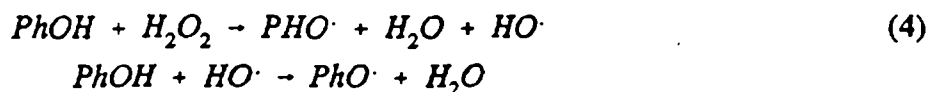
In addition, the phenolate ion can also react with oxygen:



The radicals that are formed according to Equations (1) or (2) can react with another phenol molecule according to the following equation:



Hydrogen peroxide reacts with another phenol molecule according to the following equations:



The above reactions were demonstrated to take place at elevated pressures (35 atm) and temperatures (180-210°C) and pressures (35 atm) (Shibaeva *et al.*, 1969) indicating a high activation energy of radical formation while Hay *et al.* (1959) reported oxidative coupling to take place at room temperature in the presence of copper (I) salt. The results of this study indicate that such reactions are also feasible at room temperatures with the surface of GAC serving as a catalyst.

The results of the extraction experiments (Figure 2) indicate that o-cresol polymers are

difficult to desorb from the surface of GAC since a very low extraction efficiency was achieved for the carbons used in the oxid isotherm procedure. Weight measurements conducted on these carbons after extraction and drying confirmed that essentially all of the non-desorbed adsorbate is still retained on the carbon surface. The amount of irreversibly adsorbed o-cresol was calculated from the data collected from the oxid adsorption isotherm tests and extraction experiments. The results are given in Figure 3 together with oxid and anoxic Freundlich adsorption isotherms for o-cresol. It is important to note that the amount of irreversibly adsorbed o-cresol remained essentially constant over a three orders of magnitude range of aqueous phase concentrations. This indicates that the capacity of GAC to promote the chemical reaction and, consequently, the capacity of GAC for the products of that reaction are practically constant.

Oxygen uptake measurements conducted using an aerobic respirometer were always performed on triplicate samples to obtain statistically significant results. The oxygen consumption rate measured for the adsorption system with the initial o-cresol concentration of 1957.7 mg/L and 2.0 g of GAC is depicted in Figure 4. The total amount of oxygen consumed during the equilibration period ranged from 82.8 to 88.0 mg. Based on the equilibrium liquid phase concentration measurements and the data presented in Figure 3, the corresponding amount of irreversibly adsorbed o-cresol ranged from 532.2 to 535.8 mg. The results of this test together with several other tests involving different masses of GAC and different initial o-cresol concentrations are summarized in Figure 5. The results of similar experiments performed with 2-ethylphenol and 2-chlorophenol are presented in Figures 6 and 7, respectively.

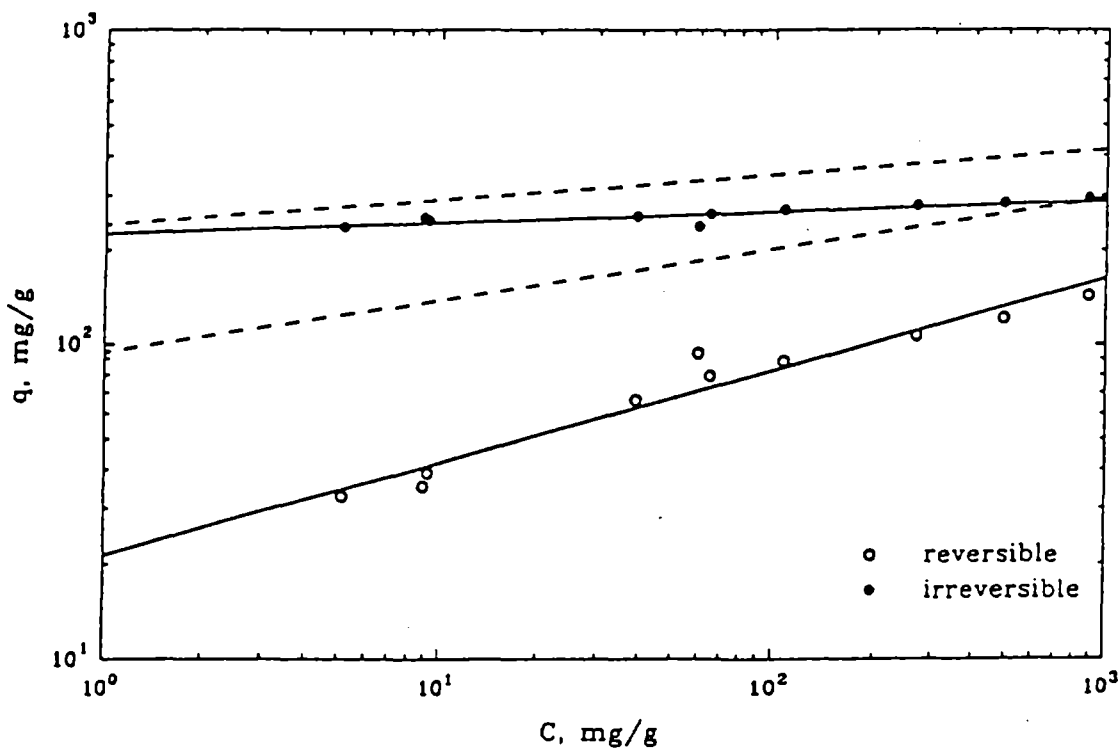


Figure 3. Reversibly and Irreversibly Adsorbed o-Cresol

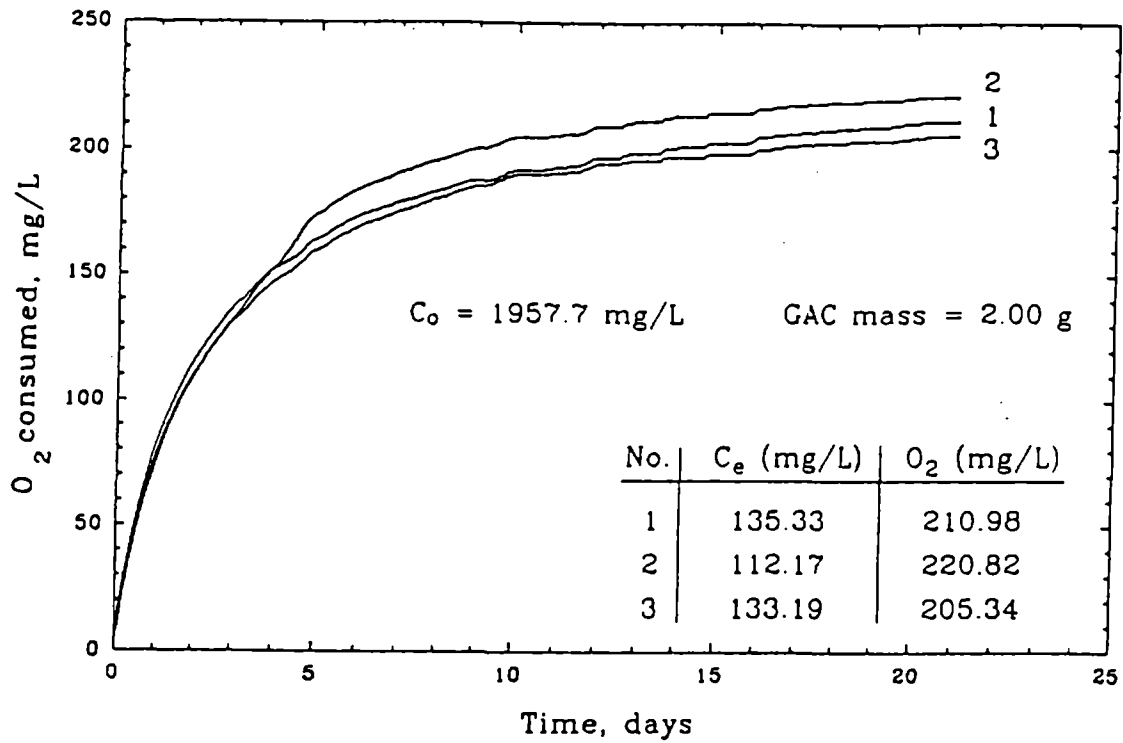


Figure 4. Rate of Oxygen Uptake During the Adsorption of o-Cresol

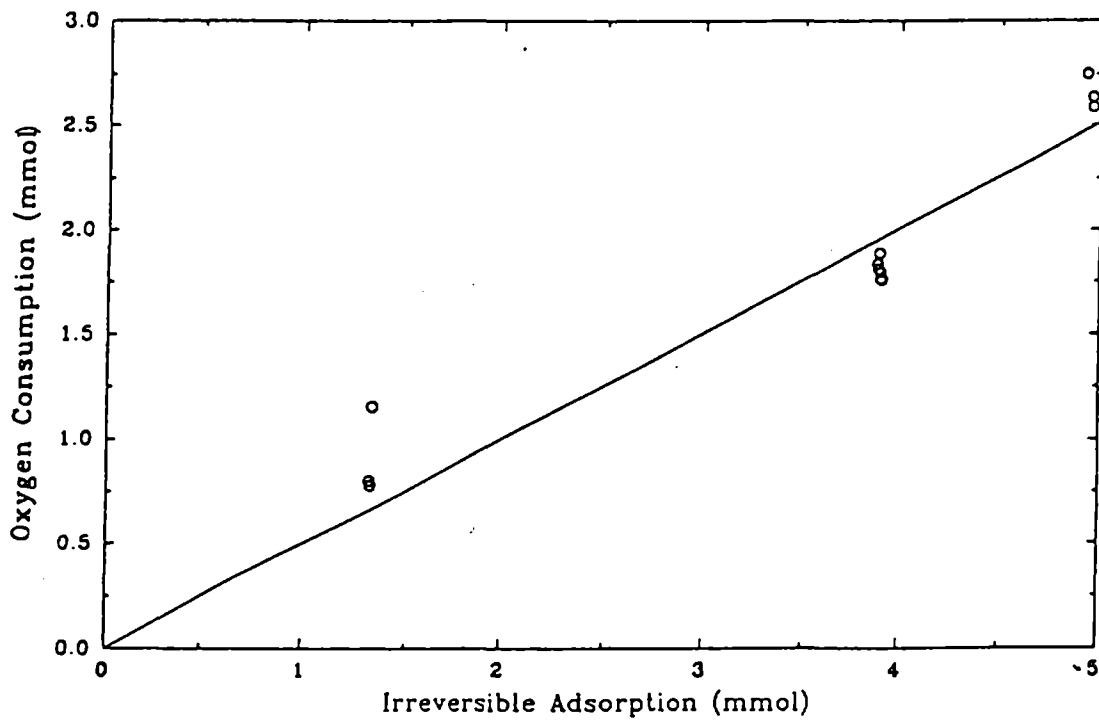


Figure 5. Total Oxygen Consumption for Polymerization of o-Cresol

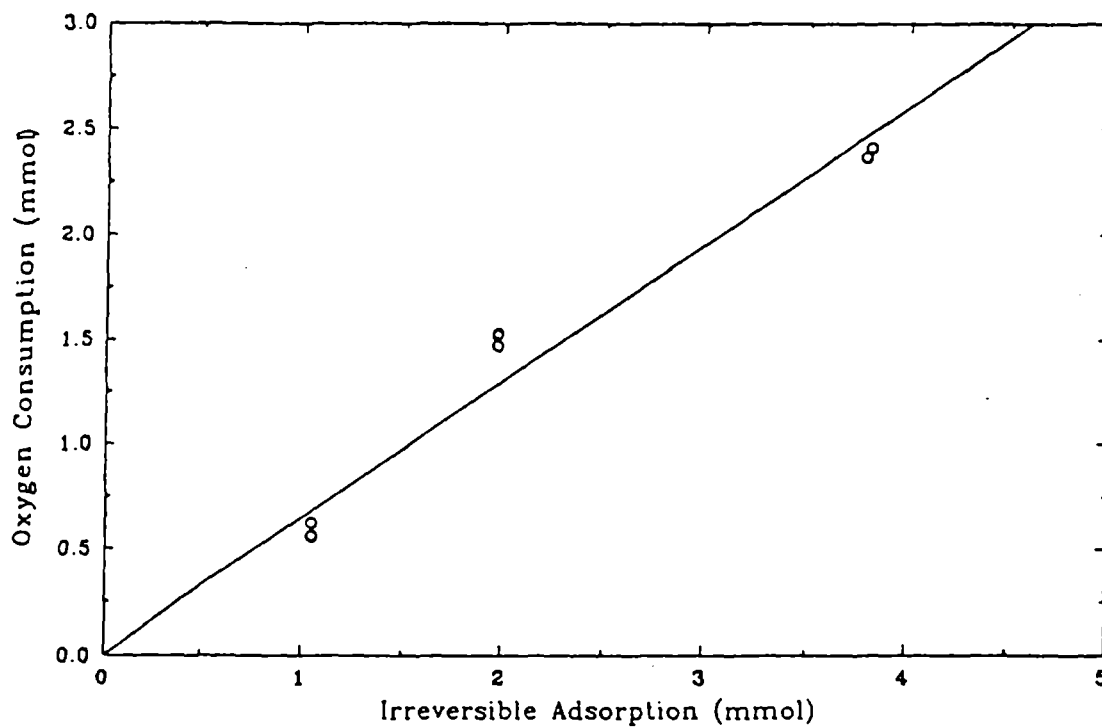


Figure 6. Total Oxygen Consumption for Polymerization of 2-Ethylphenol

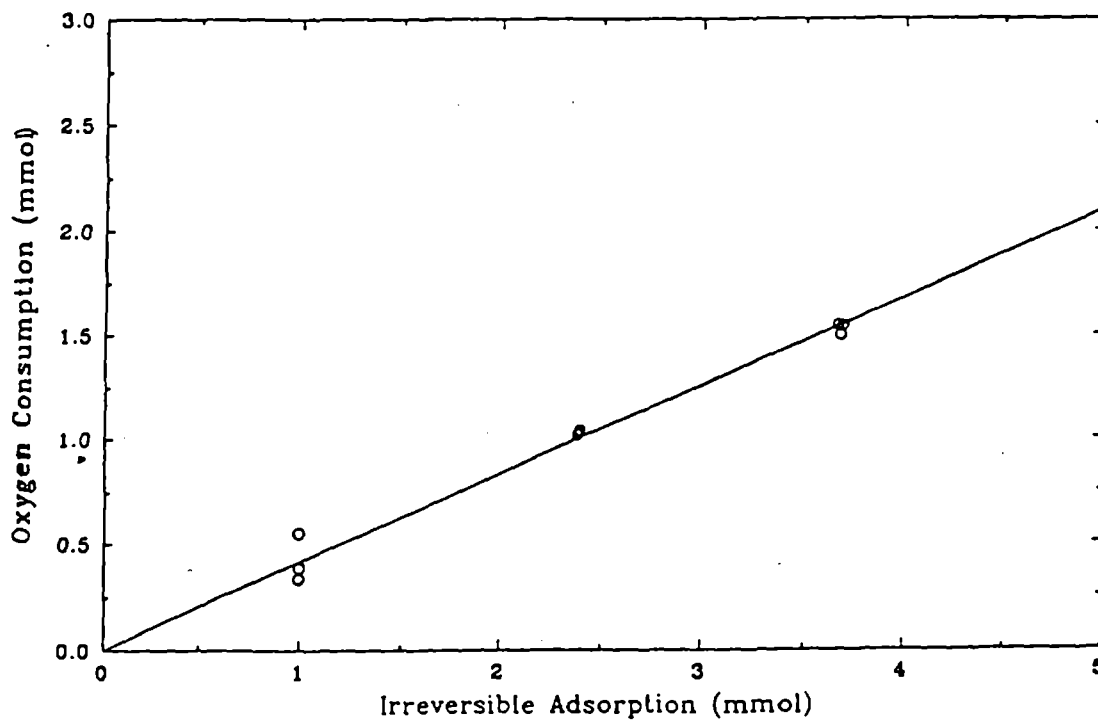


Figure 7. Total Oxygen Consumption for Polymerization of 2-Chlorophenol

As is apparent from Figures 5, 6, and 7, the amount of oxygen consumed during the adsorption of phenolic compounds is linearly proportional to the amount of irreversibly adsorbed compound. The coefficient of proportionality was 0.5026 for o-cresol, 0.6519 for 2-ethylphenol, and 0.4198 for 2-chlorophenol. Equations 1 to 4 suggest that the proportionality coefficient should be 0.25. However, that value pertains only to the first step of oxidative coupling (radical formation) of phenol in aqueous solution. The system employed in this study was much more complex than that and involved oxidative coupling of substituted phenols. Consequently, the coefficient of proportionality was above that suggested by Shibaeva *et al.* (1969).

All the organic compounds tested for the effect of molecular oxygen on the adsorptive capacity of GAC belong to different classes of organic compounds and differ in their affinity towards oxidative coupling. In most cases, the relative affinity of different adsorbates towards polymerization on the surface of GAC can be related to their tendencies to undergo oxidative coupling as solutes. Reactivity of these compounds in oxidative coupling reactions can be characterized by "critical oxidation potential" (COP). The notion of the COP was introduced by Fieser (1930). Fieser (1930) tested several phenols and amines with oxidizing agent of known redox potentials to determine the threshold oxidation potential required to oxidize each compound in a water-alcohol mixture at 35°C. COP is used in this study to determine the relative order of susceptibility of a compound towards polymerization on the surface of GAC. Figure 8 shows the amount of irreversibly adsorbed compound as a function of the COP. The values of the COP for most of the compounds presented in Figure 8 are as measured by Fieser (1930), while several COP values were calculated using the approximate values that Fieser established for substituents.

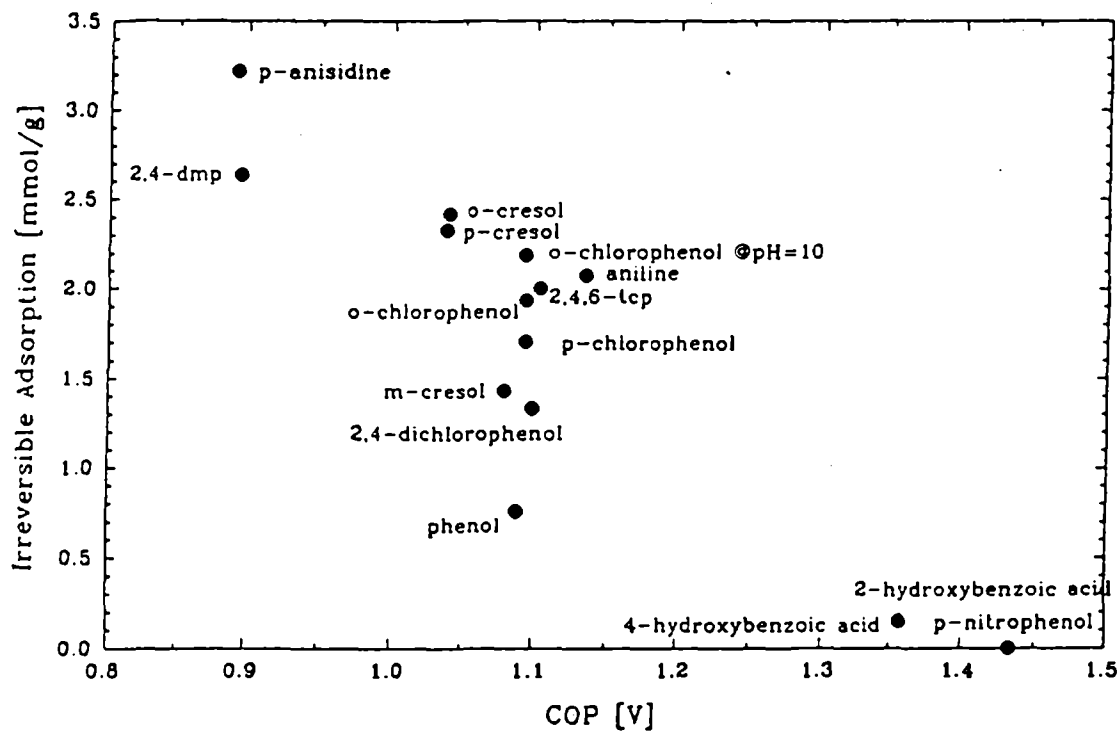


Figure 8. Irreversible Adsorption vs. Critical Oxidation Potential

In general, unsaturated groups increase the COP while the saturated ones decrease it. Furthermore, the modified hydroxyl and amino groups cause the greatest decrease in the COP. Among the compounds investigated, the nitro group caused the highest increase in the COP, which can explain the observed lack of polymerization of nitrophenols on the GAC surface. The other functionality that significantly increases the COP is the carboxyl group. However, the magnitude of the increase is lower than that measured for the nitro group. Since 4-hydroxybenzoic acid polymerized on the carbon surface, it can be concluded that the threshold potential encountered in the adsorption system is somewhere between the COP of the nitro and the carboxyl substituted phenols.

Another important observation of Fieser (1930) is that the multiple substitution of the same functional group further emphasize the change in COP in the same direction. Since the methyl functional group decreases the COP, the amount of irreversible adsorption for 2,4-dimethylphenol should be above that observed for 2-methylphenol or 4-methylphenol. Such behavior is documented in Figure 8. Similar behavior was demonstrated for the adsorption of 2-chlorophenol and 2,4-chlorophenol but in the opposite direction of the relationship observed for the methylphenols since the chlorine functionality belongs to the group of substitutes that increase the COP. However, the average amount of irreversible adsorption for 2,4,6-trichlorophenol was found to be above that computed for 2,4-dichlorophenol. This can be attributed to the fact that the value of the dissociation constant, pK_a , is 7.9 for 2,4-dichlorophenol and 5.99 for 2,4,6-trichlorophenol (Drahanovsky and Vacek, 1971), indicating that most of 2,4-dichlorophenol was present in the neutral form at pH 7.0 while the predominant species in the case of 2,4,6-trichlorophenol was the phenolate ion. Shibaeva *et al.* (1969) and Denisov (1980) found that the reaction of phenolic anions with oxygen is much faster than the reaction of the corresponding phenols. Furthermore, Chin *et al.* (1985) found the rate of aerobic coupling of phenol using cuprous chloride as a catalyst to be second order with respect to the solution pH when the pH values were below the pK_a value. These studies suggest that phenoxy radicals are formed much more readily from phenolate ions than from the neutral species, which explains the observed behavior of polysubstituted chlorophenols.

CONCLUSIONS

This study clearly delineates the important role of molecular oxygen on the adsorption of phenolic compounds by activated carbon. The presence of molecular oxygen induced polymerization of these compounds on the carbon surface resulting in a significant increase in the adsorptive capacity of GAC when compared to that attainable under anoxic conditions. The capacity of GAC to promote polymerization reactions and the adsorptive capacity for the reaction products remained constant over three orders of magnitude of equilibrium aqueous phase concentrations. Solvent extraction of GAC loaded with adsorbate in the presence of molecular oxygen yielded very low extraction efficiencies while almost 100% of adsorbate can be recovered from the carbon surface if the adsorption phase was carried out under anoxic conditions.

The amount of oxygen consumed during the adsorption of three different adsorbates was linearly proportional to the amount of irreversibly adsorbed compound. Critical oxidation potential was successfully used to establish relative susceptibility towards polymerization and, consequently, the amount of irreversible adsorption among the compounds tested in this study.

ACKNOWLEDGEMENTS

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