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Carbon-Catalyzed Oxidative Coupling of Phenolic Compounds

E. Y. Osei-Twum,[1] N. S. Abuzaid,[1] G. Nahkla[2]

[1]Research Institute and [2]Department of Civil Engineering, King Fahd University of Petroleum and Minerals, P.O. Box 1472, Dhahran, 31261, Saudi Arabia

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Adsorption onto granular activated carbon (GAC) is one of the most commonly used methods for water and waste water treatment, especially those containing organic compounds that persist in the environment and resist biodegradation. It has been known for some time now that certain phenolic compounds are difficult to remove and recover from activated charcoal (Suzuki et al. 1978; Goto et al. 1986). Seewald et al. (1983) have found several peaks in the thermal gravimetric analysis (TGA) curves for phenol and have inferred the influence of surface reaction on the adsorption process. Similar observation was latter reported by Magne and Walker (1986). Recently, Grant and King (1990) showed that phenolic compounds can undergo oxidative coupling reactions on activated carbon surface. Their results indicated that the reactions are influenced by (i) contact time, (ii) pH, (iii) temperature, (iv) dissolved oxygen, and (v) the nature of the phenolic compound. Their results were supported with mass chromatograms of the extracts from the carbon. The chromatograms indicated the formation of oligomers. However, the identities of the compounds resulting from the reaction were not provided.

In a recent study, Cooney and Xi (1992) found that, in addition to the findings of Grant and King, the oxidative coupling reactions are enhanced by the presence of electron donating substituents. They observed that the substituents influence the reactions in the order $OCH_3 > CH_3 > Cl > H > COOH > CHO > NO_2$.

Thus in spite of all these studies there has been no report on the exact compounds that are formed from the reaction of phenols on the surface of GAC. Chrostowski et al. (1983) was probably the first to propose the structure -of the products of ozone-catalyzed oxidative coupling reaction of phenolic compounds in aqueous media. We report here results of our recent studies that support the assertion that in oxidizing medium, irreversible adsorption of phenolic compounds is due to oxidative coupling.

Correspondence to: E. Y. Osei-Twumm

Our results indicate that oxygen and other oxidizing agents, such as hydrogen peroxide and potassium permanganate, lead to the same products. There are only a few products of the reaction of phenols formed during their adsorption onto GAC. The major products are trimers; dimers are also formed but in lower yield. We have attempted to provide the reaction mechanisms for the formation of the products.

MATERIALS AND METHODS

Analar grade potassium permanganate, hydrogen peroxide, phenol, o-cresol and 4-nitrophenol were obtained from BDH Chemicals Co., UK. Spectra grade methanol and dichloromethane, as well as the GAC, were obtained from Fischer Scientific, USA. The organic compounds and solvents were used without any further purification. The carbon was washed several times with deionized water to remove all fines. It was then dried at 110 °C for 24 hours in an oven. It was allowed to cool for about 10 minutes and stored in a desiccator prior to use. Karl Kolb shakers which were used for loading experiments were obtained from Scientific Technical Supplies, Germany. These were equipped with temperature control from 0 to 100 °C and a variable shaking frequency.

The adsorption isotherm experiments for phenol, o-cresol, and 4-nitrophenol, under different levels of dissolved oxygen were described in details by the authors elsewhere (Abuzaid and Nakhla 1994; Abuzaid et al. 1995), and are not repeated here.

The GAC used in the adsorption experiments were extracted with organic solvents to recover the adsorbed organic compounds. The extractions were carried out in a Soxhlet extractor. The GAC samples were first extracted for 24 hours with methanol. This was followed with a 72-hour extraction with dichloromethane. The extracts were combined, dried-with anhydrous Na_2SO_4, filtered and concentrated for GC-MS analysis. Fresh GAC and the pure adsorbates were treated in the same way for GC-MS analysis.

The samples were analyzed using an HX100 (JEOL, Japan) mass spectrometer equipped with a Carl:, Erba (Italy) gas chromatograph (GC). The GC was equipped with a split/splitless injector at 250 °C. The column was fused silica, 25m x 0.25 mm i.d., with a 0.3 µm methyl silicone film. The carrier gas was helium at 6 mL/min. The oven temperature was programmed from 50 to 300 °C at 10 °/min with a zero initial time and 5 minute final time. The ion source temperature was 250 °C, emission was 100 µA, and the acceleration voltage was 5 kV. All mass spectra were acquired and processed with a JMS-DS5000 data system. The identity of the compounds were confirmed by library search using the Beaman Search/ Probability Matching algorithm. The library data was the NBS/NIH/EPA Database.

RESULTS AND DISCUSSIONS

Adsorption studies under oxic (in which oxygen or an oxidizing agent was present) and anoxic (in which the system was purged with nitrogen) were conducted for phenol, o-cresol, and 4-nitrophenol. In the case of phenol adsorption studies of two other dissolved oxygen (DO) levels were performed out, vide supra. Potassium permanganate and hydrogen peroxide were used as the oxidizing agents. Single-solute isotherms for each of the compounds were obtained using the Freundlich equation; $q = kc^{1/n}$ (Abuzaid and Nakhla 1994; Abuzaid et al. 1995). Our results for o-cresol and 4-nitrophenol also indicate that oxygen enhances their adsorption, which is what other research groups also found (Vidic and Suidan 1991).

The phenol isotherms for the anoxic condition as well as those with hydrogen peroxide and potassium permanganate have been reported previously by the authors (Abuzaid et al. 1995) Both oxidizing agents show appreciable increase in the uptake of phenol by GAC. Thus the oxidative coupling reaction is not limited to oxygen alone; in general oxidizing conditions lead to enhanced adsorption of phenolic compounds.

Abuzaid and Nakhla (1994) recently reported the effect of different levels of DO on the equilibrium of adsorption of phenol and o-cresol by GAC. It was found that oxygen concentration has a direct effect on the adsorption of phenol.

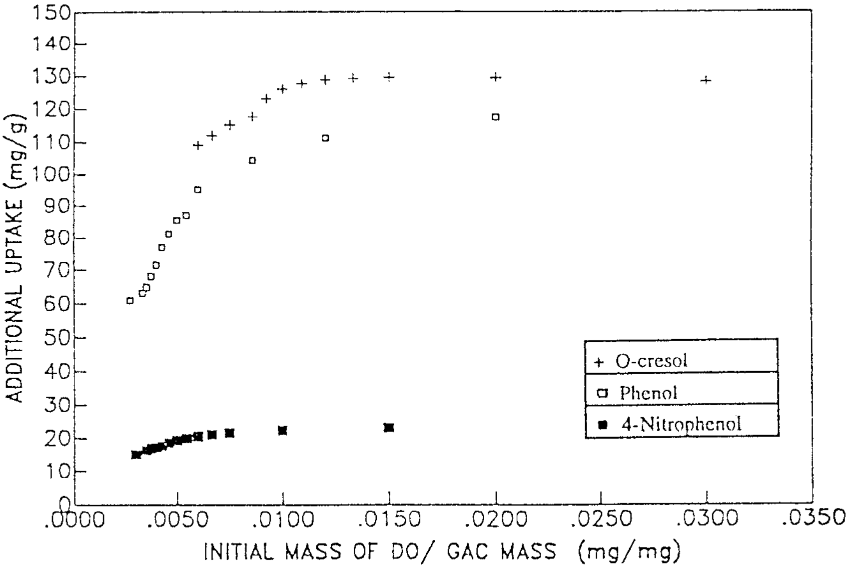


Figure 1. Relationship between additional uptake and ratio of initial DO to GAC mass for o-cresol, phenol and 4-nitrophenol at 21 °C and pH 7.

In their studies Cooney and Xi, (1992), vide supra, reported that electron donating substituents enhanced the adsorption of the phenolic compound while electron withdrawing groups had the opposite effect. In this study we chose two compounds at the extreme end of the scale together with phenol which was about midpoint between them. Our results showed that o-cresol had the highest enhanced adsorption with nitrophenol coming far behind phenol, see Figure 1. This supports the observations of Cooney and Xi (1992).

Figure 1 goes beyond showing that the adsorption capacity is dependent on the nature of the substrate. It illustrates that the enhancement in adsorptive capacity is limited by both the mass of oxygen and the availability of adsorption sites, i.e. mass of GAC. The data depict an almost linear increase in the incremental adsorption capacity with increasing DO:GAC ratio to a plateau beyond which the DO:GAC does not exert any appreciable effect on the incremental adsorption capacity. Thus at low DO:GAC ratio, the enhancement in capacity is limited by mass of oxygen in the test environment while at high DO:GAC ratio corresponding to low GAC masses, it is limited by availability of adsorption sites for oligomerization.

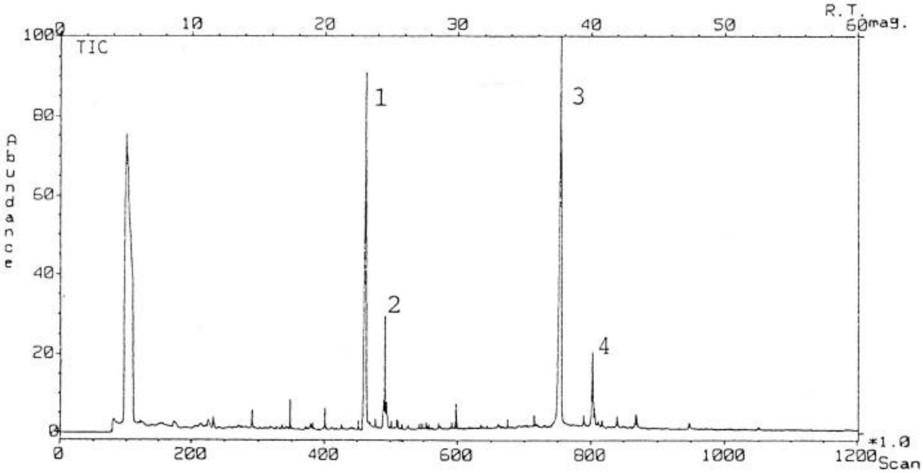


Figure 2. GC-MS total ion chromatograms for phenol adsorbed under anoxic conditions at 21 C°and pH 7.

The compounds that were adsorbed onto the GAC were extracted with methanol and dichloromethane and the extract was analyzed by GC-MS (see experimental section). Under anoxic conditions the extract was found to contain mainly phenol with very small amount of products, while under oxic conditions the extract had approximately 45% of the products in addition to the phenol. Figure 2 shows the total ion chromatogram (TIC) of phenol adsorbed under oxic conditions. The TIC shows four major products with retention times 23.15 (1), 24.6 (2), 37.73 (3 and 40.08 (9;) minutes.

The mass spectra of peaks 3 and 4 are given in Figure 3. These compounds have their molecular ions at m/z 276 and 278, respectively. From Figure 2 it is observed that compound 3 is the most abundant of the products. The mass spectrum shows the molecular ion as the base peak. There are ions at m/z 249 and 247 that are indicative of elimination of CO and CHO from the molecular ion. The spectrum shows a weak ion at m/z 259 which indicates the possible elimination of the hydroxyl radical.

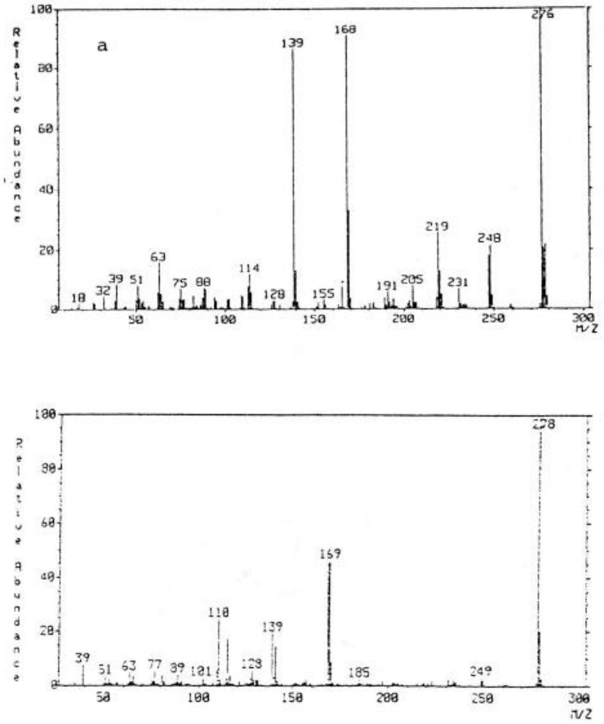
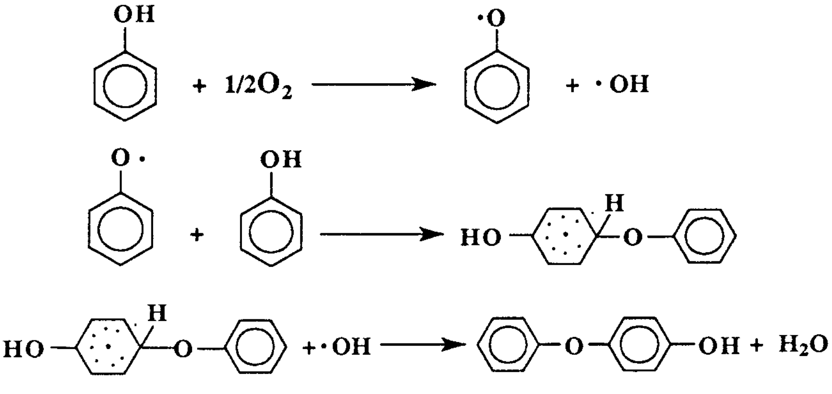


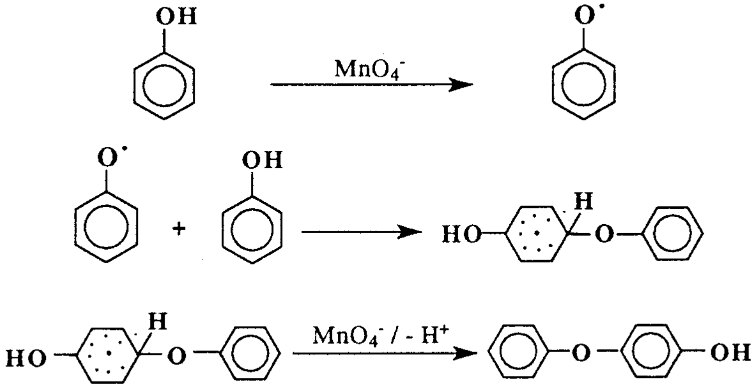
Figure 3. Mass spectra of trimeric products from the oxidative coupling of phenol on GAC.

The unambigious identification of this compound has not been made. It has tentatively been identified as a trimer of hydroxyquinone type. Compound 4, unlike the other three compounds, has the base peak at m/z 150; the molecular ion is rather weak.This compound has also been tentatively identified as ((p-phenoxy)-4-phenoxy)phenol. It must be mentioned again that the products found were the same under both oxic and anoxic conditions. To ensure that all these compounds were not originally in the starting material, a sample of the phenol was analyzed and found to have gas chromatographic purity.Chrostowski et al. (1983) proposed radical mechanism for the oxidative coupling of phenolic compounds by ozone and oxygen in aqueous media. They seem to have proposed that hydroxyl radicals were the main species involved in the oxidative coupling reaction. We propose here a similar mechanism for the reaction involving oxygen. However, we have atomic oxygen as the radical species involved in the initiation process. Scheme 1, is the proposed mechanism involving oxygen. In the reaction involving hydrogen peroxide, we expect hydroxyl radicals to be involved in such reaction.



Scheme 1: Free radical mechanism for the reaction of oxygen with phenol.

A large number of metal oxidants are known to be single-electron oxidants and will hence give radical intermediates when they react with anions. The permanganate anion is known to be one of such metal oxidants (Nonhebel et al. 1979).



Scheme 2: Permanganate-catalyzed free radical reaction of phenol.

In the reaction between the phenols and all the oxidizing agents, we obtained the same products; We proposed that the reaction involving the permanganate anion occurs via radical intermediates which arise from reaction between MnO_4- and the phenolate anion.The reaction mechanism is shown in Scheme 2. The findings of this study have a number of implications in the treatment of phenolic compounds by activated carbon. Contaminated ground water, landfill leachates and waste streams are often deficient in dissolved oxygen. To, therefore, improve the adsorption of these compounds it may be necessary to aerate the waste water during treatment.

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