Activated Carbon Catalyzes Reactions of Phenolics During Liquid-Phase Adsorption

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Various phenolic compounds in aqueous buffer solutions were contacted batchwise with powdered activated carbon. Relatively slow, but continual, decreases in the solution phenolic concentrations were measured over a period of several weeks. The decreases were due to oxidative coupling reactions of the phenolics which occurred on the carbon surface subsequent to adsorption. The effects of time, pH, dissolved oxygen, and the molecular nature of the phenolic were determined.

Introduction

Phenolic compounds are present in many types of wastewaters, and are often removed by adsorption in beds of granular activated carbon (GAC). A key to the economic use of GAC adsorption is the ability to regenerate and reuse the GAC. However, conflicting observations have been found by researchers concerning the thermal regeneration or solvent regeneration of phenolic-laden GACs.

Robertaccio (1976) reported complete desorption of phenol adsorbed on activated carbon using aqueous buffers. Similarly, Zogorski and Faust (1978) concluded that 2,4-dichlorophenol adsorbed on activated carbon could be completely (that is, reversibly) desorbed by distilled water. In contrast, Yonge et al. (1985) found that only 3-15% of several phenolic compounds adsorbed from aqueous solution could be desorbed by water. Suzuki et al. (1978) tried thermal desorption of organic compounds adsorbed onto activated carbon and found that phenol and phenolic derivatives were generally poorly removed.

Grant and King (1990) were perhaps the first to explain clearly these conflicting findings. They showed that phenolic compounds can undergo oxidative coupling reactions on activated carbon surfaces and that these reactions produce polymeric products which are adsorbed so strongly to the carbon that they are essentially "irreversibly adsorbed." Grant and King determined that these reactions are promoted by (a) longer contact times, (b) higher pH values, (c) higher temperatures, (d) the presence of dissolved oxygen, and (e) the nature of the phenolic compound.

Vidic and Suidan (1991) and Vidic et al. (1990) have shown that dissolved oxygen enhances the equilibrium adsorption capacity of activated carbon, at pH 7.0, for *o*-cresol, phenol, *o*-chlorophenol, *m*-ethylphenol, and natural organic matter. They correctly inferred that this enhancement was due to "polymerization of adsorbate on the surface of the carbon" during the two-week contacting period.

The oxidative coupling of phenolics has been well-known for over two decades (Taylor and Battersby, 1967). The general mechanisms, as discussed by Musso (1967), are quite clear. Phenolate radicals are formed from phenolate anions by the loss of one electron (this is why higher pH values, which cause phenolate anions to exist, promote oxidative coupling) or, alternatively, are formed from a phenol by the loss of a proton, as well as the loss of one electron. Such phenolate radicals give stable molecular products by coupling (a dimer thus formed may couple with another phenolate radical to give a trimer and so forth). Grant and King, however, were the first to show that activated carbon can catalyze and thereby accelerate such reactions (presumably by enhancing the removal of electrons from phenolate anions).

No studies, even the thorough one of Grant and King, have examined the *kinetics* of activated-carbon catalyzed oxidative coupling reactions of phenolic compounds in any detail. The results given by Grant and King, by Vidic and Suidan, and by Vidic et al. all consist of data on *equilibrium* adsorption capacities. This study examines the kinetics of these reactions for the first time. Details of more than 50 kinetic runs for roughly 20 phenolics and nonphenolic aromatics, with the variation of solution pH, carbon dose, dissolved oxygen content and so on can be found in the thesis of Xi (1992). We will present in this article only the most important or most representative results.

The implications of oxidative coupling for both solvent regeneration and for thermal regeneration are fairly obvious. Coupling creates higher molecular weight species which, by virtue of their higher molecular weights, are more strongly adsorbed to the carbon, are very much less soluble in solvents, and are very much less volatile in hot regeneration gases than the original phenolics. As Suzuki et al. (1978) have shown in regard to thermal regeneration, heating of an organic-laded carbon can result in (a) desorption (volatilization) of adsorbed species, (b) thermal decomposition or cracking of adsorbed species, and (c) polymerization of adsorbed species. They showed that phenolic compounds gave large residues when carbons were heated to 800°C, whereas alkanes, alcohols and large-sized glycols did not. Thus, the formation of higher phenolics can be expected to create severe difficulties in thermal regeneration.

Materials and Methods

Filtrasorb 400 granular activated carbon (Calgon Corp., Pittsburgh) was ground to less than 325 mesh, acid-washed with 1N HCl several times to remove stray inorganic matter, rinsed repeatedly with distilled water, dried (and sterilized) at 150°C and then stored in sealed vials until use. All stock solutions of the phenolic compounds tested were prepared at 10 mM concentration in standard 0.1-M ionic strength buffers at pH 2, 7, or 12 using distilled water and reagent-grade chemicals.

For each compound tested, a predetermined amount of the powdered activated carbon was weighed into a clean 25 mL borosilicate glass vial and 20 mL of the stock solution was added. A control vial, identical except for the lack of any carbon, was also prepared. Each day, these vials were agitated on a shaker device for 4 h to assure good carbon/solution contact, and then they were allowed to stand in a 30°C thermostatted water bath for 12–14 h to let the carbon settle (the bath was used to prevent seasonal changes in the room temperature from being an uncontrolled variable). Samples of clear supernatant (100 μL) were drawn, diluted with buffer and assayed for the organic concentration by UV spectroscopy at a suitable wavelength (usually at a peak in the range of 260–310 nm). The controls were treated in the same fashion as the vials containing carbon. Analyses were done for up to 40 days, during which time no significant changes in the organic concentrations in the control vials were noted (hence, selective evaporative losses of the organic and biological consumption were assumed to be negligible in all samples). Repeatability of concentration measurements, as determined by duplicate analyses done each day, was on the order of 1–2%.

Kinetics of Adsorption vs. Reaction

We first carried out experiments with a compound and a pH value for which reaction was predicted to be negligible (this was later confirmed). We used *o*-hydroxybenzoic acid (salicylic acid) at a pH of 2. Powdered F-400 carbon (0.0700 g) was contacted with 20 mL of a 10-mM pH 2 solution of salicylic acid in a glass vial with continuous shaking, and samples were withdrawn after 5, 10, 20, 30, 60 and 300 min. Final samples were withdrawn after two days. The samples were filtered to remove any traces of carbon and then were analyzed. The salicylic acid concentration fell rapidly over the first 0–10 min, and by 20–30 min the concentration had reached a steady value of about 3.6 mM. There was no further decline over the next two days. This experiment showed that adsorption equilibrium with the finely powdered carbon that we used was achieved for a "typical" substituted phenol in a time of roughly 30 min.

For other phenolics, after the initial rapid adsorption process had occurred, a slow but steady decline in solution concentration over a period of many days and weeks was observed. These slow subsequent changes were obviously due to oxidative coupling reactions which took place on the carbon surface, producing strongly adsorbed polymeric products. With the conversion of the originally adsorbed phenolic species (P) to polymeric derivatives (PP, PPP, and so on) more of species P was then able to transfer from the solution to the carbon surface, thereby decreasing the concentration of species P in the solution.

We have recently developed a model for the adsorption/reaction processes occurring, which can be fitted to the types of concentration vs. time data presented in this article. The model assumes that phenolic species P adsorbs and reaches adsorption equilibrium in a relatively short time (for example, 30 min). The amount which adsorbs is determined using a Langmuir adsorption isotherm equation (the two parameter values required are estimated for the compound being modeled based on equilibrium data from the literature). Then it is assumed that the adsorbed P molecule reacts via two possible mechanisms to form a dimer: either with a P molecule in free solution, or with an adjacently adsorbed P molecule. This reduces the concentration of adsorbed monomeric P on the carbon surface and allows more P from free solution to adsorb. The reaction which forms the dimer is modeled as a relatively slow second-order irreversible reaction. It is further assumed that the product PP is so strongly adsorbed that it cannot desorb to any significant extent. Only one reaction parameter is involved—the forward rate constant k_1, which is obtained by trial-and-error matching of the shape of the concentration vs. time data to the model. Either mechanism leads to the same shape of curve, the only difference being in the magnitude of the rate constant value. Thus, which mechanism is correct cannot be determined from the modeling procedure. Details of the model and an example of its fit to the data (which is generally excellent) will not be given here, as the results are relatively trivial.

Results for Phenol

Figure 1 shows results for phenol (initial concentration 10 mM) in a pH 12 buffer for two different amounts (W) of added activated carbon. It is clear that: (a) reactions occurred which caused the phenol concentration to fall continually over the entire 40 day period of the tests; (b) the initial amount of phenol adsorbed was greater for $W = 0.0700$ g than for $W = 0.0350$ g, as one would expect; and (c) the reaction rate was much higher for $W = 0.0700$ g than for $W = 0.0350$ g. This shows clearly the catalytic influence of the activated carbon.

Figure 2 shows the effect of pH on phenol adsorption and reaction at constant W. At pH 2 and pH 7, the phenol is essentially 100% undissociated (its pK_a is 10.0); hence, the initial amount adsorbed is the same at both pH values (the concentration decrease is from 10 mM to about 6.3 mM for both). At pH 12, however, the phenol is essentially totally ionized. It is well known that ionized forms of species adsorb less effectively to activated carbon than do their undissociated

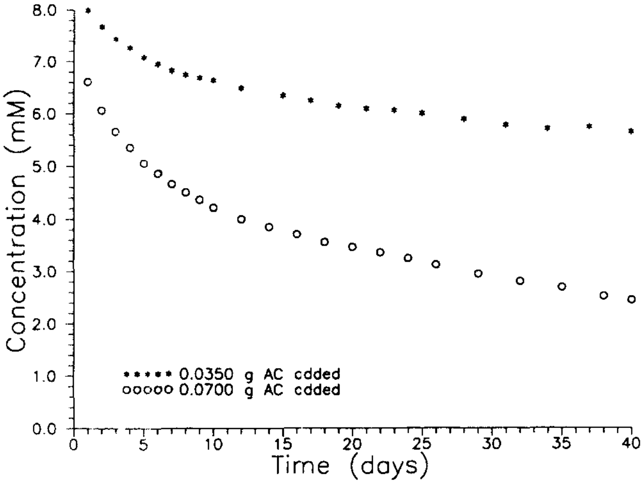

Figure 1. Effect of activated carbon amount on the reaction of phenol at pH 12.

forms. Thus, the initial amount adsorbed is less than at pH 2 and pH 7. However, the main effect to be noted is that at pH 2 the reaction rate is very small, whereas at the two higher pH values the reaction rate is much faster. The change in the phenol concentration over the 40 day period is somewhat larger at pH 12 than at pH 7, but it is clear that pH is the important determinant of reaction, not the degree of dissociation of the phenol.

The effect of dissolved oxygen on the reaction of phenol is shown in Figure 3, for constant pH and carbon weight. Three identical vials were used. In one, the headspace (about 5 mL) was allowed to contact only pure N_2 whenever the vial was opened (daily), while in the others contact with either room air or with pure O_2 was allowed. Additionally, for the "N_2" case, the stock solution was purged of dissolved oxygen (DO) before the experiment began by bubbling N_2 through it. The effect of DO is quite clear. Although oxidative coupling can occur in the absence of any DO (as Grant and King (1990) have explained), the presence of DO does markedly accelerate the oxidative coupling reactions.

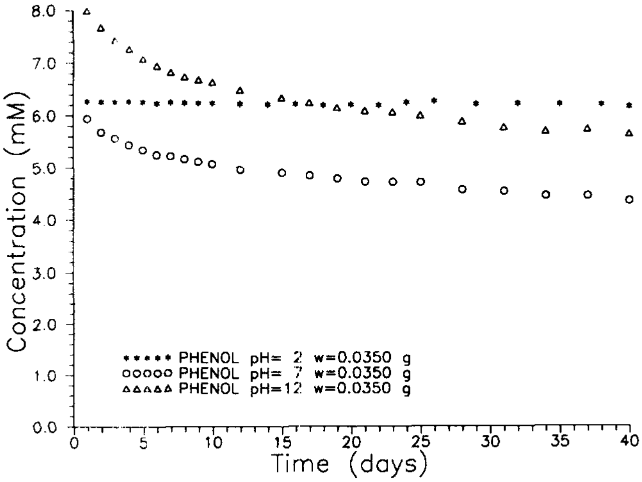

Figure 2. Effect of pH on phenol reaction at constant added activated carbon.

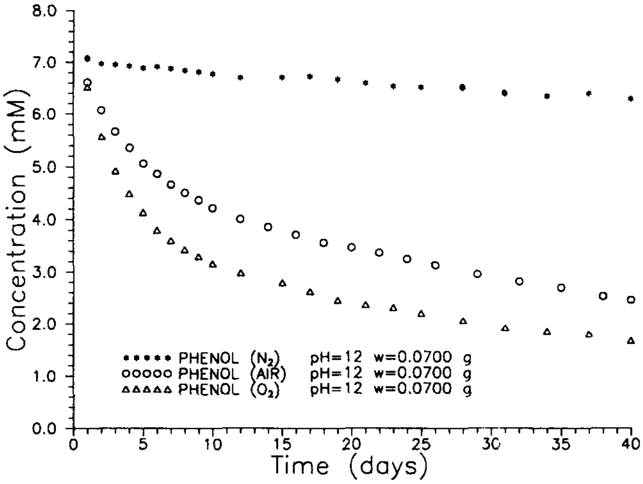

Figure 3. Effect of dissolved oxygen on phenol reaction (constant pH and W).

While the effect of pH in promoting coupling has been seen before (by Grant and King) and the effect of DO in promoting coupling has been seen before (by Grant and King, Vidic and Suidan, and Vidic et al.), these previous studies have shown only their effects on equilibrium adsorption capacities, not on the kinetics.

Results for Substituted Phenols

The effect of having a substituent group on the phenol molecule was assessed at pH 2 and pH 12 using $-OCH_3$, $-CH_3$, $-Cl$, $-COOH$, $-CHO$ and $-NO_2$ as the substituents. Our results, some of which are shown in Figure 4, show that the oxidative coupling reaction is accelerated according to:

$$OR > R > \mathrm{Cl} > H > \mathrm{COOH} > \mathrm{CHO} > \mathrm{NO_2}$$

where R represents CH_3 and H denotes the case of phenol itself. The sequence is identical to that denoting whether the substituent group repels electrons, and thus creates a higher

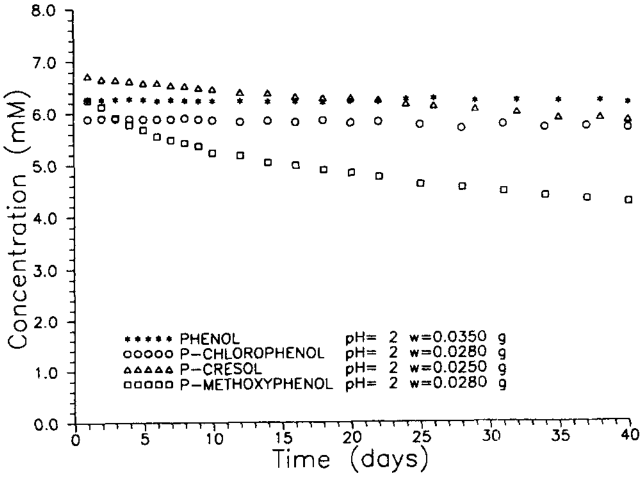

Figure 4. Effect of substituent group (para position) at pH 2.

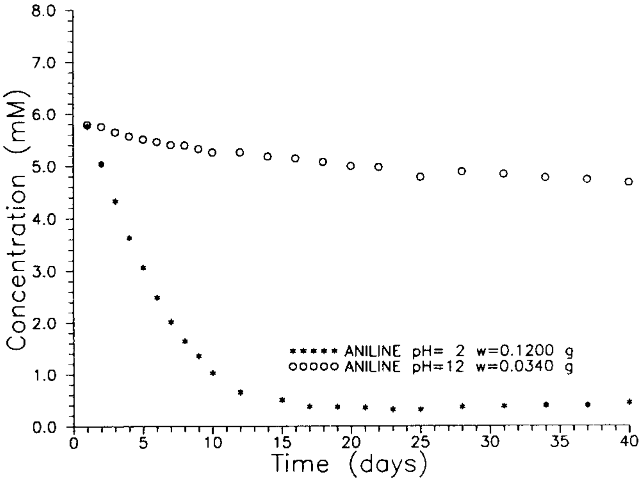

Figure 5. Reactivity of aniline at pH 2 and pH 12.

electron density on the aromatic ring, or whether the substituent group attracts electrons, and thus reduces the electron density on the aromatic ring (Morrison and Boyd, 1983). Thus, $-OR$ (for example, methoxyphenol) was highly reactive and $-NO_2$ (nitrophenol) was unreactive (indeed, $-COOH$, $-CHO$ and $-NO_2$ substituents all caused the phenol molecule to become essentially unreactive to any degree, even at pH 12).

A study was also carried out with chlorophenols and with cresols to determine the effect of the position (ortho, meta, para) of the substituent group on reactivity. The effect on reactivity was in the order ortho > para > meta, although the differences were not very large. Again, this sequence can be explained by what is known about the effect of position on the density of the electron cloud on the aromatic ring, and by consideration of steric hindrance effects.

Other Compounds

Studies were also conducted with other types of aromatic compounds, such as aniline, biphenol and β-naphthol. We will report here only the results for aniline. Figure 5 shows that aniline (a base which is ionized at low pH, in contrast to phenol, an acid which is ionized at high pH) is very reactive at low pH and much less reactive at high pH (the amount of carbon used was made higher at pH 2 than at pH 12 in order to try to enhance the reaction effect at pH 2). The results for aniline are as expected, based on molecular-level chemical arguments.

Conclusions

We have shown that phenolic compounds undergo oxidative coupling reactions subsequent to adsorption from aqueous solution. These reactions are catalyzed by activated carbon, and are enhanced by: (a) high pH, (b) increased carbon amount, (c) dissolved oxygen, and (d) the presence of electron repelling substituent groups. Grant and King (1990) and others have shown, using GC/MS analysis of solvent-extracted phenolic-laden activated carbons, that the reaction products are indeed predominately polymeric forms of the phenolic compounds, and that they are extremely difficult to desorb in any significant quantity. This information, taken as a whole, has important implications regarding the regenerability of activated carbons which have been used to adsorb phenolic compounds from wastewaters.

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