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Oxidative coupling and the irreversible adsorption of phenol by graphite

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Abstract

Uptake of phenol by graphite, and regeneration by methanol extraction, was measured to evaluate irreversible adsorption of phenols to carbon surfaces. The emphasis of this work was to identify the role of oxidative coupling, which has been invoked to explain irreversible phenol sorption by activated carbons. Graphite was chosen as a model carbon surface to eliminate potentially confounding effects of microporosity present in other types of carbonaceous sorbents. The isotherm data were well described by the Langmuir–Freundlich isotherm from pH 3 to 9. At pH 12, measured uptakes were higher than expected based on model predictions, suggesting the occurrence of an adsorption mechanism besides physisorption. One oxidative coupling product, 2,2′-dihydroxybiphenyl, was obtained exclusively after adsorption at pH values above 7, and appeared both in aqueous solution and in the methanol regenerant solution. The fraction of total uptake that was not recoverable by methanol extraction decreased with increasing phenol concentration in solution, suggesting preferential sorption by high-energy sites. However, absolute irreversible adsorption increased with phenol concentration in solution. Both fractional irreversible adsorption and 2,2′-dihydroxybiphenyl oxidative coupling product recovery as a function of pH and contact time demonstrated that irreversible sorption of phenol by graphite could not be explained by an oxidative coupling mechanism alone.

Keywords: Graphite; Oxidative coupling; Irreversible adsorption; Phenol; Dihydroxybenzene

1. Introduction

Sorption reversibility is a phenomenon that is of considerable interest today in multiple contexts, including bioavailability of contaminants sorbed to soils and sediments, and the use of sorbents for in-process recovery of industrial chemicals. The recovery of phenol from aqueous waste streams generated during petroleum refining, coal processing, resin manufacture and steel production represents an attractive approach to minimize pollutant discharge and improve process economics. In many cases recovery of phenol from carbonaceous adsorbents such as activated carbons is limited by low yields. The factors contributing to irreversible adsorption by activated carbon were shown to be consistent with an oxidative coupling mechanism [1], discussed in more detail below. In this regard, the microporous nature of activated carbon may play an important role. Phenolic multimers formed by the oxidative coupling reaction could themselves become entrapped or block pores and entrap other molecules. This study was designed to investigate the mechanisms of irreversible adsorption of phenol on graphite, as part of broader work investigating a range of carbonaceous adsorbents [2]. In contrast to most studies conducted to date, the use of graphite provides the opportunity to isolate how the adsorbent surface influences adsorption and desorption, without confounding effects of microporosity.

Phenolic compounds are adsorbed strongly by activated carbon and may interact with carbon surfaces in several ways, depending on the adsorption conditions. The physical adsorption (*physisorption*) of phenolic compounds to carbon surfaces is thought to arise from dispersion forces acting between π-electrons in the molecule and π-electrons in the graphitic basal planes on the surface [3]. Physisorption is reduced as a result of π-electron localization (via

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surface oxidation or doping) and is increased when electron-withdrawing substituent groups on the phenol molecule decrease the electron density of the ring [1,3–5]. Phenol could form hydrogen bonds with polar oxygen centers on the carbon surface [3]; however, the importance of this mechanism depends on the degree of competition with water, which increases with increasing surface oxidation [6] but can be reduced by employing a nonpolar solvent barrier [7]. Physical adsorption processes dominate at short equilibration times, low temperatures, low pH, and low concentrations of molecular oxygen. In contrast, *oxidative coupling*, a polymerization reaction catalyzed by carbon surfaces in which phenol multimers are formed through C–O and C–C linkages, becomes important under opposite conditions in each of the above respects [8–10].

Oxidative coupling of aqueous phenol can yield reaction products shown in Fig. 1 [8,11], including dihydroxybiphenyls and phenoxyphenols, in good agreement with proposed theory [12]. Such products have been identified in organic solvent extracts of phenol-loaded carbons [6,8–10,16]. All proposed mechanisms for oxidative coupling of phenols include two steps [12–15]. The first (and rate controlling) step involves either a hydrogen atom loss (by phenol) or an electron loss (by phenolate) to form a phenoxy radical. This is followed by a second step that involves a coupling of the highly reactive phenoxy radical to another phenoxy radical, to a phenolate ion or to a phenol molecule, forming a dimer. By the same mechanism, oxidative coupling reactions can involve dimer molecules forming trimers and higher molecular weight multimers (Fig. 1). A possible role of catalysts in the reaction is to lower the activation energy of the initial radical formation step and promote electron transfer to oxygen or an alternative electron acceptor. Many features of phenol irreversibility are consistent with oxidative coupling [1,8]. Grant and King [8] showed that the irreversible adsorption of phenol and several substituted phenols by microporous activated carbons correlated with their critical oxidation potential [17], a relative measure of how easily a given compound can be oxidized. A similar correlation was later found by Vidic et al. [18] for other substituted phenols. Acidic surface oxygen groups have been shown to reduce phenol uptake, reduce the formation of oxidative coupling products, and increase reversibility [6,8]. Possible mechanisms include localization of basal plane electrons and increased competition from water [6]. Increasing the concentration of surface lactone groups (as measured by the Boehm titration technique) was shown to reduce the temperature dependence of activated carbon surface resistance and the difference between phenol uptake in the presence and absence of molecular oxygen [19].

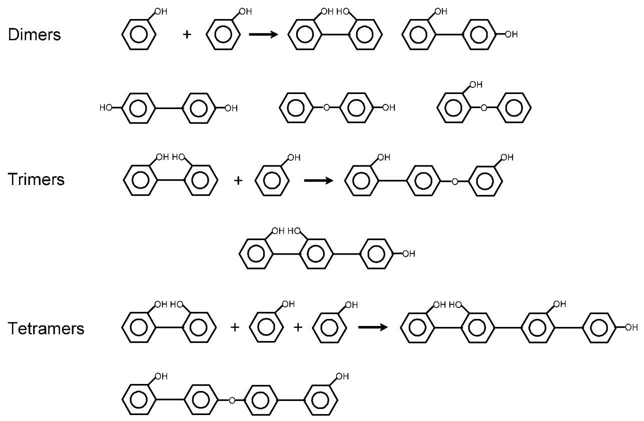

Fig. 1. Structures of selected oxidative coupling products.

Finally, *chemisorption* may occur between phenol and specific sites on the surface, and could be partly responsible for irreversible adsorption. Magne and Walker [20] proposed that irreversible chemisorption could occur on oxygen-free sites located at the edges of the graphene layers, whereas others have proposed that phenolic groups [8] and oxygen-containing basic groups (e.g., chromene, pyrone) can promote irreversible adsorption [21]. Terzyk [19] has proposed that phenol molecules or phenoxy radicals react with active sites on a carbon surface, which can result in covalent bonding to the surface.

In this study we attempt to more clearly identify the role of oxidative coupling vis-à-vis chemisorption. Previous work has confirmed the presence of oxidative coupling products (with the composition $C_{6n}H_{4n+2}O_n$) in acetone [6,8], methylene chloride [9,10], and supercritical carbon dioxide [16] extracts of loaded carbons. In this work we quantify, for the first time, both oxidative coupling product formation and irreversible phenol sorption. Specific objectives of this work were to evaluate (i) the reversibility of phenol sorption by graphite; (ii) the ability of graphite to act as an oxidative coupling catalyst; and (iii) the correlation between irreversible adsorption of phenol by graphite and oxidative coupling product formation.

2. Conceptual model

The conceptual model guiding this work is shown in Fig. 2. The physical system is composed of an aqueous liquid phase and a solid adsorbent phase. The adsorbent is considered to have very low microporosity, especially as compared to activated carbons and carbon fibers, but not a complete absence of structural heterogeneity. Two mechanisms are proposed for phenol adsorption, Fig. 2a: (i) physisorption (A ↔ B), which is reversible and driven by hydrophobic interactions; and (ii) chemisorption (B → C), which is irreversible and possibly caused by reaction to specific active sites on the surface. Chemisorbed phenol can quench the occupied site (species C) or become a site for further reaction (species G). Upon adsorption, phenol can react via oxidative coupling catalyzed by the carbon surface, to form multimers. Such multimers either physisorb to the surface (species D), desorb to the solution phase (species F) or chemisorb to specific sites (species E). Note that species D may physisorb so strongly to the carbon surface that it may not be recovered