



RAPID COMMUNICATION

IMPACTS OF DISSOLVED OXYGEN ON THE SORPTION OF HUMIC SUBSTANCES AND THE SUBSEQUENT INHIBITION OF *o*-CRESOL UPTAKE BY GRANULAR ACTIVATED CARBONTANJU KARANFIL, MARK A. SCHLAUTMAN and WALTER J. WEBER JR^{*}

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Abstract—The impacts of dissolved oxygen (DO) on the sorption of natural and model humic substances by granular activated carbon (GAC) were investigated. Among five substances tested, the sorptions of only two, polymaleic acid (PMA) and peat humic acid, were affected by the presence of DO. The uptake of the target compound *o*-cresol on virgin GAC and on GAC preloaded with PMA under oxic and anoxic conditions was also examined. The oxic and anoxic preloading conditions had similar effects on subsequent *o*-cresol reactions under both oxic and anoxic sorption conditions. A reduction of approximately 20% in *o*-cresol uptake observed under anoxic conditions by GAC preloaded under each condition is attributed to a decrease in the adsorption capacity of the GAC by preloading. In the presence of oxygen, however, an observed reduction of about 45% in *o*-cresol uptake by preloaded GAC appears to result from a combination of decreased adsorption and inhibited *o*-cresol polymerization.

Key words—Humic substances, dissolved oxygen, oxidative coupling, *o*-cresol

INTRODUCTION

Granular activated carbon (GAC) is widely used for the removal of target synthetic organic compounds (SOCs) in wastewater and water treatment applications. However, the presence of background dissolved organic materials (DOMs), frequently of humic and/or fulvic character, in the solution matrix of many waters and wastewaters reduces the operational life and performance of GAC adsorbers (Weber and Smith, 1989; Summers *et al.*, 1989; Carter *et al.*, 1992). Dissolved organic carbon (DOC) concentrations attributable to DOMs have been reported to range from 1 to 60 mg/l, depending on geographic location and climate (Thurman, 1985). GAC adsorbers are usually located after initial pretreatment processes in water treatment practice, which can reduce raw water background DOMs by 10–90% (Randtke, 1988). A report by Roberts and Summers (1982) on a study of 13 water treatment plants around the world indicated that concentrations of total organic carbon (TOC) entering GAC filters ranged from 1 to 16 mg/l, with an average value of 4 mg/l. Because of their polydisperse physical and chemical properties and their significantly different adsorption characteristics relative to target SOCs, background DOMs usually create a long active sorption zone within GAC fixed-bed adsorbers. As a result, fresh GAC layers in the adsorbers are continuously *fouled* or *preloaded* by the background DOMs, which significantly reduces the

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GAC capacity for the subsequent sorption of target SOCs.

Oxidative coupling of phenolic compounds on GAC has been reported widely in the presence of dissolved oxygen (DO) (e.g. Grant and King, 1990; Vidic *et al.*, 1990; Vidic and Suidan, 1991; Vidic, 1992) and free and combined chlorine (e.g. Voudrias *et al.*, 1985a; Voudrias *et al.*, 1985b; Voudrias *et al.*, 1987). In these systems, GAC surfaces are thought to act as catalysts for the oxidative coupling reactions. Polymerizations of this nature are particularly important in water treatment operations, given the potential for formation of hazardous products from these types of reactions (Voudrias *et al.*, 1985c). In addition to reducing GAC sorption capacities for target SOCs, however, preadsorption or preloading of background DOMs may also “poison” the catalytic effects of clean GAC surfaces on such compounds as phenols, thus minimizing the potential effects of polymerization reactions. Chin *et al.* (1993) recently reported inhibition of phenol coupling on GAC in column studies by syringic acid and by relatively high concentrations of fulvic acids (over 30 mg/l TOC). The authors hypothesized that inhibition of phenol coupling resulted from either free radical scavenging (leading to cross-coupling reactions) or from competition for active sites on the GAC surface.

A final consideration is the potential impact of DO on the sorption of background DOMs themselves by GAC. If the preloading of GAC by background DOMs is sensitive to the presence of DO, one might

expect this to affect subsequent target SOC reactions in GAC adsorbers. There has been only one report to date of enhanced sorption of DOMs by GAC in the presence of DO (Vidic and Suidan, 1991). Although Chin *et al.* (1993) reported inhibition of phenol coupling by fulvic acids, they did not evaluate the impacts of DO on the sorption of the fulvic acids in their column experiments. Because of the paucity of data on this topic, the present study was performed in order to determine the potential importance of DO for the GAC applications in the water and wastewater treatment plants. The objectives of this study, therefore, were to: (i) investigate the impacts of DO on the sorption of natural and model humic substances, and (ii) examine the effects of preloaded GAC on the subsequent uptake of *o*-cresol in the presence and absence of DO.

MATERIALS AND METHODS

Materials

Natural and model humic substances. The natural and model organic materials investigated here were selected because of their common use in attempts to characterize the behavior of humic substances and DOMs. A commercial humic acid (Aldrich) was purified following the procedure described by Kilduff and Weber (1992). Polymaleic acid (PMA) was synthesized according to the procedure described by Spiteller and Schnitzer (1983). Peat humic acid (International Humic Substances Society) and 1.8 K polystyrene sulfonate (PSS) (Polysciences) were used as received. Stock solutions were prepared by dissolving the materials in deionized water at pH 12, adjusting the pH to 7 with 1 M HCl, and filtering the solutions through 0.45- μ m membrane filters (Gelman Science), except for the PSS stock solution, which was directly prepared in deionized water at pH 7. Huron River Water (HRW), a source of natural aquatic DOMs, has been collected and characterized by Carter *et al.* (1992). Sodium azide was added to a concentration of 100 mg/l after its collection and it was stored in 55 gal stainless steel containers at 6 °C in a cold room to minimize the chance of biological activity until its use.

***o*-Cresol.** *o*-Cresol (Sigma) was obtained as highest possible purity grade and used without further treatment.

GAC. Two different U.S. standard mesh sizes, 80/100 and 30/40, of Filtrasorb (F-400) granular activated carbon (Calgon) were prepared as described previously by Carter *et al.* (1992).

Methods

Measurement techniques. All natural and model humic substances were quantified by TOC analysis (Schimadzu TC-500) and u.v. spectrophotometry at 254 nm (Varian DMS 200). The same linear correlations between these two different measurements were obtained for each substance before and after the sorption isotherm experiments. *o*-Cresol was quantified by measurement of u.v. absorbance at 270 nm. An oxygen microprobe (YSI 530) having a detection limit of 0.1 mg/l was used to measure DO concentrations.

Isotherm experiments. All humic and *o*-cresol sorption experiments were conducted at pH 7 and room temperature (21 ± 2 °C). The humic solutions were buffered with 0.001 M Na_2HPO_4 , while the *o*-cresol solutions were buffered with 0.01 M Na_2HPO_4 so that direct comparisons could be made

with literature results for *o*-cresol uptake. Two-week and four-week equilibration times were chosen for *o*-cresol and humic substances, respectively, based on preliminary studies. Deionized water for stock solutions and all glassware for the isotherm experiments were autoclaved before use to minimize the chance of biological activity during the isotherm experiments. In the preliminary studies, control samples containing 100 mg/l sodium azide and standard biological plating techniques after completion of the isotherm experiments both showed that biological interference over the time periods of isotherm was insignificant.

The effects of DO on the sorption of natural and model humic substances were examined in isotherm experiments using three different initial oxygen conditions. For the first condition, designated "oxic", a 60-ml air headspace was left in each isotherm bottle (Wheaton, 160 ml), which provided approximately 18 mg total initial oxygen in the bottle. For the second condition, termed "oxygen limited", bottles were completely filled with an air-saturated stock solution, providing approximately 1.4 mg initial DO. For the third condition, "anoxic", bottles were completely filled in an anaerobic chamber with a N_2 -purged stock solution, thereby obtaining a maximum of 0.05 mg initial DO in each bottle. For *o*-cresol uptake by GAC, only oxic and anoxic isotherms were conducted.

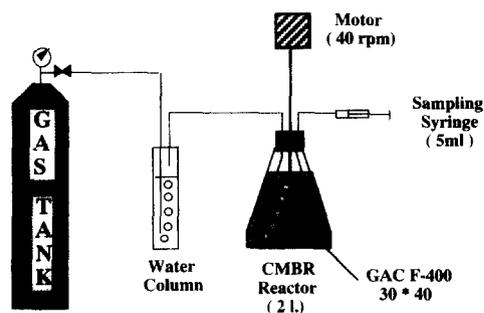


Fig. 1. Completely-mixed batch reactor (CMBR) system for GAC preloading.

Preloading of GAC. Preloading of GAC with an oxygen-sensitive humic model substance, PMA, was conducted in the completely-mixed batch reactor (CMBR) shown schematically in Fig. 1. The preloading was done at pH 7 in 0.01 M Na_2HPO_4 under both oxic and anoxic conditions by continuously bubbling either air or nitrogen, respectively, through each system over the course of the preloading. Preliminary studies revealed that no significant PMA desorption occurred within 30 days at the *o*-cresol isotherm conditions.

Modeling of *o*-cresol isotherm results. The Freundlich isotherm model was used to describe the experimental isotherm data:

$$q_e = K_f C_e^n$$

where: q_e is the solid-phase concentration (mg/g) of sorbate at equilibrium with C_e , the solution-phase solute concentration (mg/l); K_f (mg/g)(l/mg) n , the Freundlich pre-exponential parameter, is a measure of overall adsorption capacity at a specified solution concentration; and, the exponential term, n , is related to the magnitude of the adsorption driving force and to the distribution of adsorption energy sites on the adsorbent (Weber *et al.*, 1991). Linear geometric mean functional regression of the log-transformed experimental data was used to determine the parameters $\log K_f$ and n (Smith and Weber, 1988; Olmstead and Weber,

1990). Confidence intervals (95 %) were also determined for each parameter based on the regression of log-transformed data.

RESULTS AND DISCUSSION

Verification of the impact of DO on *o*-cresol uptake by virgin GAC

Replicate *o*-cresol sorption experiments on virgin GAC were run, two each under oxic and anoxic conditions. The resulting isotherms are shown in Fig. 2, and the Freundlich isotherm parameters are listed in Table 1. The oxic isotherm confidence intervals for

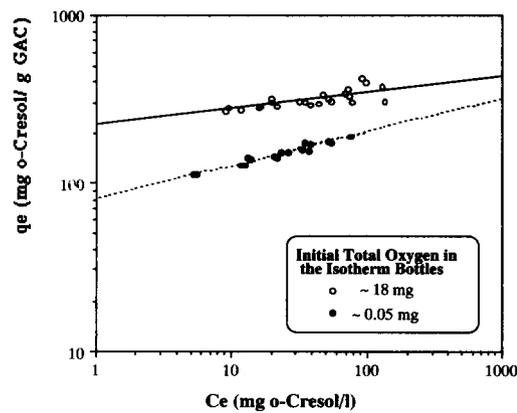


Fig. 2. Data (points) and Freundlich model fits (lines) for sorption of *o*-cresol on virgin GAC in the presence and absence of dissolved oxygen.

the Freundlich parameters overlap the oxic isotherm parameters reported by Vidic and Suidan (1991) for the same type of GAC, while the anoxic isotherm parameters given in Table 1 are slightly, but statistically, different than corresponding values given by Vidic and Suidan. The findings for virgin GAC in

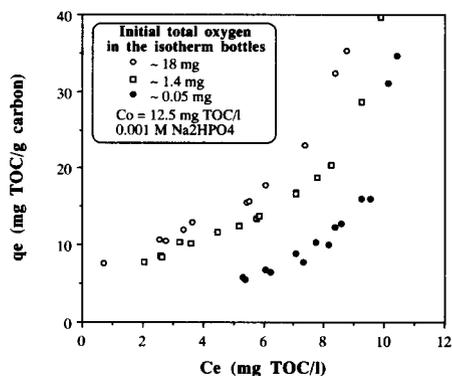


Fig. 3. The influence of dissolved oxygen on the sorption of polymaleic acid (PMA).

the two studies can be considered comparable, particularly given likely differences in GAC surface characteristics due to different storage conditions and/or different carbon lots.

It has been reported in the literature that oxidative coupling of phenolic compounds occurs readily on GAC in the presence of DO, but not when oxygen is purged from the solutions (Grant and King, 1990; Vidic *et al.*, 1990; Vidic and Suidan, 1991). In the context of this work, it is presumed that the uptake of *o*-cresol by GAC determined by the loss of *o*-cresol from solution under anoxic conditions involves little or no oxidative coupling or other polymerization reactions. Under these conditions, the uptake is therefore referred to as *adsorption*. Conversely, under oxic conditions where observed uptake likely involves significant polymerization of *o*-cresol, such uptake is referred to as *sorption*.

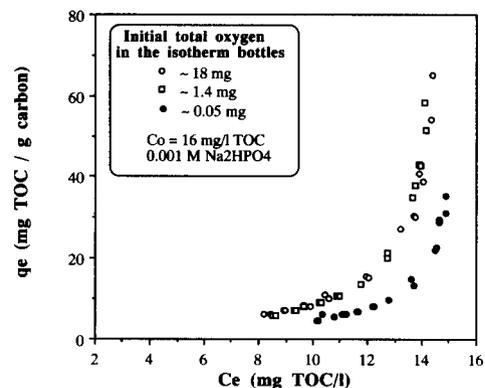


Fig. 4. The influence of dissolved oxygen on the sorption of peat humic acid.

Impacts of DO on the sorption of natural and model humic substances by GAC

In order to test the sensitivity of humic sorption to initial DO concentrations, three sets of isotherms were run for each substance. As indicated in Figs 3 and 4, respectively, both PMA and peat humic acid sorption showed a dependence on DO, the effect being greater for PMA than for peat humic acid. The dependence was not directly proportional to initial DO concentrations, however, as shown by the larger deviations between the anoxic and oxygen-limited and oxic conditions. This indicates that oxygen-sensitive DOMs may have a finite capacity for utilizing DO on GAC surfaces. No impact of DO was detected for PSS, purified Aldrich humic acid, or Huron River Water, as exemplified for the latter in Fig. 5. It can not be explained fully at this time why the sorption of some humic-type substances by GAC can be affected by the presence of DO, while that of others is not; additional studies in our laboratory are examining this phenomenon in more detail. Two major difficulties

Table 1. Freundlich isotherm parameters for the sorption of *o*-cresol on virgin and preloaded GAC*

GAC	Oxic conditions		Anoxic conditions	
	K_F (mg/g)(L/mg) ⁿ	n (-)	K_F (mg/g)(L/mg) ⁿ	n (-)
Virgin	224.89 (244.22–207.08)	0.095 (0.118–0.072)	79.16 (84.73–73.96)	0.201 (0.222–0.180)
Preloaded with PMA under air-saturated conditions	117.09 (187.53–73.10)	0.137 (0.251–0.022)	60.84 (62.20–59.50)	0.214 (0.220–0.207)
Preloaded with PMA under oxygen-free conditions	127.87 (189.95–86.07)	0.105 (0.206–0.004)	64.05 (69.07–59.40)	0.202 (0.225–0.179)

*Numbers in parentheses represent 95% confidence intervals

faced in understanding the impacts of DO on the sorption of humics or DOMs are the system specific but unknown characteristics of these substances and the almost “irreversible” sorption of large humic macromolecules on GAC. From an engineering

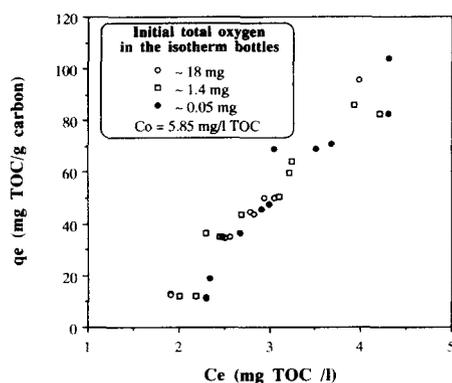


Fig. 5. The influence of dissolved oxygen on the sorption of background organic matter from Huron river water.

design perspective, however, it is clear that DO concentration can be an important experimental variable when measuring sorption equilibrium and rate parameters for humic substances on GAC. From a research and development point of view, it is equally clear that compounds chosen to model the sorption of DOMs or humic substances on GAC must be chosen carefully, because responses to such system parameters as DO concentration may well vary.

The impacts of GAC preloading on the uptake of o-cresol

Because *o*-cresol sorption on activated carbon is faster than that of typical background DOMs, the active zone for its uptake is expected to move more slowly through a GAC adsorber than that for uptake of DOMs, in which case a separation between the mass transfer zones should exist. During transport within an adsorber, most *o*-cresol sorption will thus occur on GAC surfaces which have been preloaded to varying levels by DOMs.

As noted earlier, the sorption of PMA, the material used to model DOM preloading effects in this study, was observed to be sensitive to the presence of DO. GAC was thus preloaded with this material under both oxic and anoxic conditions to determine whether PMA sorbed on the GAC surface by these two different methods would affect the reactivity of the GAC surface differently with respect to subsequent *o*-cresol adsorption and polymerization. The GAC was preloaded to the same surface coverage in both cases, as illustrated in Fig. 6. Oxic and anoxic *o*-cresol isotherms were then run using each of these two preloaded GACs. The Freundlich parameters obtained from the data fits for these isotherms are given in Table 1.

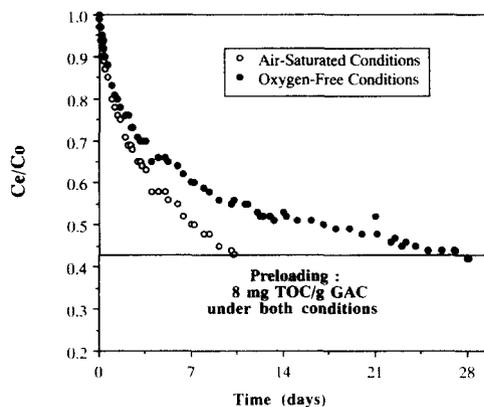


Fig. 6. Preloading of GAC (30/40) under air-saturated and oxygen-free conditions with PMA.

The results presented in Table 1 show that preloading of GAC with PMA under either oxic or anoxic conditions creates a “parallel” shift in the *o*-cresol isotherm; that is, the value of n remains statistically constant, but the K_F term in the Freundlich equation decreases significantly. The effect of PMA preloading was greater for the *o*-cresol isotherms conducted under oxic conditions than it was for those measured under anoxic conditions. The impact of preloading on oxic and anoxic *o*-cresol isotherms can

be assessed by comparing the ratio of K_F values obtained for each preloaded GAC to the K_F values obtained for virgin GAC. For *o*-cresol adsorption under anoxic conditions, this ratio has values of 0.77 and 0.81 (i.e. ~ 20 % decrease) for GAC preloaded under air-saturated and oxygen-free conditions, respectively. The corresponding values for *o*-cresol sorption under oxic conditions are 0.52 and 0.57 (~ 45 % decrease), respectively. These results clearly show the separate impacts of preloading on *o*-cresol adsorption and polymerization on GAC surfaces.

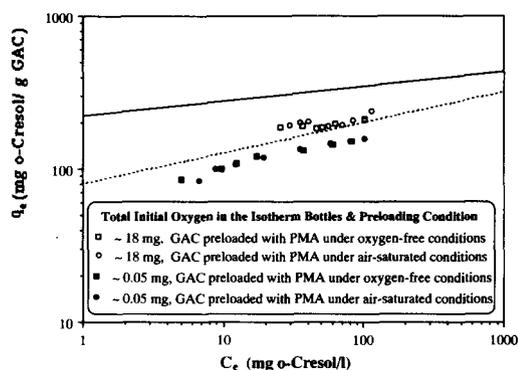


Fig. 7. The influence of different PMA preloading conditions on the uptake of *o*-cresol. The solid and dashed lines are the Freundlich model fits for uptake of *o*-cresol by virgin GAC under oxic and anoxic conditions, respectively.

Chin *et al.* (1993) have hypothesized that the role of humic substances in inhibiting phenolic coupling on GAC surfaces may be as free radical scavengers. Our results, however, do not seem to be consistent with this hypothesis. For example, Fig. 7 compares the effects of preloading GAC with PMA under oxic and anoxic conditions with respect to the subsequent inhibition of adsorption and polymerization of *o*-cresol. This figure illustrates that the oxic and anoxic isotherms for *o*-cresol are not significantly affected by the oxygen-conditions of PMA preloading. If PMA were only scavenging DO in our systems, then the preloading conditions should affect subsequent *o*-cresol reactions on the GAC surface, based on the oxygen-sensitivity data for PMA presented in Fig. 3. Instead, Fig. 7 indicates that the extent of surface coverage may be the most significant factor relative to the effects of preloading on the adsorption and polymerization of *o*-cresol.

It should be noted that the surface coverage of the GAC by PMA in the preloading experiments was not very high (~ 8 mg TOC/g GAC). This is significantly lower than levels which are usually obtained even in water treatment applications. As evident from Fig. 3, this level represents only the lower surface coverage ranges examined in the sorption isotherms for PMA. It is therefore likely that preloading at the higher surface coverages normally experienced in water and wastewater treatment applications (e.g. see Fig. 5)

will significantly inhibit both adsorption and polymerization of phenolic compounds

CONCLUSIONS

The following conclusions can be drawn from the results presented above :

(i) it is clear that the presence of DO can be important for the sorption of some natural and model humic materials by GAC and not for others, but the mechanism or factors responsible for this effect cannot be elucidated at this time;

(ii) preloading of GAC by PMA, an oxygen sensitive model humic material, was shown to decrease the subsequent adsorption of *o*-cresol by approximately 20 % and, at the same time, decrease oxidative coupling of the *o*-cresol by about 25 %;

(iii) although PMA is an oxygen-sensitive model humic substance, its inhibition effects on *o*-cresol adsorption and polymerization are similar when preloaded to the same level of GAC surface coverage under oxic and anoxic conditions; and,

(iv) polymerization of *o*-cresol in full-scale GAC adsorbers, which are generally extensively preloaded by DOMs, may not be significant for many practical applications because preloading may significantly inhibit oxidative coupling of *o*-cresol.

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