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## Evaluation of Activated Carbon as a Reactive Cap Sorbent for Sequestration of Polychlorinated Biphenyls in the Presence of Humic Acid

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### Abstract

This study investigated the interferences caused by high humic acid concentrations on the adsorption of coplanar and noncoplanar polychlorinated biphenyls (PCBs) on coconut shell activated carbon. In particular, the research focuses on the application of activated carbon as a reactive cap for contaminated sediment sites, a possible intervention to reduce contaminant flux through pore water, and to organisms in aquatic environments. Kinetic and equilibrium studies were conducted using activated carbon as a sorbent for individual PCB congeners including BZ 1, 52, 77, 153, and 169, respectively, in the presence and absence of humic acid. Results showed that preloading of activated carbon with humic acid significantly reduced the adsorption affinity for all selected PCB congeners. Experiments conducted without preloading of activated carbon demonstrated that desorption upon subsequent spiking with humic acid (simulating long-term exposure to pore water that contains high humic acid concentrations) was not found to be statistically significant, and varied with coplanarity of PCBs. Results provide important information for the design of reactive caps in sediments where high concentrations of dissolved organic carbon are found, and highlight the importance of considering site conditions when designing effective reactive caps.

**Key words:** reactive cap sorbent; activated carbon; PCBs; humic acid; SEM

### Introduction

**S**EDIMENTS THAT ARE CONTAMINATED with hydrophobic organic contaminants (HOCs) that are toxic, bioaccumulative, and persistent are of major concern both from the perspective of human health and the health of aquatic ecosystems. These sediments can be treated using *ex situ* treatment methods following environmental dredging or *in situ* treatment methods such as monitored natural recovery and capping technologies. To date, monitored natural recovery and sand caps have been used as an *in situ* treatment method, whereas reactive capping has been piloted but has not yet seen widespread use as a remediation technique. Reactive capping can be accomplished both by mixing reactive material into a sediment bed (Zimmerman *et al.*, 2004; Werner *et al.*, 2005), by depositing loose granular material over the sediment bed, or by binding the reactive material into a geotextile that is deployed on the contaminated sediment bed (McDonough *et al.*, 2008). There is substantial information available for adsorption of aromatic compounds (Walters and Luthy,

1984; Zimmerman *et al.*, 2004; Cornelissen *et al.*, 2006) and chlorinated compounds (Karanfil *et al.*, 1999; Sotelo *et al.*, 2002) on activated carbon. Zimmerman *et al.* (2004) have shown a 92% reduction in polychlorinated biphenyl (PCB) aqueous concentration and 84% reduction in polycyclic aromatic hydrocarbon (PAH) aqueous concentration, and up to 89% reduction in PCB flux to overlying water with addition of 3.4 wt.% of activated carbon to sediments. Cornelissen *et al.* (2006) have shown a significant reduction in pore water concentrations of PAH by addition of 2 wt.% of activated carbon to sediments. The studies have also shown an increase in effectiveness with the increase in contact time from 1 month to 6 months (Millward *et al.*, 2005; Werner *et al.*, 2005).

Significant research has investigated activated carbon as a sorbent for organic pollutants, but the remediation process for contaminated sediments requires understanding the influence of high concentrations of background natural organic acids, like humic acids, that influence the efficacy of treatment and fate of organic contaminants. The adsorption efficiency of activated carbon can be reduced in the presence of ubiquitous humic and other substances that occur naturally (Pirbazari *et al.*, 1989; Matsui *et al.*, 2003). The concentration of dissolved organic carbon (DOC) in sediment pore water has been reported to be as high as 200–2,500  $\mu\text{M}$  (0.6 to 7.5 g/L) for the upper ~20–30 cm of sediments (Burgie, 2001). The objective

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of this study was to evaluate the adsorption affinity of coconut shell activated carbon for PCBs in the presence of humic acid to understand its potential use in reactive capping for *in situ* remediation of contaminated sediments. In the present study, several kinetic and isotherm experiments have been conducted to determine the sorption behavior of these contaminants on activated carbon in the presence of humic acid at concentrations relevant to sediment porewater.

The reduction in adsorption affinity of activated carbon by humic substances can be attributed to two mechanisms: pore blockage caused by humic acid or competition of HOCs with humic acid for adsorption sites. The adsorption system in the presence of humic acid is complex, and consists of freely dissolved HOCs and humic acid, dissolved HOC-humic acid complexes, adsorbed HOC and humic acid, and adsorbed complexes. To control the competition between humic acid molecules and HOCs for adsorption sites, understanding the relationship between the optimum pore size region for adsorption of target HOC and pore size region for DOC adsorption is important (Karanfil *et al.*, 2006). Large humic molecules cannot enter the micropore network, and can block access to the large internal pore structure of activated carbon (Pignatello *et al.*, 2006). For effective adsorption of HOCs the size distribution of micropores in activated carbon should be about twice the kinetic diameter of the contaminant, which has been reported to reduce the pore blockage caused by DOC (Quinlivan *et al.*, 2005). The molecular weight of DOC also plays an important role, as microporous carbon can be affected by low molecular weight DOC and mesoporous carbon by high molecular weight DOC (Newcombe *et al.*, 2002; Li *et al.*, 2003). Therefore, the pore blockage effect of DOC has been reported to be reduced by using activated carbon with large micropores and mesopores (Li *et al.*, 2003). Besides pore structure, surface chemistry can also significantly affect the adsorption of organic compounds on activated carbon. Some studies showed that hydrophobic carbon surfaces, which are present with coconut shell-based activated carbon or coal-based activated carbon, can be more effective for adsorption of organic compounds compared to hydrophilic carbon surfaces, like some of the chemically modified activated carbon, due to interference of water adsorption with HOC adsorption (Newcombe *et al.*, 1997, 2002; Quinlivan *et al.*, 2005). Taking these factors into consideration, coconut shell activated carbon was selected for this study, and a comparison of select adsorption behavior between coconut shell and coal-based activated carbon is provided. McDonough *et al.* (2008) have studied the performance of coal-based activated carbon in the presence of simulated pore water at a very low concentration of dissolved organic matter. In this research coconut shell activated carbon, which is more porous than coal-based activated carbon, has been evaluated at very high concentrations of humic acid.

Contaminant flux from sediments to overlying waters has been ascribed to various processes including bioturbation by epibenthic and infaunal organisms, mechanical scouring, uprooting of macrophytes, in addition to pore water flux by diffusion and advection (Butcher *et al.*, 2004). Therefore, the goal of this research was focused on development of a thin layer cap that can be deployed over a contaminated sediment bed for sequestration of contaminants as well as isolation of contaminated sediments from the overlying water body. The action of a reactive cap is to reduce or eliminate mechanisms

responsible for contaminant transport (bioturbation, scouring, uprooting), and to provide reactivity to reduce contaminant flux associated with diffusive and advective mechanisms. The fate and transport of contaminants in this type of system requires knowledge of how complexation with and interference from natural organic acids influences partitioning to the solid surface of a sorbent that can be used in the reactive cap. Therefore, it is important to evaluate the performance of a sorbent in the presence of natural organic acids such as humic acid that can be found in high concentrations under typical site conditions.

## Materials and Methods

### Chemicals

Ultrahigh purity chemicals and GC-grade solvents including hexane, methanol, and acetone were used for all experiments and were obtained from Fischer Scientific (Agawam, MA). The five PCB congeners were selected for this research on the basis of number of chlorine atoms and coplanarity to represent a wide range of hydrophobicity. The PCB congeners used were 2-chlorobiphenyl, 2,2',5,5'-tetrachlorobiphenyl, 3,3',4,4'-tetrachlorobiphenyl, 2,2',4,4',5,5'-hexachlorobiphenyl, and 3,3',4,4',5,5'-hexachlorobiphenyl (BZ 1, 52, 77, 153, and 169, respectively). 2,4,6-Trichlorobiphenyl (BZ 30) was used as an internal standard because of no overlapping with peaks of other selected PCB congeners and 2,4,5,6-tetrachloro-*m*-xylene (TCMX) was used as a surrogate standard. These PCB congeners and TCMX were purchased (Ultra Scientific, North Kingstown, RI) either in neat form or dissolved in hexane. Humic acid sodium salt (Sigma-Aldrich, St. Louis, MO) was used as a representative natural organic matter. Aldrich humic acid was used in this study to attain worst-case analysis by obtaining very high concentration of humic acid solution, which could not be achieved otherwise by using sediment pore water. Sodium azide (EMD Chemicals Inc., San Diego, CA) was used as bactericide to avoid biological growth in the experiments and sodium sulfate anhydrous (Fisher Scientific, Morris Plains, NJ) was used in a preparatory step for GC analysis of samples.

**Activated carbon.** The sorbent used in this study was coconut shell activated carbon, OLC 12×40 (Calgon Carbon Corporation, Pittsburgh, PA). This material was selected because it is widely used for removal of trace organic compounds and it has high microporosity. Table 1 shows the properties of the material. Coal-based Calgon F400 was also

TABLE 1. TYPICAL PROPERTIES OF COCONUT SHELL AND F400 ACTIVATED CARBONS

	Coconut shell	F400
Particle size [ASTM D-2862] <sup>a</sup>	12×40 US Mesh	12×40 US Mesh
Ash Content (Base Material) [ASTM D-2866] <sup>a</sup>	3% w/w	9% w/w
Bulk Density [ASTM D-2854] <sup>a</sup>	0.50 g/cm <sup>3</sup>	0.52 g/cm <sup>3</sup>
Iodine Number [BSC 90-032] <sup>a</sup>	1,050 mg/g	1,000 mg/g

<sup>a</sup>Values obtained from Calgon Corp.

used for some of the studies to compare the performance of these two activated carbons; its properties are also shown in Table 1.

#### Batch experiments

Batch experiments were used to determine the kinetics of PCB adsorption on activated carbon and to determine the adsorption affinity of activated carbon for PCBs in the presence and absence of humic acid. All the experiments were conducted in separate batches of 125 mL deionized (DI) water using acetone as a carrier solvent for PCB congeners. Acetone was used to prepare the stock solution because of a lack of significant interference of acetone on PCB adsorption on activated carbon (Pirbazari and Weber, 1981). For quality assurance purposes, duplicates were prepared in all the experiments and controls were used to account for any kind of PCB loss other than adsorption on activated carbon. The effect of humic acid was determined by preloading activated carbon with humic acid, and by adding humic acid after 48 h of equilibration to investigate whether desorption of PCBs occurs.

**Preloading of activated carbon.** The preloading of activated carbon was done with 1 g/L of humic acid solution prepared in DI water. Sodium azide was added to the humic acid stock solution at a concentration of 100 mg/L to avoid biological growth. All of the samples were equilibrated for 48 h at 150 rpm on a rotary shaker to ensure thorough mixing. Equilibration time was based on data published on adsorption kinetics of humic acid on activated carbon by Bjelopavlic *et al.* (1999) and Lorenc-Grabowska and Gryglewicz (2005). Preloaded samples having activated carbon preloaded with humic acid along with the humic acid solution were used as such for further experimentation to mimic site conditions with very high concentrations of humic acid.

#### Kinetic studies

Batch experiments were conducted for the duration of 1 month to evaluate the kinetics of adsorption of PCBs and to determine the effect of humic acid on adsorption process. PCBs selected for this study were 2-chlorobiphenyl, 2,2',5,5'-tetrachlorobiphenyl and 2,2',4,4',5,5'-hexachlorobiphenyl. The effect of humic acid was determined by preloading of activated carbon as mentioned in the previous section. Separate batches were prepared for samples with bare activated carbon in DI water and preloaded activated carbon, which

remained in the humic acid solution used for preloading. Experiments for all three PCB congeners were conducted separately to avoid interferences in the performance of activated carbon due to competition among congeners for adsorption sites. The concentrations of PCBs used were different for each congener: 6 mg L<sup>-1</sup> for 2-chlorobiphenyl, 5 mg L<sup>-1</sup> for 2,2',5,5'-tetrachlorobiphenyl, and 0.08 mg L<sup>-1</sup> for 2,2',4,4',5,5'-hexachlorobiphenyl. The samples were continuously mixed on a rotary shaker at 150 rpm for the duration of the experiment.

#### Isotherm studies

Separate batches were prepared at different loading rates of all PCB congeners with bare activated carbon (Table 2) and activated carbon preloaded with humic acid. The preloading time and procedure was the same as performed for the kinetic studies (above). These studies were conducted with an equilibration time of 72 h, which represents a reasonable approximation of equilibrium as shown by the kinetic experiments for bare activated carbon (this selection is discussed further in the Results section of this article). The preliminary studies were also conducted to evaluate and compare the performance of coal-based activated carbon, Calgon F400, for adsorption of 2,2',5,5'-tetrachlorobiphenyl in the presence of humic acid.

**Desorption studies.** These studies were conducted to simulate the long-term exposure of reactive cap sorbents to natural organic matter that may occur in the field. Once sampling was completed at 72 h, humic acid was added to the bare activated carbon samples to obtain the same concentration of humic acid as in preloaded samples to determine the extent of desorption for PCBs already adsorbed on activated carbon. These samples were again equilibrated for 72 h of mixing prior to the sampling.

#### Sample extraction

The supernatant of each sample was extracted into hexane using TCMX as a surrogate standard by vial liquid-liquid extraction method. Twenty milliliters of sample and 10 mL of hexane were taken into a 40-mL vial. The vials were sealed with Teflon<sup>®</sup>-lined screw caps and shaken vigorously for 30 s three times at intervals of 30 s each. The vials were then stored for at least for 24 h at 4°C. The surrogate recoveries by using this extraction method were all in the range of 70–130%. The extracts were passed through sodium sulfate to remove any

TABLE 2. SOLUBILITY LIMIT, LOG OCTANOL-WATER PARTITION COEFFICIENTS AND LOG  $K_{DOC}$  VALUES OF SELECTED POLYCHLORINATED BIPHENYL CONGENERS

PCB congener	Solubility limit in water (ppm) <sup>a</sup>	Log $K_{OW}$ <sup>a</sup>	Log $K_{DOC}$	Isotherm studies concentration range (mg/L)	Coplanarity
2-chlorobiphenyl	4.0	4.7	3.63 <sup>b</sup>	0.008–6.1	Noncoplanar
2,2',5,5'-tPCB	0.26	5.9	4.6 <sup>c</sup>	0.008–0.4	Noncoplanar
3,3',4,4'-tPCB	0.26	5.9	—	0.008–0.8	Coplanar
2,2',4,4',5,5'-hPCB	0.038	6.7	5.3 <sup>c</sup>	0.032–0.8	Noncoplanar
3,3',4,4',5,5'-hPCB	0.038	6.7	—	0.024–0.8	Coplanar

<sup>a</sup>Erickson, 1997.

<sup>b</sup>Butcher and Garvey, 2004.

<sup>c</sup>Poerschmann *et al.*, 1999.

PCB, polychlorinated biphenyl.

chemically bound water prior to injection on GC columns. The GC vials were prepared using these filtered solvents and an internal standard.

#### Gas chromatography/mass spectrometry analysis

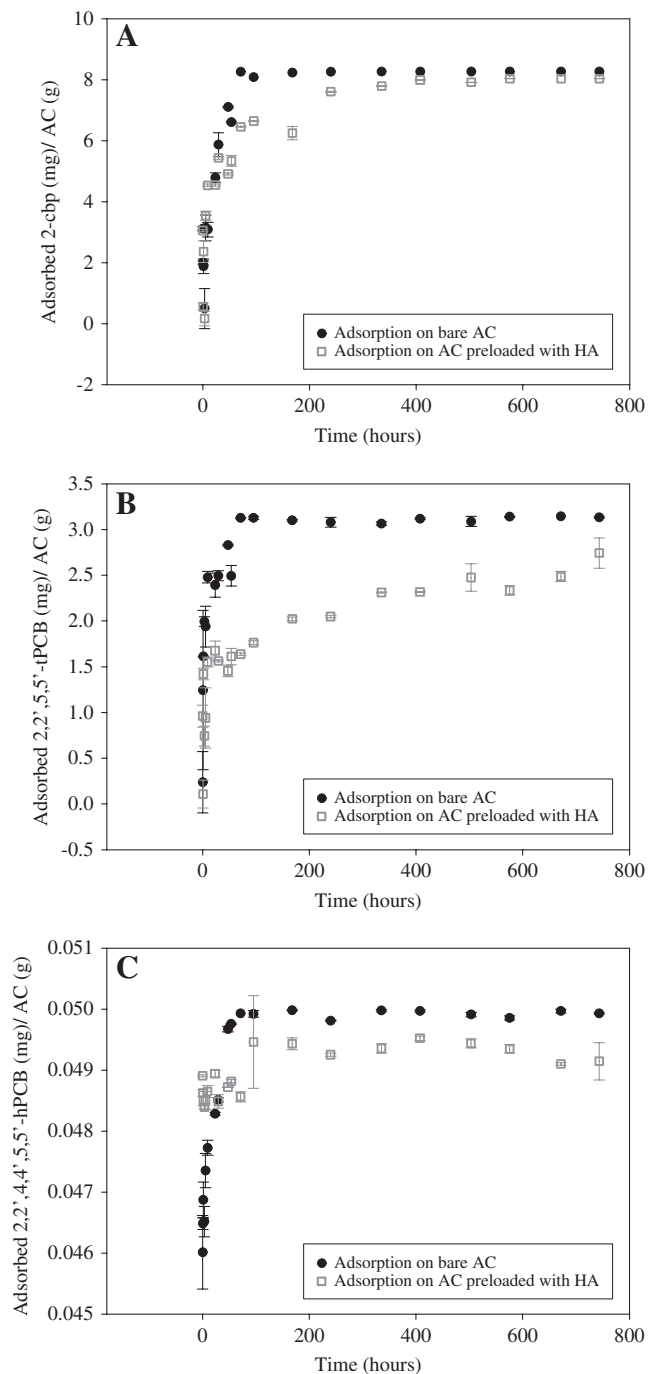
The internal standard method was used for analysis of all the samples. All extracts were analyzed using a Varian CP3800 Gas Chromatograph (GC)/Saturn 2200 Ion Trap Mass Spectrometer (MS) with a CP8400 Auto Sampler. The GC column used was a DB-5 type capillary column (Varian Factor Four VF-5 ms), 30 m long, 0.25 mm i.d. and 0.5  $\mu$ m thick. The ion trap was operated in selected scan mode (MS/MS) for each PCB congener. The column oven temperature was programmed at 40°C with a hold time of 2 min, followed by a temperature ramp up to 184°C at the rate of 12°C/min and then to 280°C at the rate of 4°C/min, with the final hold time of 2 min.

## Results and Discussions

### Kinetic studies

Experiments were conducted to obtain the equilibration time required for adsorption of PCBs on activated carbon. Figure 1 shows the kinetics of 2-chlorobiphenyl, 2,2',5,5'-tetrachlorobiphenyl and 2,2',4,4',5,5'-hexachlorobiphenyl adsorption on bare activated carbon and activated carbon preloaded with humic acid. The kinetics of 2-chlorobiphenyl (Fig. 1A) indicated equilibrium was reached at approximately 72 h for adsorption on bare activated carbon. The equilibrium for preloaded activated carbon was found to be delayed, and the impact of preloading was found to be decreased with time. Clearly, preloading activated carbon with humic acids has a significant effect on the rate of adsorption of 2-chlorobiphenyl and 2,2',5,5'-tetrachlorobiphenyl, as shown in Fig. 1. There was no discernible effect on the kinetics of the hexachlorobiphenyl adsorption (Fig. 1C), although a longer equilibration time (beyond 30 days) may have resulted in an observable change in kinetics. Figure 1B suggests that equilibrium is not yet achieved at 30 days, as the adsorbed concentration of tetrachlorobiphenyl with preloaded carbon approaches that without humic acid present. It is also important to point out that these experiments were conducted at only one concentration of each congener; the effect of humic acids on kinetics and the partitioning observed at the end of the experiments would not be expected to be identical under all conditions. The retardation effects are likely due to the pore blockage effect and more complexation of highly chlorinated congeners to humic acid compared to the monochloro-congener.

Kinetics were important to characterize not only for the conduct of isotherm experiments but also for the application of a thin reactive cap; studies conducted at Anacostia River for demonstration of specific discharge and tidal heights showed the average specific discharge of sediment pore water to the overlying water column of 5 cm/day (Draft Data Report, 2006). This underscores the significance of understanding adsorption equilibration times, as residence time in a thin layer cap may be significantly less than 24 h. Given that the residence time of porewater moving through a thin reactive cap can be as little as 4.8 h (for a 5 cm/day flux and 1 cm-thick



**FIG. 1.** Kinetics of adsorption of PCB congeners on coconut shell activated carbon (AC) in the presence and absence of humic acid (HA): (A) 2-chlorobiphenyl, (B) 2,2',5,5'-tetrachlorobiphenyl, and (C) 2,2',4,4',5,5'-hexachlorobiphenyl.

cap), a decision had to be made for how long to equilibrate samples when conducting isotherm experiments. Figure 1B demonstrates that, for some congeners and under some conditions, equilibrium is not reached even at the end of 30 days. To characterize the expected performance of these materials in a consistent manner in a reasonable time frame, 72 h was used for equilibration. Clearly, this is far shorter than

necessary to reach equilibrium, and it is longer than the residence time expected for thin reactive caps in many physical settings.

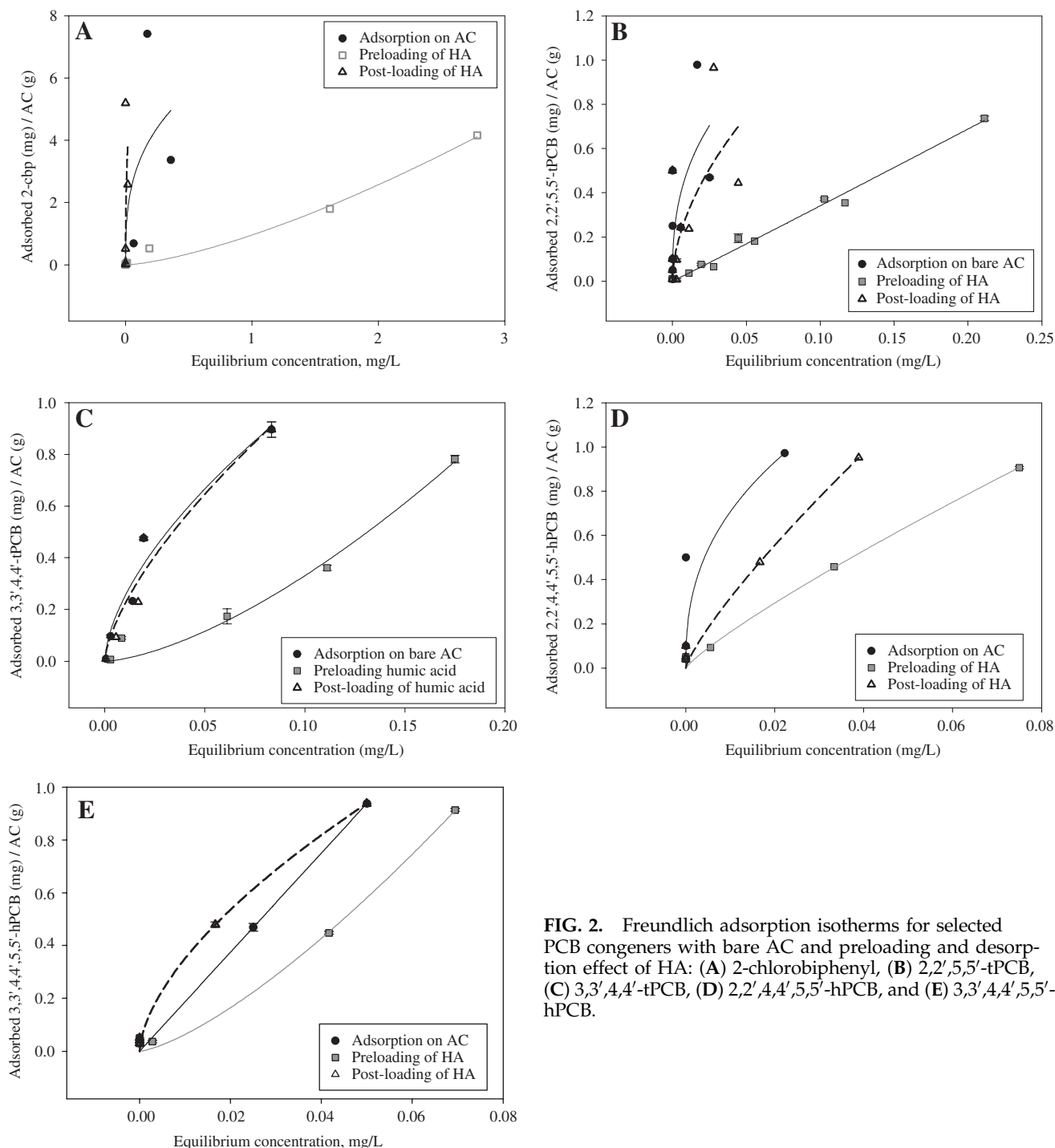
*Isotherm studies*

Isotherm studies were conducted to determine the adsorption affinity of selected PCB congeners for activated carbon in the presence and absence of humic acid. The selection of PCBs for this study was designed to obtain a range in the

degree of chlorination and coplanarity to obtain an idea of sorption behavior for a range of PCB congeners. The Freundlich model was used to obtain the isotherms using the equation:

$$q_e = K_F (C_e)^{(1/n)}$$

where  $q_e$  is the concentration of adsorbed PCB congener ( $\text{mg g}^{-1}$ ),  $K_F$  is the Freundlich Isotherm constant,  $C_e$  is the aqueous phase concentration ( $\text{mg L}^{-1}$ ) and  $1/n$  is the



**FIG. 2.** Freundlich adsorption isotherms for selected PCB congeners with bare AC and preloading and desorption effect of HA: (A) 2-chlorobiphenyl, (B) 2,2',5,5'-tPCB, (C) 3,3',4,4'-tPCB, (D) 2,2',4,4',5,5'-hPCB, and (E) 3,3',4,4',5,5'-hPCB.

TABLE 3. MODEL 1: LEAST-SQUARE MEANS-DIFFERENCED STUDENT'S *t* COMPARING ADSORPTION AFFINITY FOR ACTIVATED CARBON

PCB congener	Levels <sup>a</sup>	Least square means
2,2',4,4',5,5'-hPCB	A	0.293
3,3',4,4',5,5'-hPCB	B	0.283
2,2',5,5'-tPCB	C	0.265
3,3',4,4'-tPCB	C	0.265

Alpha = 0.050, *t* = 2.0639

<sup>a</sup>Levels not connected by same letter are significantly different.

dimensionless Freundlich exponent. Figure 2A–E shows data and Freundlich adsorption isotherms for PCB congeners studied in the presence and absence of humic acid. The humic acid interferences are shown as: (1) preloading of humic acid on activated carbon and (2) postloading of humic acid, in which activated carbon was spiked with humic acid after 72 h of PCB adsorption to simulate the long-term exposure to pore water humic acid concentrations.

In all of the isotherms, a significant reduction in adsorption affinity for activated carbon was found in the presence of humic acid as shown in Fig. 2. This reduction may be due to the pore blockage effect caused by the preloading of activated carbon with humic acid molecules prior to the entry of HOCs into the pores (Li *et al.*, 2003; Pignatello *et al.*, 2006), the hydrophobic partitioning of HOCs to dissolved humic acid (Poerschmann *et al.*, 1999), and the competition for adsorption sites by humic molecules. The studies conducted to evaluate desorption effects of humic acid showed that once PCBs were adsorbed on activated carbon there is no discernable desorption. Figure 2A–E appears to show some degree of desorption for noncoplanar congeners, whereas coplanar congeners show no desorption. However, desorption was found to be insignificant statistically in all cases, despite the appearance of slight desorption in the case of noncoplanar congeners,

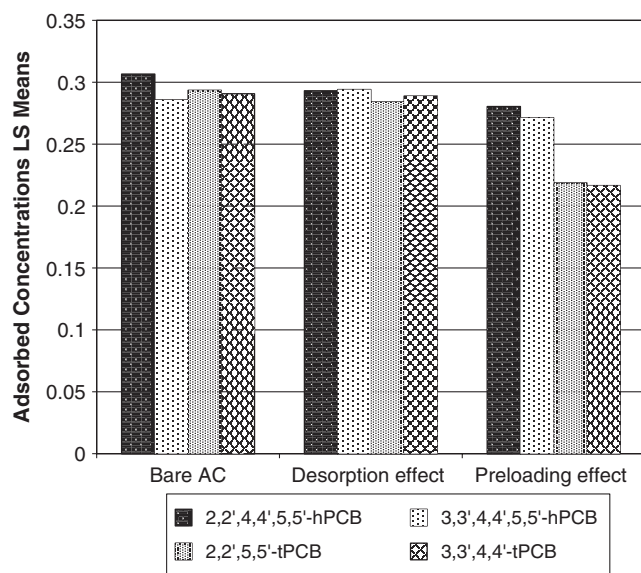


FIG. 3. Least-square (LS) means plot to determine the effects of preloading and postloading of humic acid on PCB adsorption.

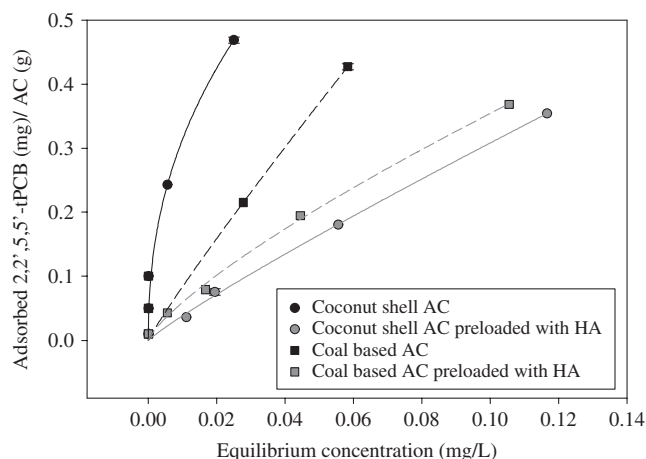


FIG. 4. Comparative isotherms for coal-based and coconut shell-based AC for 2,2',5,5'-tetrachlorobiphenyl.

which would be consistent with steric hindrances in the non-coplanar configuration leading to decreased sorption affinity (Fig. 2A–E) (Cornelissen *et al.*, 2004).

The data obtained from the isotherm studies was analyzed statistically using software JMP<sup>®</sup> 5.1. A model was developed on the Fit model platform to evaluate the performance of activated carbon for tetra- and hexachlorobiphenyls. The model was developed based on the hypothesis that performance of coconut shell activated carbon in the presence of humic acid varies with the PCB isomer and the coplanarity of the congeners. The three factors considered in this model were: PCB congener, loading rate, and adsorption density on activated carbon (including preloading and postloading of humic acid). The full factorial design was developed with these three factors along with the quadratic term of loading rate. According to the analysis of variance (ANOVA) the *p*-value was <0.0001; therefore, there is a significant effect of the isomer and coplanarity of congeners on adsorption affinity for coconut shell activated carbon in the presence of humic acid. The *F*-test was performed on each term (considering the main effects and the interaction terms between effects) of the model to determine the significance of the factors based on the value of *p* < 0.05. The Student's *t* was used to compare the adsorption affinities of all PCB congeners at  $\alpha = 0.05$ , and showed higher

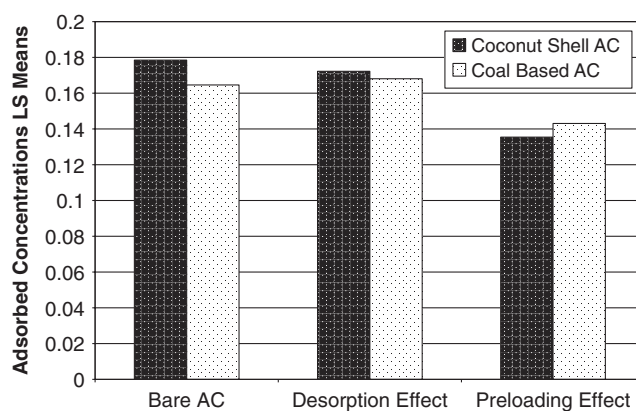


FIG. 5. LS means plot: effect of preloading humic acid on coconut shell activated carbon and coal-based activated carbon.

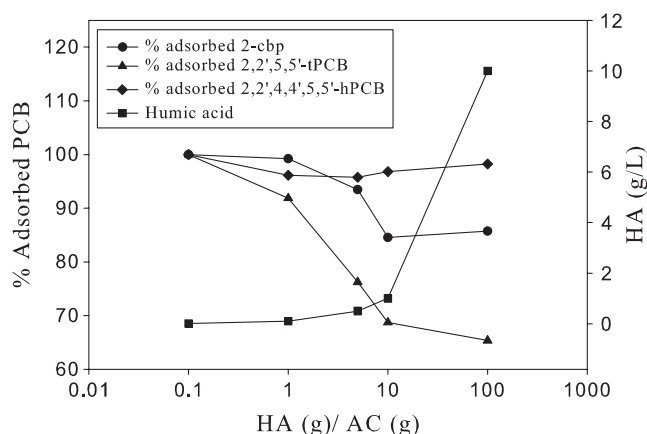


FIG. 6. Effect of different loadings of HA on adsorption of 2-chlorobiphenyl; 2,2',5,5'-tPCB and 2,2',4,4',5,5'-hPCB.m.

adsorption for hexachlorobiphenyls compared to tetrachlorobiphenyls (Table 3). The least-square means of all PCB congeners were plotted against the treatment effects (preloading/desorption effect), and it was found that the desorption due to postloading of humic acid was not significant in the case of the coplanar tetra- and both coplanar and noncoplanar hexachloro-congeners. The preloading of humic acid was found to be significant for all the congeners (Fig. 3).

The coconut shell-based activated carbon has a distinctly different pore structure than the coal-based activated carbon (Bjelopavlic *et al.*, 1999). However, when both carbon types were preloaded with humic acid, their performance was found to be similar in the presence of high concentrations of humic acid (Fig. 4). Thus, although the coconut shell-based activated carbon was clearly superior in the absence of humic acid, the presence of humic acid clearly affects the coal-based activated to a lesser extent. Model 2 was developed on JMP® 7 to determine the performance of both types of carbon in the presence of humic acid. The statistical analysis of data confirmed that preloading had statistically significant effects on both types of activated carbon (Fig. 5). Experiments were also conducted to determine the effect of humic acid on the adsorption affinity for both types of activated carbon at different loadings of humic acid and fixed loading of PCBs. The results

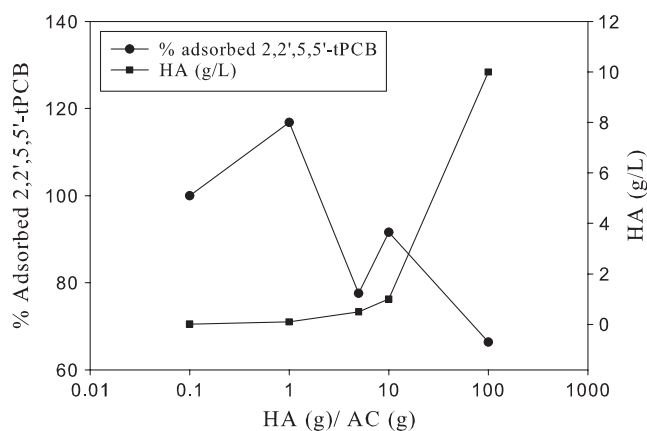


FIG. 7. Effect of different loadings of HA on adsorption of 2,2',5,5'-tPCB on coalbased AC.

TABLE 4. ADSORPTION COEFFICIENTS AND FREUNDLICH ISOTHERM CONSTANTS OBTAINED FOR SELECTED POLYCHLORINATED BIPHENYL CONGENERS ON BARE ACTIVATED CARBON AND ACTIVATED CARBON PRELOADED WITH HUMIC ACID

Congener	Freundlich Isotherm Constants					
	Nonlinear form ( $q_e = K_f C_e^{(1/n)}$ )			Linear form ( $\log q_e = \log K_f + n^{-1} \log C_e$ )		
	Bare AC	Preloaded	1/n	Bare AC	Preloaded	1/n
Coconut shell AC						
2-chlorobiphenyl	12.625	1.3862	0.336	7.002	7.414 (6.264-8.563)	0.386 (0.101-0.671)
2,2',5,5'-tPCB	16.501	2.963	0.437	2.347	7.519 (6.709-8.328)	0.249 (-0.063-0.561)
3,3',4,4'-tPCB	9.985	4.123	0.608	4.112	4.672 (3.158-6.187)	0.899 (0.519-1.280)
2,2',4,4',5,5'-hPCB	35.988	11.626	0.399	4.442	8.00 (7.211-8.788)	0.227 (-0.178-0.633)
3,3',4,4',5,5'-hPCB	17.85	12.216	1.000	18.750	7.590 (7.355-7.824)	0.271 (0.198-0.352)
Coal-based AC						
2,2',5,5'-tPCB	6.344	3.352	0.923	5.888	7.563 (6.774-8.352)	0.200 (-0.07-0.47)



for all three congeners (monochloro, tetrachloro, and hexachloro) showed that the adsorption affinity for coconut shell activated carbon decreased with the increase in humic acid concentration (Fig. 6). The effects were found to be least in the case of hexachlorobiphenyl followed by monochlorobiphenyl and then tetrachlorobiphenyl. The experiment conducted to measure the effect of humic acid loadings on coal-based activated carbon also showed a reduction in adsorption affinity for coal-based activated carbon with the increase in humic acid loadings (Fig. 7).

All the isotherms obtained using coconut shell and coal-based activated carbon were also evaluated by performing bivariate analysis on JMP<sup>®</sup> 7.1 to obtain the log-linear form of Freundlich model.

$$\log q_e = \log K_f + n^{-1} \log C_e$$

To perform this set of data analysis all the values were converted to nanogram level, and then log values were obtained for equilibrium concentration ( $\text{ng L}^{-1}$ ) and adsorbed concentration ( $\text{ng kg}^{-1}$ ). The linear fit was obtained by using Fit Y by X platform and for each  $\log K_f (\text{ng}^{(1-(1/n))} \text{L}^{(1/n)} \text{kg}^{-1})$  and  $n^{-1}$  values confidence intervals were also obtained (shown in Table 4).

#### Evaluation of isotherm coefficients

As mentioned earlier, the main aim of this research is to more completely understand the design parameters for a reactive sediment cap that considers the interference from natural organic acids. To compare materials and the sorption affinity for different congeners, adsorption coefficients ( $K_d$ ) were also estimated using a linear fit for all the isotherms (Table 4). The linear coefficients are used here to simplify interpretation of sorption affinity: this is something that is very difficult with the Freundlich coefficients due to the significance of curvature in the model. In this study, based on  $K_d$  values, the preloading effect was found to be most significant for 2-chlorobiphenyl noncoplanar 2,2',5,5'-tetrachlorobiphenyl (with 89 and 82% reduction in adsorption affinity, respectively). The effect was less dominant in the case of coplanar 3,3',4,4'-tetrachlorobiphenyl with a 59% reduction and noncoplanar 2,2',4,4',5,5'-hexachlorobiphenyl with a 68% reduction and was least in the case of coplanar 3,3',4,4',5,5'-hexachlorobiphenyl with a 32% reduction. The measure of nonlinearity for isotherms was estimated using the Freundlich isotherm coefficient ( $1/n$ ). The adsorption the trend was found to be favorable with  $1/n < 1$  (Table 4, nonlinear) for all bare activated carbon isotherms and noncoplanar congeners with preloaded humic acid, but in the case of coplanar congeners and 2-chlorobiphenyl with preloading, the value of ( $1/n$ ) was greater than 1 and the trend of the isotherm was unfavorable as shown in Fig. 2. Using the linear fit of Freundlich coefficients when  $\log K_f$  values were compared for bare activated carbon with that of preloaded activated carbon, the reduction in  $\log K_f$  values ranged from 0.101 to 0.954, again indicating a significant effect of preloading with humic acid (Table 4, linear).

#### Summary

This study demonstrated the effects of preloading and postloading (addition of humic acid after equilibration of ac-

tivated carbon with PCBs) of humic acid on adsorption affinity for coconut shell activated carbon for coplanar and noncoplanar PCB congeners. The adsorption affinity for bare activated carbon was found to be greater, with no desorption observed that was statistically significant, for highly chlorinated coplanar congeners as well as lower chlorinated noncoplanar congeners. Adsorption affinity for coconut shell activated carbon was found to be significantly affected by preloading with high concentrations of humic acid. Although PCBs had a greater affinity for coconut shell-based activated carbon than coal-based carbon, when the carbon was preloaded with humic acid, the differences between the performance of the two carbons was very small for 2,2',5,5'-tetrachlorobiphenyl. The presence of humic acid is a major factor in the design and performance of reactive caps under typical site conditions. Reactive caps that will be deployed over the sediment bed are likely to encounter high concentrations of natural organic matter. Therefore, it is important to evaluate the performance of sorbents that will be used in the mat in the presence of high organic acid concentrations. This study showed that sorbent material exposure to humic acid prior to the sorption of contaminants affects performance significantly; remedial designs that rely on reactive caps containing sorbents need to understand the influence of dissolved organic carbon on sorption properties.

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#### Author Disclosure Statement

The authors declare that no conflicting financial interests exist.

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