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Evaluation of reactive cap sorbents for in-situ remediation of contaminated sediments

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EVALUATION OF REACTIVE CAP SORBENTS FOR *in-situ* REMEDIATION OF CONTAMINATED SEDIMENTS

BY

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DISSERTATION

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In
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DEDICATION

In memory of

Shri Bihari Lal Sharma

(December 21, 1918 – February 29, 2008)

This dissertation is dedicated to my Grand pa. You will always be my inspiration and will always be remembered.

ACKNOWLEDGMENT

"A teacher affects eternity; he can never tell where his influence stops"

Henry Adams

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ABSTRACT

EVALUATION OF REACTIVE CAP SORBENTS FOR *in-situ* REMEDIATION OF CONTAMINATED SEDIMENTS

By

Bhawana Sharma

University of New Hampshire, September 2008

Contaminated sediments can be treated using in-situ treatment methods that aim to either degrade or sequester contaminants, reducing their bioavailability. The main purpose of this research was to develop and evaluate a reactive capping mat that can be used for in-situ remediation of contaminated sediments. This study investigated the interferences caused by humic acid on the adsorption of co-planar and non-co-planar polychlorinated biphenyls (PCBs) including 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 and polycyclic aromatic hydrocarbons (PAHs) including naphthalene, phenanthrene and pyrene on two types of sorbents being evaluated for use in a mat: activated carbon and organoclays. Several kinetic and isotherm studies have been conducted using several formulations of activated carbons and organoclays as sorbents to treat individual PCB congeners and PAHs. The results showed that preloading of sorbents with humic acid, and simultaneous adsorption of humic acid and contaminant, significantly reduced the adsorption capacity for all selected PCB congeners and PAHs. Experiments conducted without preloading of sorbent surfaces demonstrated that desorption upon subsequent spiking with humic acid, to simulate the long-term exposure to porewater that contains high humic acid concentrations, was not pronounced and varied with co-planarity of PCBs and number of rings of PAHs. Also, humic acids were found to interfere to a much greater extent with adsorption to activated carbon than with organoclay formulations evaluated in this work.

Experiments were also conducted to determine the effects of Suwannee River fulvic acid (FA), humic acid (HA) and natural organic matter (NOM) obtained from International Humic Substance Society (IHSS) and pore water isolated from sediment of the Hudson River and the Passaic River to understand the influence of different fractions of dissolve organic carbon that will be present in real site conditions. The results demonstrated enhancement in adsorption of PCB and PAH in presence of fulvic acid on both type of sorbents including activated carbon and organoclay but the effect of humic acid and NOM varied with contaminant. The humic acid had more reducing effect on PCB adsorption as compared to NOM and NOM had more reducing effects on PAH adsorption.

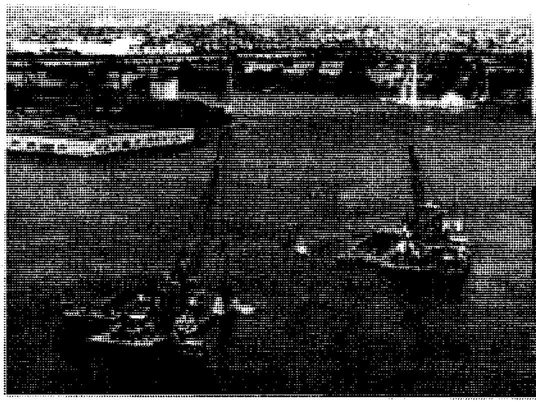
A structural analysis using Scanning Electron Microscopy for activated carbon and X-Ray Diffractometry, Atomic Force Microscopy and Scanning Electron Microscopy for organoclay were conducted to observe differences caused by humic acid on the surfaces of the sorbents. BET surface area analysis has also been conducted to determine the surface area of activated carbon and organoclays. Thermo gravimetric analysis of organoclays was done to determine the % organic content which increases the hydrophobicity and thereby adsorption capacity of organoclays. This research indicate that organic acids, which are quite concentrated in sediment porewater, have a significant impact on the efficacy of reactive cap components and are an essential factor in the design and ultimate performance of this type of in-situ sediment management approach.

CHAPTER 1

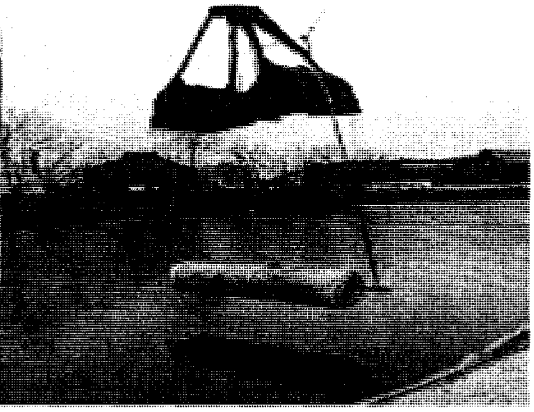
INTRODUCTION

Objectives

In the1990s, the extent and severity of sediment contamination was brought into consideration and the USEPA planned to take actions to reduce the risk posed by contaminated sediments to fish as well as to humans and wildlife. In 1997, the EPA estimated about 10% of sediments (top 5 cm that represents biologically active zone) under national water surfaces to be contaminated with toxic chemicals (USEPA, 1997). This estimate fostered the requirement to set up goals and objectives for remediation of contaminated sediments. According to the EPA the assessment and subsequent actions needed to be based on "sound science" and "site specifications" (USEPA, 1998). Based on the hierarchical approach for the evaluation of treatment methods, first of all source control should be assessed followed by in-situ remediation such as natural recovery or capping technology and finally ex-situ treatment methods such as dredging (wet) or dry excavation (Cushing, 1999).



Dredging



Reactive Core Mat

In dredging technology, sediments are removed from the given site followed by treatment and disposal. Contaminated sediments should not be removed from a site if it is more harmful compared with leaving them in place or using alternative management strategies such as in-situ remediation using capping technology.

Figure 1.1 shows the concentration profile in Cottonwood Bay (Mountain Creek Lake, Dallas, Texas, 1994-97) the field site selected for the deployment of the reactive capping mats deployed in this study. In this figure it is shown that the concentration of contaminants first increases with the increase in depth and then decreases with further increase in depth. Also, it was also observed in the M2.40 core that the concentration of cesium-137 was highest around 45 cm, for DDT the first peak was observed from 30 – 50 cm and second DDT peak was observed around 65 cm and for Dieldrin first peak around 50 cm and second around 65 cm. In the MCL-4 core the concentration of DDT was found to be high from 20-80 cm depth.

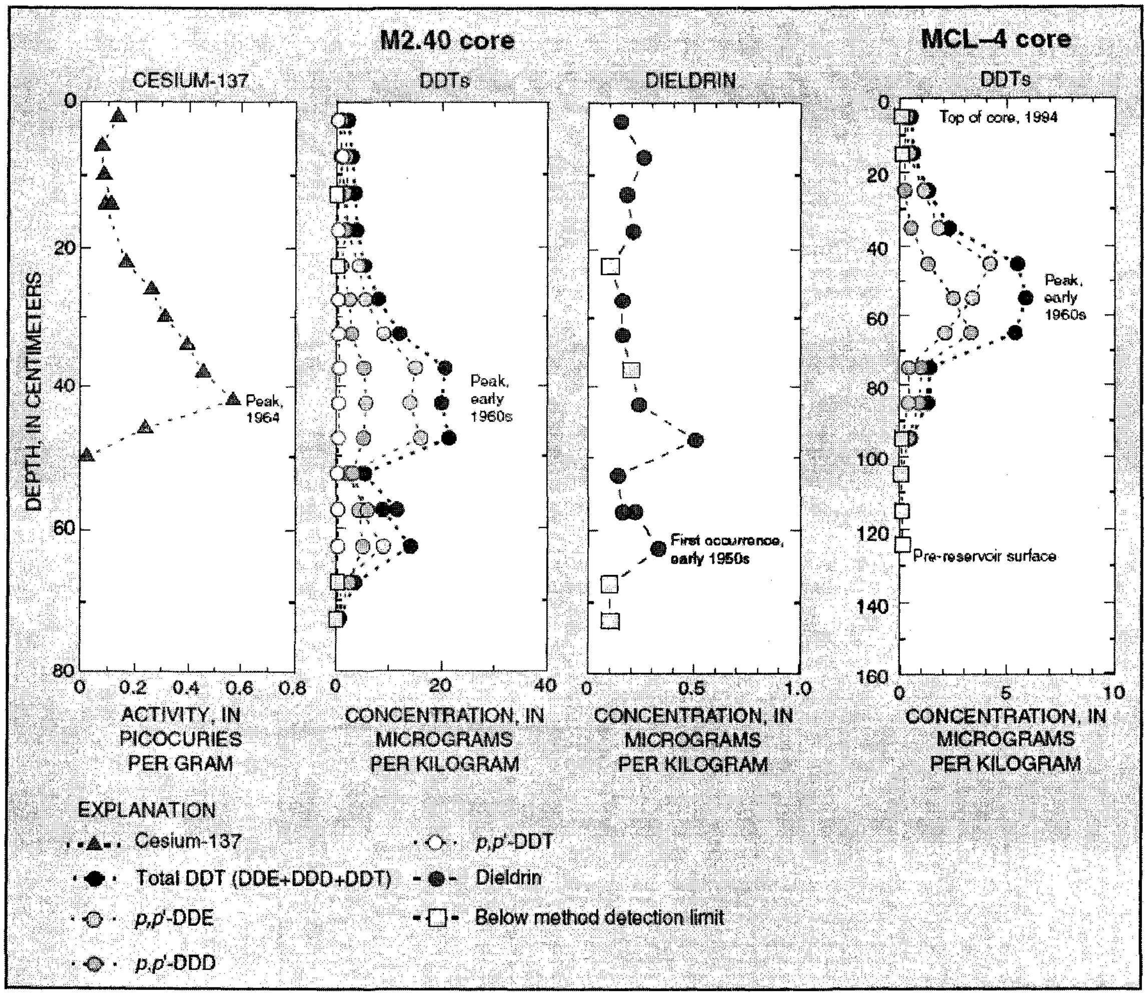


Figure 1.1 Contaminant Concentration Profile in Study Field Site

(Source: USGS, Water-Resource Investigations Report 03-4082)

This shows that the concentration profile of different contaminants can vary with depth. Therefore, dredging of the top layer might expose the higher concentrations of the contaminant present at that depth in the sediments. These types of sites should be either dredged deep enough to remove high concentrations of all contaminants of concern, which can be very expensive, or alternative technology should be used such as reactive capping technology.

The contaminant flux from sediments to overlying water is governed by various processes including bioturbation, mechanical scouring, uprooting of macrophytes in addition to the pore water flux by diffusion and advection. Therefore, the goal of this research is focused on development of a reactive capping mat, containing sorbent amendment mixture, which 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 in-situ remediation process for contaminated sediments requires understanding of the influence of high concentrations of background natural organic acids, like humic acids, that influence the efficacy of treatment and fate of organic contaminants. To get a better understanding of the entirety of the process and improved quality of the reactive capping mat, six sigma analyses which includes DMAIC (i.e. Define, Measure, Improve, Analyze and Control), was used as a helpful tool. When the project was at the definition phase the SIPOC model (i.e. Suppliers, Inputs, Process, Outputs, and Customers) was developed to achieve the goal of defining quality, characteristics and identification of factors or variables which may impact the process (Figure 1.2). During experimentation the random factors such as presence of natural organic matter were considered to be a major factor of the design in order to estimate the actual performance of the sorbents that could be observed after deployment of the reactive caps in the real site conditions.

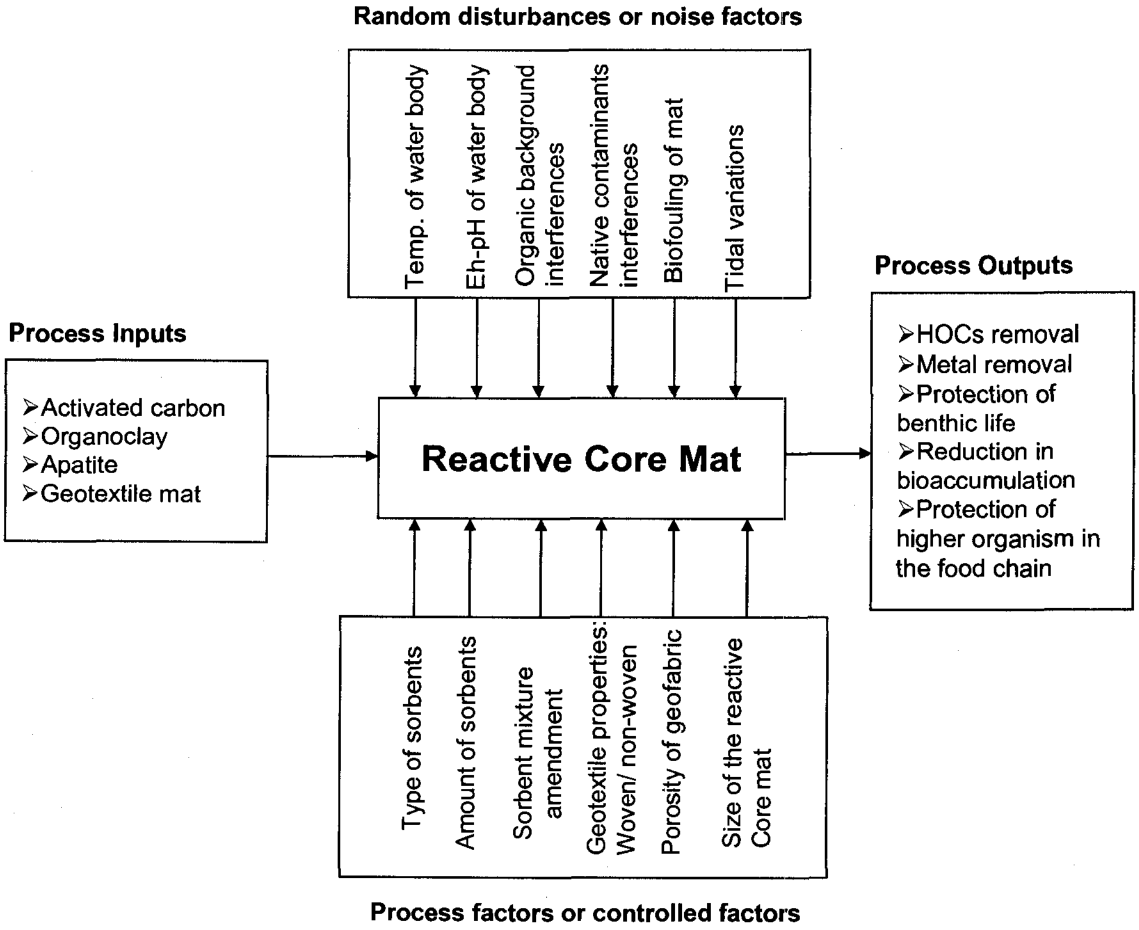


Figure 1.2: SIPOC Model for Reactive Core Mat

In this study the performance of different formulations of activated carbon and organoclay were evaluated in the presence and absence of natural organic matter for sequestration of persistent hydrophobic organic contaminants. The effect of natural organic matter, which is ubiquitous in nature and is important in governing the fate and transport of hydrophobic organic contaminants, on the efficacy of the sorbents was immensely studied in the form of various fractions such as humic acid and fulvic acid and natural organic matter (as a whole) in the colloidal and non-colloidal form.

Dissertation Organization

This dissertation has been organized in the form of a compilation of papers. The effect of humic acid on the performance of activated carbon for PCB sequestration (chapter 2), different formulations of organoclay on PCB sequestration (chapter 3), PAH adsorption on activated carbon and organoclay (chapter 4) and the effect of different fractions of natural organic matter on activated carbon and organoclay (chapter 5) have been discussed in detail.

Chapter 2 focuses on the interferences caused by humic acid on the adsorption capacity of coconut shell and coal based activated carbon for co-planar and non-coplanar PCBs. In this chapter results have been produced from kinetics studies to demonstrate the effects of humic acid on the adsorption kinetics of PCBs and isotherm studies to show the effect on the adsorption capacity of activated carbon due to preloading with humic acid. Scanning electron micrographs were produced to show the differences in the porous structure of coal based and coconut shell based activated carbon and to show the pore blockage effect caused by preloading activated carbon with high concentrations of humic acid.

Findings: The results showed that preloading of activated carbon with humic acid significantly reduced the adsorption capacity for all selected PCB congeners. Experiments conducted without preloading of activated carbon demonstrated that desorption upon subsequent spiking with humic acid was not found to be statistically significant and varied with co-planarity of PCBs. Slight desorption was found for non-coplanar tetrachlorobiphenyl as compared to the mono-chloro-congener and the co-planar tetra-and hexa-congeners which did not show any observable desorption. Desorption was found to be observable in the case of non-coplanar hexachlorobiphenyl but the phenomenon was found to be insignificant statistically.

Chapter 3 discusses the performance of three different formulations of organoclays, which have different base clay and organic cations, for adsorption of co-planar and non-coplanar PCBs in the presence and absence of humic acid. This chapter was focused on adsorption of organic contaminants on organoclay and the effect of humic acid on the adsorption of PCBs onto organoclay. Chapter 3 demonstrates the kinetics of adsorption of PCB on two different formulations of organoclay and isotherm studies to show effect of humic acid on adsorption capacity of organoclays for PCB congeners.

Findings: Studies showed a significant reduction in the performance of organoclays due to preloading with high concentrations of humic acid for all selected PCB congeners. The reduction in sorption affinity due to preloading ranged from 46 % to 96% depending on the congener and the composition of organoclay. Desorption studies that were conducted to simulate the long-term exposure to high humic acid concentrations in the sediment pore water (in typical site conditions) also showed effects that were less pronounced compared to preloading effect and varied with the composition of organoclay and PCB congener. No desorption was noticed in case of 2-

chlorobiphenyl adsorption on CETCO and Biomin Inc. organoclay but significant desorption was observed in the case of Polymer Ventures organoclay that had different base clay as compared to CETCO and Biomin Inc. that had same base clays. Desorption effect on adsorption of 2, 2', 5, 5'-tPCB was found to be similar for CETCO and Polymer Ventures organoclay. The statistical analysis done to evaluate the performance of CETCO organoclay for tetra- and hexa- chlorobiphenyl showed preloading effect to be more pronounced in case of co-planar congeners compared to their non-coplanar isomers and desorption effects were not substantial in any case.

Chapter 4 compares the performance of activated carbon and organoclay for PAH adsorption in the presence and absence of humic acid. This chapter illustrates the effect of humic acid on adsorption of small ringed PAHs that are readily transported in sediment pore water. Chapter 4 explains the effect of humic acid on the kinetics of PAH adsorption on activated carbon and organoclay and shows the effect of preloading the sorbent with high concentration of humic acid on selected PAHs.

Findings: The performance of bare organoclay was found to be better for naphthalene and pyrene compared to activated carbon. The preloading effect was found to be significant for both the sorbents for phenanthrene and pyrene though there was negligible effect on naphthalene adsorption. Desorption effects were not found to be significant for naphthalene for both the sorbents but it was statistically significant for phenanthrene and pyrene adsorption on organoclay. This shows that if these sorbents are exposed to very high concentrations of natural organics such as 1g L^{-1} (as in the case of this study) then it can affect the performance of the reactive core mat. Also, long term exposure of organoclay to natural organic matter might affect the performance by desorption depending on the sorption pattern of target compounds and their partition coefficients for humic acid.

Chapter 5 illustrates the effect of different fractions of natural organic matter (that plays a significant role in fate and transport of hydrophobic organic contaminants) on the adsorption of PCB and PAH on activated carbon and organoclay. This chapter also demonstrates the effect of colloidal and non-colloidal pore water on the performance of sorbents. Chapter 5 also discusses the effect of natural organic matter present in Cottonwood Bay, Texas (study field site) on the performance of the sorbent mixture that was present in the reactive core mats deployed in the field for six months.

Findings: Results showed a significant effect of Aldrich humic acid on 2, 2', 5', 5'-tetrachlorobiphenyl adsorption on both the sorbents. There was a slight enhancement of the adsorption capacity of organoclay for 2, 2', 5', 5'-tetrachlorobiphenyl in the presence of Suwannee River fulvic acid but no effect was observed for activated carbon. There was no effect of Suwannee River NOM on 2, 2', 5', 5'-tetrachlorobiphenyl adsorption on both the sorbents. In the case of phenanthrene adsorption, no effect of any fraction of natural organics was noticed for organoclay. In the case of activated carbon the effects of Aldrich humic acid, Suwannee River humic acid, Suwannee River fulvic acid and Suwannee River NOM were found to have similar reducing effect. A significant effect of Hudson River porewater (high aquatic humics) was observed on the performance of both the sorbents for both the contaminants, although only a small effect was found for the Passaic porewater (which was low in humics).

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CHAPTER 2

EVALUATION OF COCONUT SHELL ACTIVATED CARBON AS A REACTIVE CAP SORBENT FOR SEQUESTRATION OF PCBS IN PRESENCE OF HUMIC ACID

Abstract

This study investigated the interferences caused by humic acid on the adsorption of co-planar and non-coplanar polychlorinated biphenyls on activated carbon. Kinetic and equilibrium studies were conducted using activated carbon as a sorbent for individual PCB congeners including 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) in the presence and absence of humic acid. The results showed that preloading of activated carbon with humic acid significantly reduced the adsorption capacity 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 co-planarity of PCBs. Analysis of surface properties using Scanning Electron Microscopy demonstrated observable pore blockage caused by humic acid on the surfaces of the activated carbon.

Introduction

Sediments 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 attenuation and capping technologies. To date monitored natural attenuation and sand caps have been used as an in-situ treatment method and now reactive capping is gaining attention for its potential effective use. Reactive capping can be accomplished both by mixing reactive material into a sediment bed (Zimmerman et al. 2004; Werner et al. 2005) or by binding the reactive material into a geotextile and deploying it over a contaminated sediment bed (Mc Donough et al. 2008). There is substantial information available for adsorption of aromatic compounds (Zimmerman et al. 2004; Walters et al. 1984; and Cornelissen et al. 2006) and chlorinated compounds (Sotelo et al. 2002; and Karanfil et al. 1999) on activated carbon. Zimmerman et al. (2004) have shown a 92% reduction in polychlorinated biphenyl (PCBs) aqueous concentration and 84% reduction in polycyclic aromatic hydrocarbon (PAHs) aqueous concentrations 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 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 one month to six months (Werner et al. 2005; and Millward 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; and Matsui et al. 2003). The objective of this study was to evaluate the adsorption capacity of coconut shell activated carbon for PCBs in the presence of humic acid in order 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, which can occur at very high concentrations in sediment pore water. The concentration of dissolved organic carbon (DOC) in sediment pore water has been reported to be as high as 200 -2500 μM (0.6 g/L to 7.5 g/L) for the upper ~ 20-30 cm of sediments (Burgie et al. 2001).

The reduction in adsorption capacity 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 (Li et al. 2003; and Newcombe et al. 2002). 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 (Quinlivan et al. 2005; Newcombe et al. 2002; and Newcombe et al. 1997). Taking this into consideration, coconut shell activated carbon was selected for this study. McDonough et al. (2008) have studied the performance of coal based activated carbon in the presence of simulated pore water at 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 the pore water flux by diffusion and advection (Butcher et al. 2004). Therefore, the goal of this research is focused on development of reactive capping mat (containing a sorbent amendment mixture) or in general 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

Ultra high purity chemicals and GC-grade solvents including hexane, methanol and acetone were used for all experiments and were obtained from Fischer Scientific

(Agawam, MA, USA). The five PCB congeners were selected for this research on the basis of number of chlorine atoms and co-planarity 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 surrogate standard. These PCB congeners and TCMX were purchased (Ultra scientific, North Kingstown, RI, USA) either in neat form or dissolved in hexane. Humic acid sodium salt (Sigma-Aldrich, St. Louis, MO, USA) was used as a representative natural organic matter. Aldrich humic acid was used in this study in order 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, USA) was used as bactericide to avoid biological growth in the experiments and sodium sulfate anhydrous (Fisher Scientific, Morris Plains, NJ, USA) was used in preparatory step for GC analysis of samples.

Activated carbon: The sorbent used in this study was coconut shell activated carbon, OLC 12 x 40 (Calgon Carbon Corporation, Pittsburg, PA, USA). This material was selected because it is widely used for removal of trace organic compounds and it has high microporosity (Figure 2.1). Table 2.1 shows the properties of the material. Coal based Calgon F400 was also used for some of the studies to compare the performance of these two activated carbons.

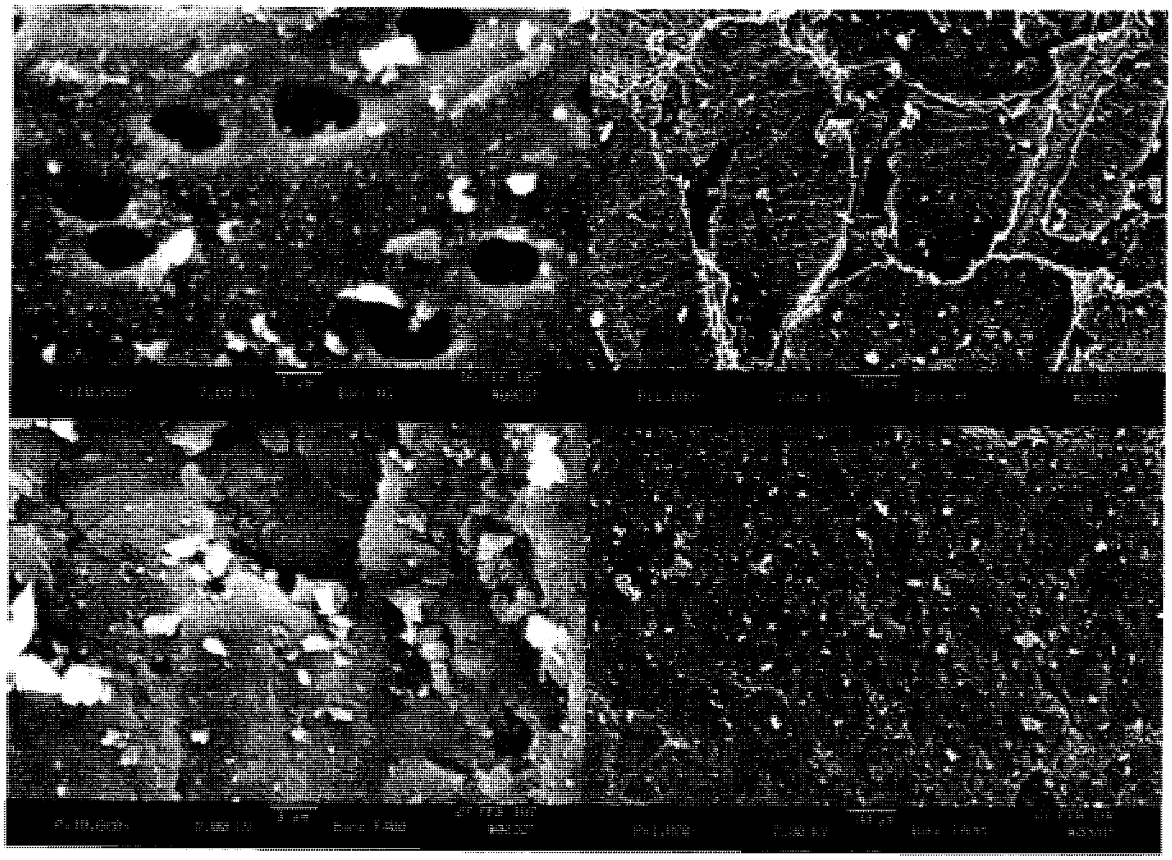


Figure 2.1: Comparative SEM image for coconut shell AC (top two images) and coal based AC (bottom two images).

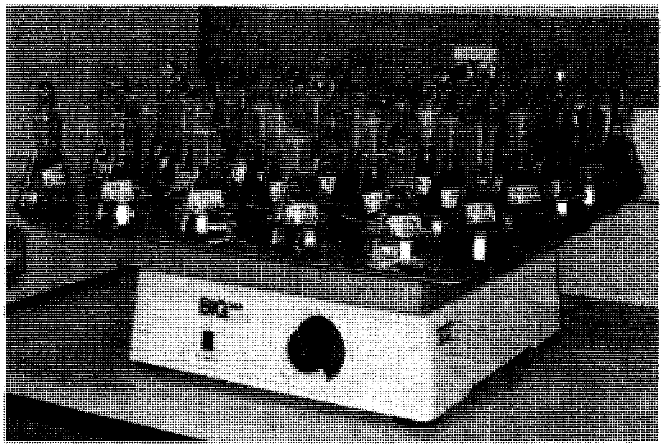
Table 2.1 shows the properties of the material. Coal based Calgon F400 was also used for some of the studies to compare the performance of these two activated carbons.

Table2.1. Typical Properties of Coconut Shell Activated Carbon:

Particle size [ASTM D-2862]*	12 x 40 US Mesh
Ash Content (Base Material)[ASTM D-2866]*	3% w/w
Bulk Density [ASTM D-2854]*	0.50 g/ cm^3
Iodine Number [BSC 90-032]*	1050 mg/g
BET Surface Area of Bare AC	872.05 m^2/ g

Batch Experiments

Batch experimentation method was used to determine the kinetics of PCB adsorption on activated carbon and to determine the adsorption capacity 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 et al. 1981). For quality assurance purpose duplicates were prepared in all the experiments (error bars in each plot represent standard deviation between duplicates) 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 in two ways: Preloading effect and Desorption effect.



Preloading of Activated Carbon: The preloading of activated carbon for kinetics and isotherm experiments was done with 1g/L of humic acid solution prepared in de-ionized (DI) water. A 10% sodium azide was added to the humic acid stock solution to avoid biological growth. All the samples were equilibrated for 48 hours at 150 rpm on a rotary shaker to ensure thorough mixing. 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.

SEM sample preparation: Scanning electron micrographs were obtained for bare activated carbon and activated carbon preloaded with humic acid. The preloaded samples were prepared with 0.1 and 1 g/L humic acid solution containing 10% sodium azide. In case of the lower loading of humic acid no effect was found as compared to the higher (1g/L) loading of humic acid (Figure 2.2). This also confirmed that in case of 1 g/L humic acid pores are blocked not due to sodium azide but due to high concentration of humic acid (Figure 2.2).

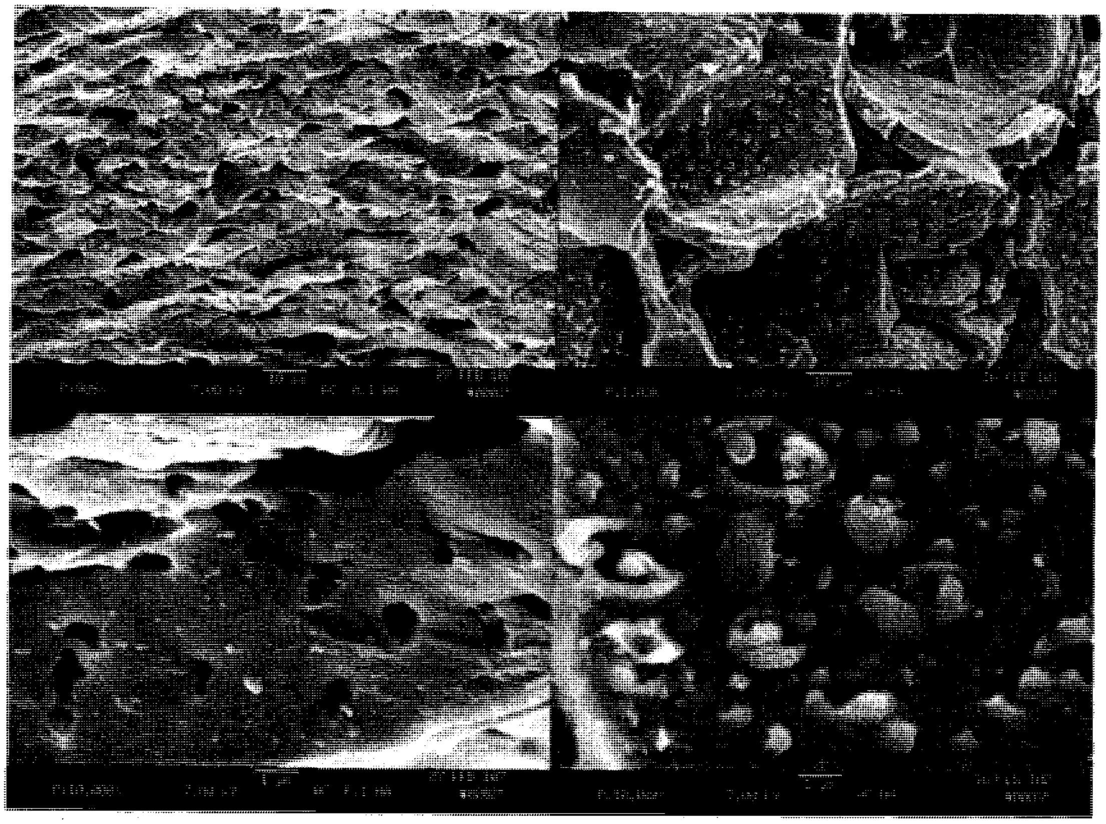


Figure 2.2: Comparative SEM image for coconut shell AC preloaded with 0.1 g/L humic acid solution (upper and bottom left) and coconut shell AC preloaded with 1 g/L (upper and bottom right).

Kinetic Studies

Batch experiments were conducted for the duration of one 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 humic acid solution as 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^{-1} for 2-chlorobiphenyl, 5 mg L^{-1} for 2, 2', 5, 5'-tetrachlorobiphneyl and 0.08 mg L^{-1} 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 2.2) and activated carbon preloaded with humic acid to obtain adsorption isotherms. The preloading time and procedure was the same as performed for the kinetics studies (above). As mentioned earlier in preloaded samples humic acid was present in two forms (i) humic acid adsorbed on activated carbon due to preloading (ii) humic acid in dissolved form in DI water matrix. These studies were conducted for the equilibration time of 72 hours which represents a reasonable approximation of equilibrium as shown by the kinetics experiments for bare activated carbon. 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.

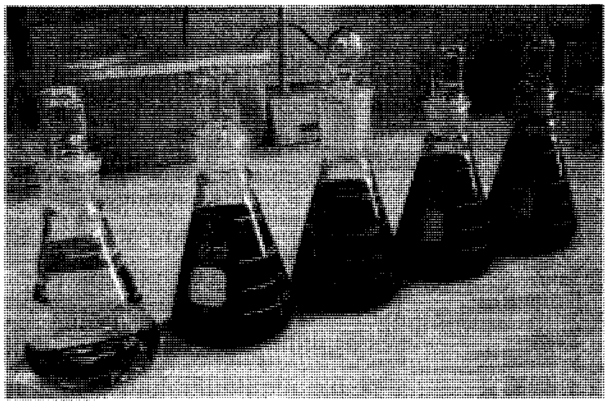
Table 2.2: Solubility limit, Log Octanol-water partition coefficients and Log K_{DOC} values of selected PCB congeners

PCB congener	† Solubility Limit in water (ppm)	† Log K_{OW}	Log K_{DOC}	Isotherm Studies Concentration Range (mg/L)
2-cbp	4.0	4.7	3.63*	0.008 – 6.108
2,2',5,5'- tPCB	0.26	5.9	4.6 **	0.008 – 0.400
3,3',4,4'- tPCB	0.26	5.9	-	0.008 – 0.800
2,2',4,4',5,5'- hPCB	0.038	6.7	5.3**	0.032 – 0.800
3,3',4,4',5,5'- hPCB	0.038	6.7	-	0.024 – 0.800

* Butcher et al. 2004; ** Poerschmann et al. 1999; † Erickson, 1997

Desorption studies: These studies were conducted to simulate the long term exposure of reactive cap sorbents to natural organic matter that can occur in site conditions. Once sampling was completed at 72 hours, 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 hours of mixing prior to the sampling.

Determination of HA Effects



Batch experiments were conducted to obtain the adsorption behavior of 2-chlorobiphenyl, 2, 2', 5, 5'-tetrachlorobiphenyl and 2, 2', 4, 4', 5, 5'-hexachlorobiphenyl at different loadings of humic acid. These experiments were conducted at fixed loading of PCB with varied loading rates of humic acid with respect to activated carbon. The activated carbon was preloaded with different loading rates of humic acid for 48 hours prior to the spiking of PCB. These experiments were also allowed to equilibrate for 72 hours. Experiments were also conducted to determine the effect of different loadings of humic acid on coal based activated carbon for adsorption of 2, 2', 5, 5'-tetrachlorobiphenyl.

Sample Extraction and Analysis

The supernatant of each sample was extracted into hexane using TCMX as a surrogate standard by vial liquid-liquid extraction method. Twenty ml of sample and ten ml of hexane was taken into a 40 ml vial. The vials were sealed with Teflon® lined screw caps and shaken vigorously for 30 seconds three times at intervals of 30 seconds each. The vials were then stored for at least for 24 hours at 4° C. The surrogate recoveries by using this extraction method were found to be in the range of 70-130%. The extracts were then passed through sodium sulfate to remove any chemically bound water prior to running on GC columns. The GC vials were prepared using these filtered solvents and an internal standard.

Gas Chromatography/ Mass Spectrometry Analysis

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-5ms), 30 m long, 0.25 mm ID and 0.5 μm 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 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 held time of 2 minutes.

Results and discussions

Kinetic studies:

Experiments were conducted to obtain the equilibration time required for adsorption of PCBs on activated carbon. Figure 2.3 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 (Figure 2.3-A) indicated equilibrium was reached at approximately 72 hours 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. Smaller compounds like 2-chlorobiphenyl that have higher diffusivity (Schaffner et al., 1997) can more rapidly enter micropores which sieve the larger humic acid molecules. Equilibrium was reached at approximately 72 hours for 2, 2', 5, 5'-tetrachlorobiphenyl and 50 hours for 2, 2', 4, 4', 5, 5'-hexachlorobiphenyl adsorption on bare activated carbon and activated carbon preloaded with humic acid (Fig. 2.3 B-C). The preloading effect was significant for tetrachlorobiphenyl and was found to gradually decrease with time but remained significant for the duration of the experiment.

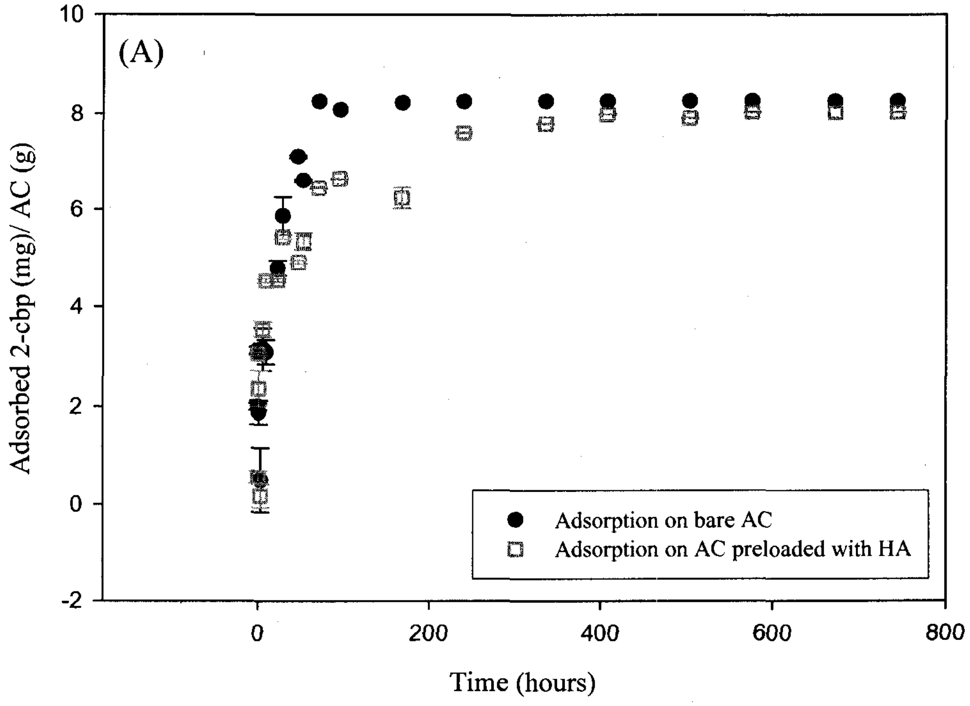
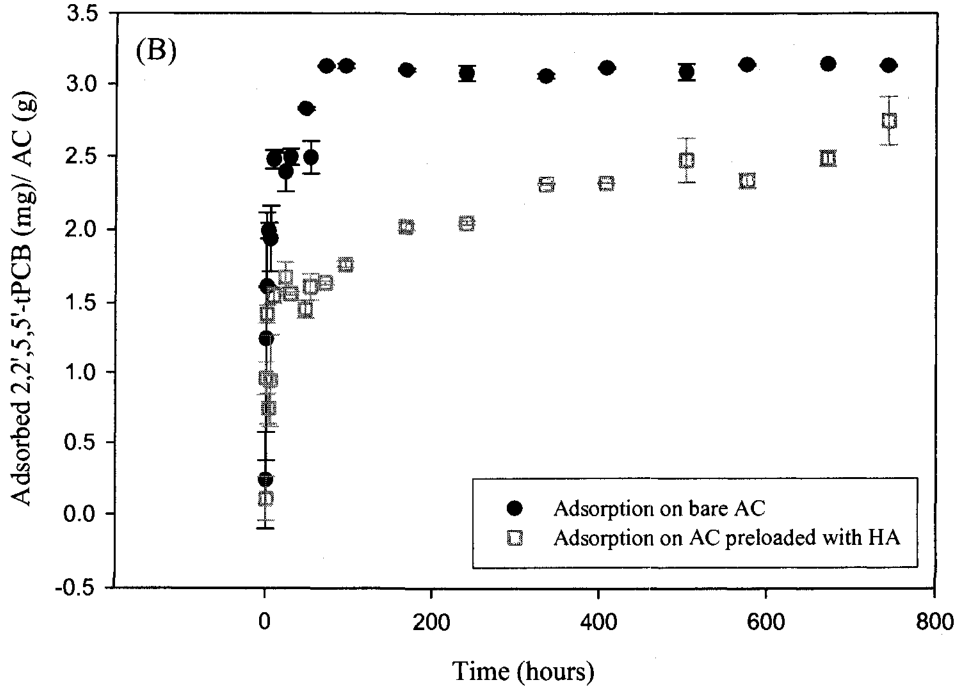


Figure 2.3 A: Kinetics of adsorption of PCB congeners on coconut shell AC in presence and absence of HA: 2-chlorobiphenyl



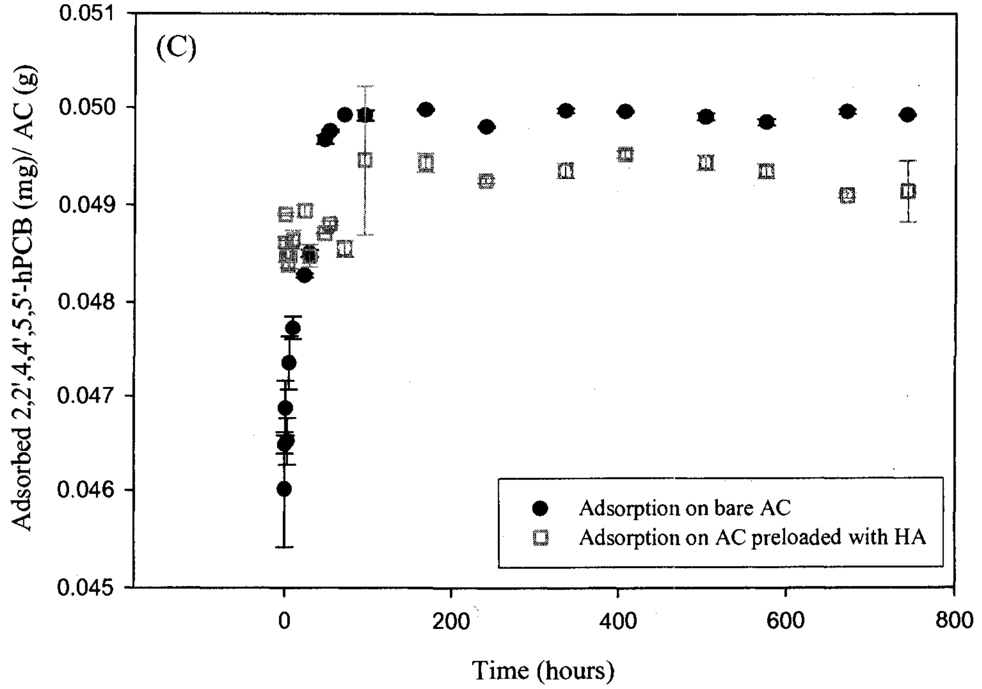


Figure 2.3: Kinetics of adsorption of PCB congeners on coconut shell AC in presence and absence of HA: (B) 2, 2', 5, 5'-tetrachlorobiphenyl and (C) 2, 2', 4, 4', 5, 5'-hexachlorobiphenyl.

The effect of preloading on hexachlorobiphenyl was found to be very low (due to very low concentration of hexa-chloro biphenyl used in the experiment) and remained consistent with time. This study showed that preloading of activated carbon with humic acid appeared to increase the time required to reach equilibrium. These retardation effects could be due to the pore blockage effect and more complexation of highly chlorinated congeners to humic acid as compared to mono-chloro-congener. Greater complexation with humic acid is expected from more highly chlorinated congeners as shown by K_{DOC} complexation constants reported in table 2.2, which increase with the increase in hydrophobicity of the compound (Pirbazari et al. 1989).

Kinetics was important to characterize not only for the conduct of equilibrium 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 that 24 hours.

Isotherm studies:

Isotherm studies were conducted to determine the adsorption capacity of 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 co-planarity 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 amount of adsorbed (mg g^{-1}), K_F is the Freundlich Isotherm constant, C_e is the equilibrium concentration (mg L^{-1}) and $1/n$ is the dimensionless Freundlich exponent. Figure 2.4 shows data and Freundlich adsorption isotherms for all above mentioned PCB congeners in the presence and absence of humic acid. The humic acid interferences were obtained as: (i) preloading effect of humic acid on activated carbon and (ii) desorption effect in which activated carbon was spiked with humic acid after PCB adsorption to simulate the long term exposure to pore water humic acid concentrations.

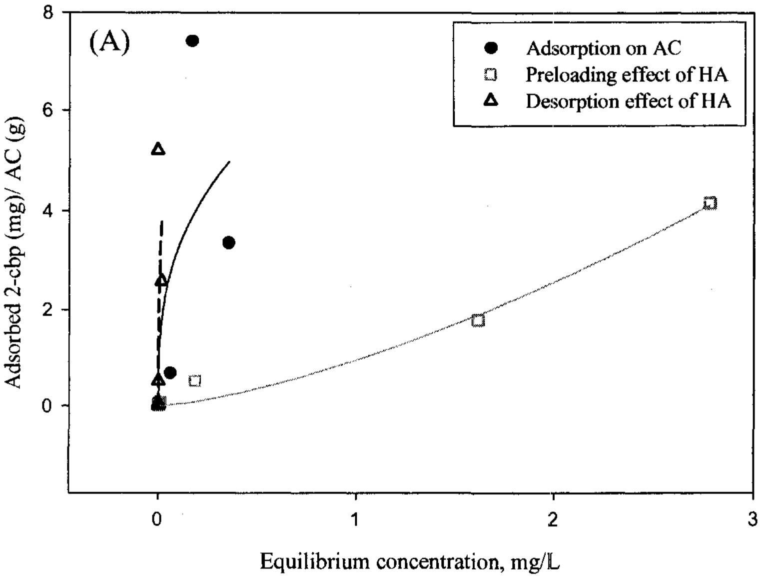
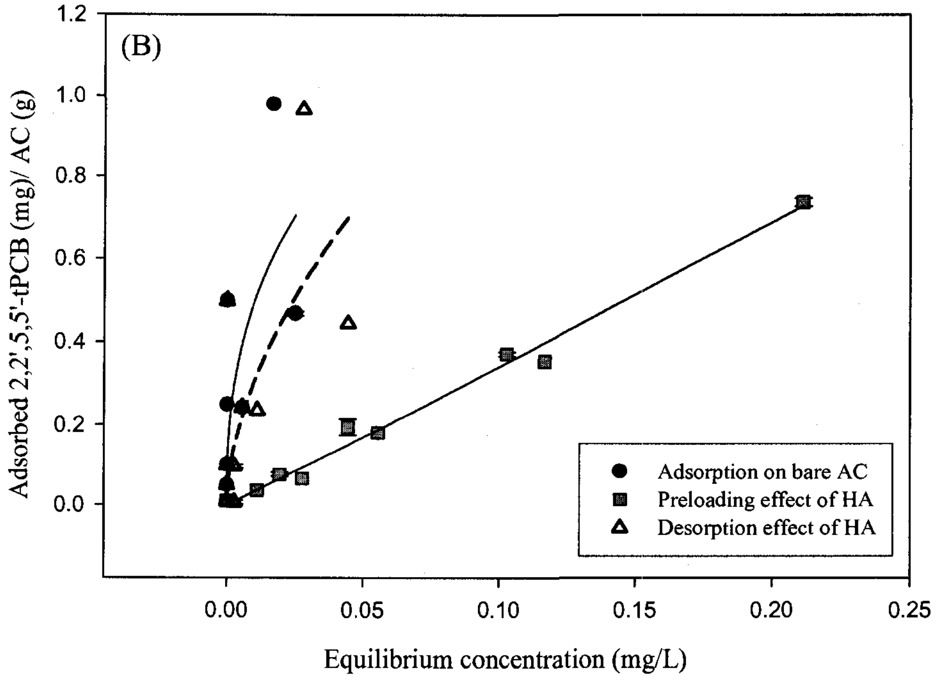


Figure2.4 A. Freundlich Adsorption Isotherms for selected PCB congeners with bare AC and preloading and desorption effect of HA: 2-chlorobiphenyl



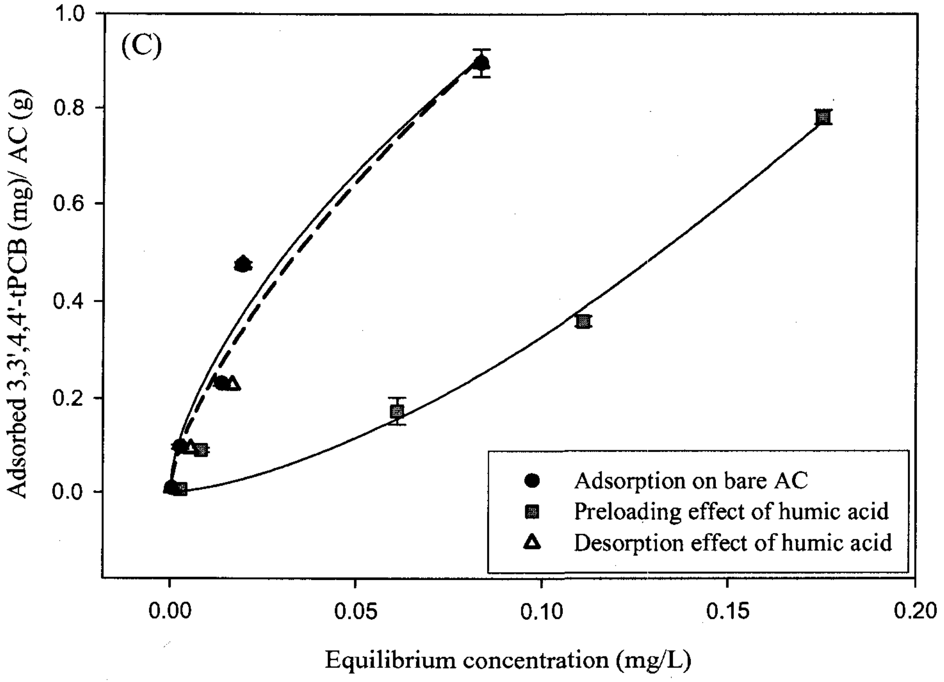
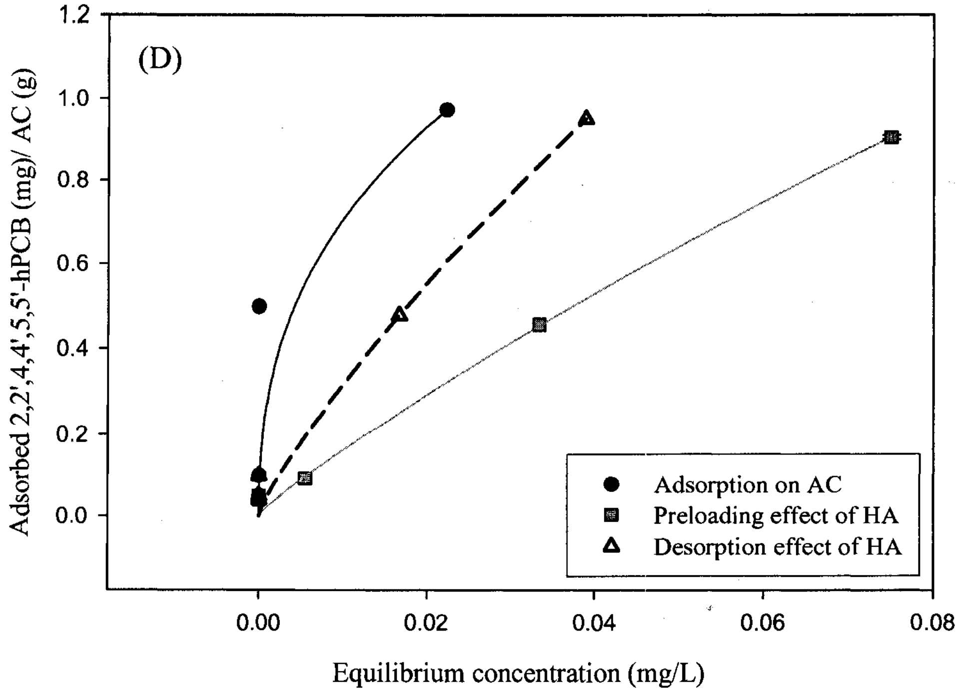


Figure 2.4 B - C. Freundlich Adsorption Isotherms for selected PCB congeners with bare AC and preloading and desorption effect of HA: (B) 2, 2', 5, 5'-tPCB (C) 3, 3', 4, 4'-tPCB



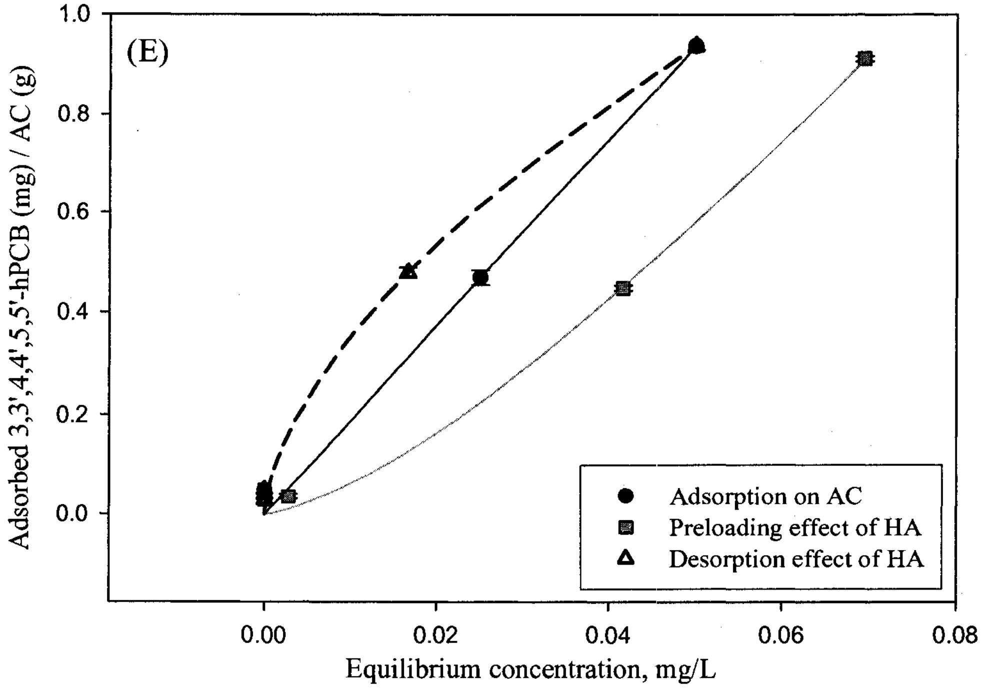


Figure 2.4 D - E. Freundlich Adsorption Isotherms for selected PCB congeners with bare AC and preloading and desorption effect of HA: (D) 2,2',4,4',5,5'-hPCB (E) 3,3',4,4',5,5'-hPCB

In all of the isotherms, a significant reduction in adsorption capacity of activated carbon was found in the presence of humic acid as shown in figure 2.4. 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 (Pignatello et al. 2006; and Li et al. 2003) and the hydrophobic partitioning of HOCs to dissolved humic acid (Poerschmann et al. 1999). When activated carbon is preloaded with humic acid, the larger humic acid molecules that cannot enter the micro- and mesopores block the pore channels by clump formations (Pignatello et al. 2006). These types of formations due to preloading of activated carbon by humic acid molecules were observable in scanning electron micrographs (SEM) as shown in figure 2.2. The studies conducted to evaluate desorption effects of humic acid showed that once PCBs were adsorbed on activated carbon there is negligible desorption that varied with the co-planarity of the congener. Slight desorption was found for non-coplanar tetrachlorobiphenyl (Figure 2.4 B) as compared to the mono-chloro-congener (Figure 2.4A) and the co-planar tetra-and hexa-congeners (Fig. 2.4 C & E) which did not show any observable desorption. Desorption was found to be observable in the case of non-coplanar hexachlorobiphenyl in figure 2.4 D but the phenomenon was found to be insignificant statistically (Figure 2.5). This slight variation in desorption effect between co-planar and non-coplanar PCBs can be explained by the steric hindrances in the non-coplanar configuration which decrease sorption affinity (Cornelissen et al. 2004).

The data obtained from the isotherm studies was analyzed statistically using software JMP® 7. A model was developed on the Fit model platform to evaluate the performance of activated carbon for tetra- and hexa-chlorobiphenyls. The model 1 was developed based on the hypothesis that performance of coconut shell activated carbon varies with the degree of chlorination of the congener and the co-planarity of the congeners in the presence of humic acid (table 2.3). The three factors considered in this model were: PCB congener, loading rate and treatment (preloading/desorption effects). The full factorial design was developed with these three factors along with the quadratic term of loading rate.

Table 2.3: Specifications for Statistical Model 1

Model 1 specification
PCB congener
Loading Rate
Treatment on AC
PCB congener*Treatment on AC
PCB congener* Loading Rate
Treatment on AC* Loading Rate
PCB congener*Treatment on AC* Loading Rate
Loading I* Loading Rate
Loading I* Loading Rate *PCB congener
Loading I* Loading Rate *Treatment on AC
Loading I* Loading Rate *Treatment on AC*PCB congener

According to analysis of variance (ANOVA) the p-value was < 0.0001, therefore, the model is significant and there is a significant effect of the number of chlorine atoms and co-planarity of congeners on adsorption capacity of coconut shell activated carbon in presence of humic acid (details in additional information). F-test was performed on each term (main effects and interaction terms) of the model to determine the significance of the factors based on the p-value < 0.05. The Student's t was obtained to compare the adsorption affinities of all PCB congeners at $\alpha = 0.05$ and showed higher adsorption for hexa-chlorobiphenyls compared to tetra-chlorobiphenyls (table 2.4).

Table 2.4: LS Means Differences Student's t

Alpha = 0.050 t = 2.0639			
PCB congener	Levels *		Least Square Means
2,2',4,4',5,5'- hPCB	A		0.2934
3,3',4,4', 5, 5'- hPCB	B		0.2837
2, 2', 5, 5' - tPCB		C	0.2654
3,3',4,4'-tPCB		C	0.2653

* Levels not connected by same letter are significantly different

The least square means of all PCB congeners were plotted against the treatment effects (preloading/ desorption effect) and it was found that the desorption effect of humic acid was not significant in the case of co-planar (tetra- and hexa- congeners) and both hexa-chloro-congeners. The preloading effect of humic acid was found to be significant for all the congeners (Figure 2.5).

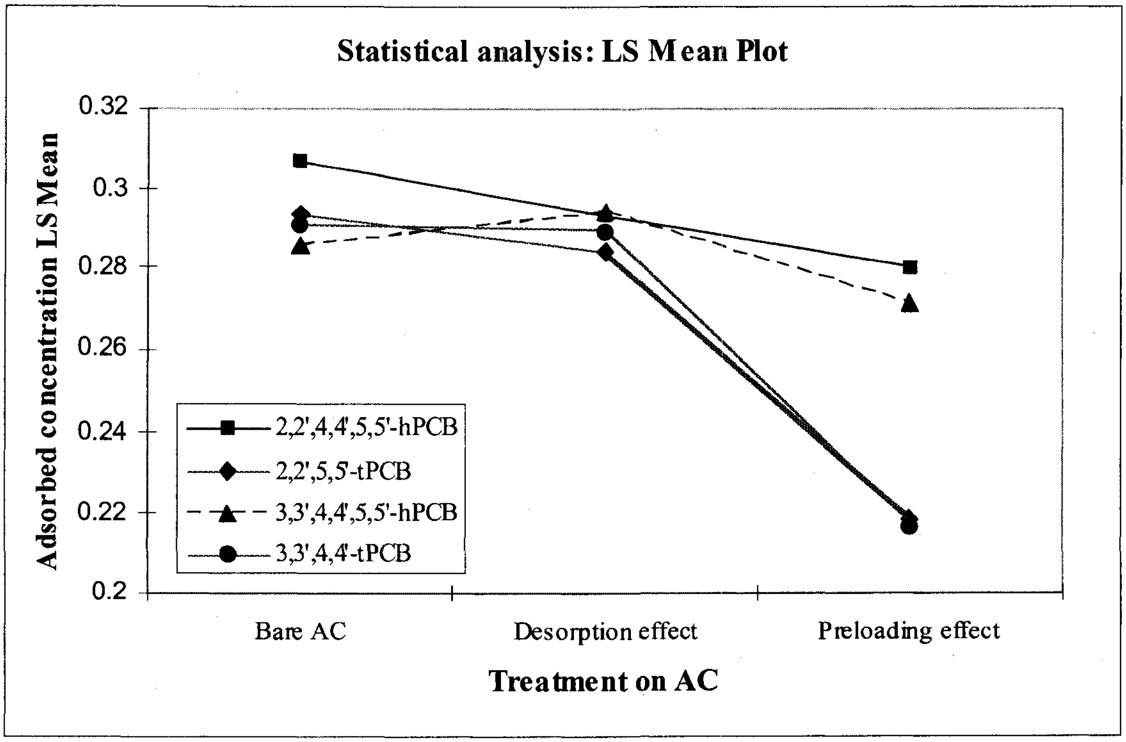


Figure 2.5: LS Mean Plot to determine the effects of AC treatments on PCB adsorption

The coconut shell based activated carbon has a distinctly different pore structure than the coal based activated carbon. The coal based activated carbon has a less porous structure compared to that of coconut shell activated carbon which can be seen in comparative SEM images for both types of activated carbon (Figure 2.1). However, when both carbon types were preloaded with humic acid, their performance was found to be similar (Figure 2.6). Model 2 was developed on JMP ® 7 to determine the performance of both types of carbon in presence of humic acid (table 2.5). The statistical analysis of data also confirmed that humic acid has similar effects on both types of carbons (Figure 2.7).

Table 2.5: Specifications for Statistical Model 2

Model 2 specification:
Type of AC
Treatment
Type of AC*Treatment
Loading rate
Type of AC*Loading rate
Treatment*Loading rate
Type of AC*Treatment*Loading rate
Loading rate*Loading rate

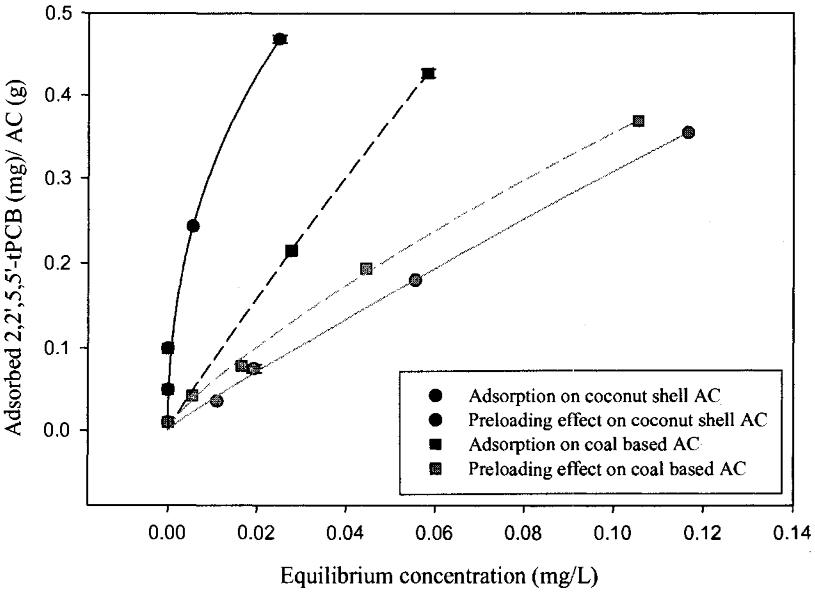


Figure 2.6: Comparative Isotherms for Coal Based and Coconut Shell based AC for 2, 2', 5, 5'- tetrachlorobiphenyl

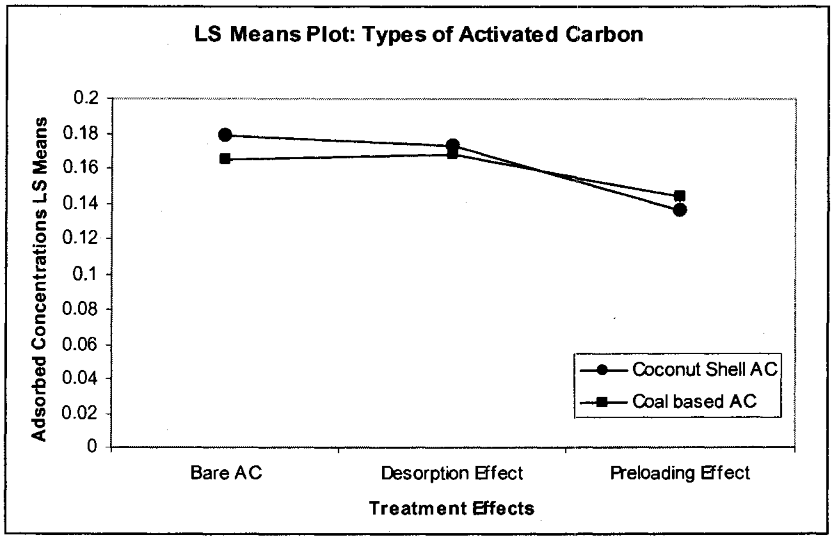


Figure 2.7: Least Square Means plot: Preloading effect of humic acid on coconut shell activated carbon and coal based activated carbon

Experiments were also conducted to determine the effect of humic acid on the adsorption capacity of both types of activated carbon at different loadings of humic acid and fixed loading of PCBs. The results for all three congeners (mono-chloro, tetrachloro- and hexa-chloro) showed that the adsorption capacity of coconut shell activated carbon decreased with the increase in humic acid concentration (Figure 2.8).

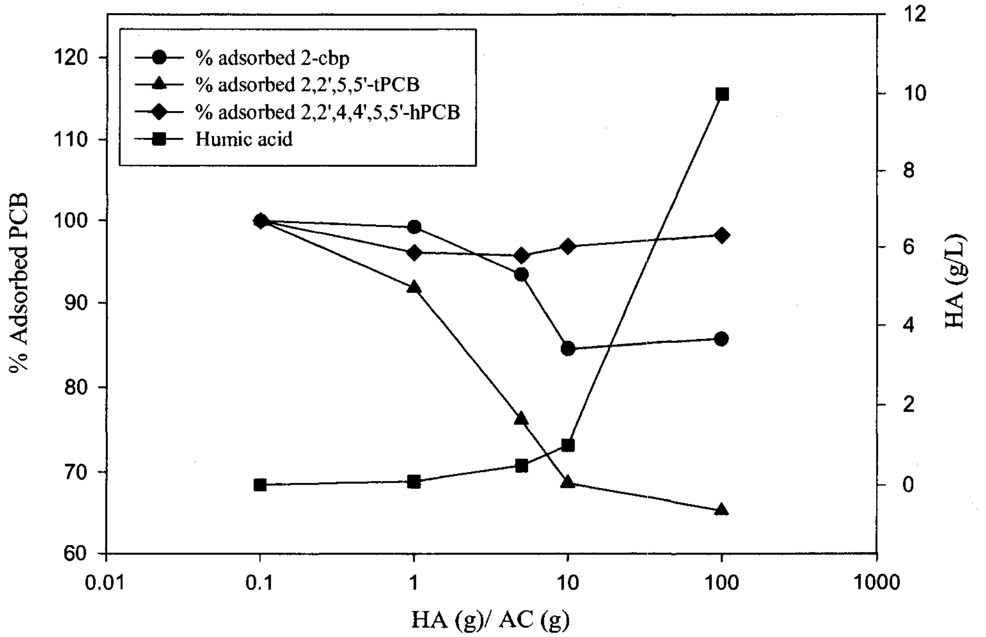


Figure 2.8: Effect of different loadings of HA on adsorption of 2-chlorobiphenyl; 2, 2', 5, 5'-tPCB and 2, 2', 4, 4', 5, 5'-hPCB

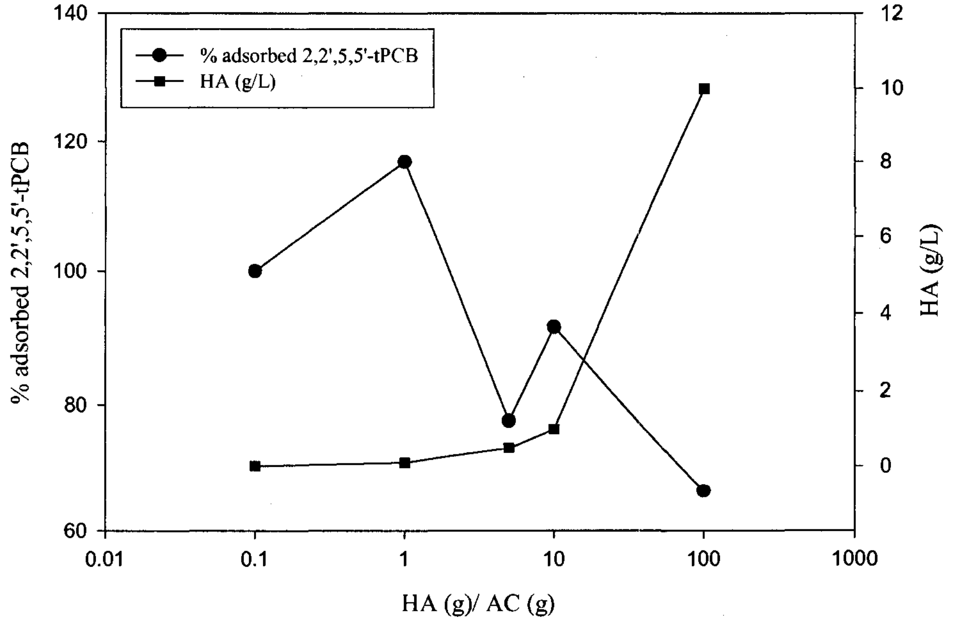


Figure 2.9: Effect of different loadings of HA on coal based activated carbon

The effects were found to be least in case of hexa-chlorobiphenyl followed by mono-chlorobiphenyl and then tetra-chlorobiphenyl. The experiment conducted to measure the effect of humic acid loadings on coal based activated carbon also showed reduction in adsorption capacity of coal based activated carbon with the increase in humic acid loadings (Figure 2.9).

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

$$log\ qe = log\ Kf + n^{-1} log\ Ce$$

To perform this set of data analysis all the values were converted to nano gram level and then log values were obtained for equilibrium concentration (ng L $^{-1}$) and adsorbed concentration (ng kg^{-1}). The linear fit was obtained by using Fit Y by X platform and for each log Kf (ng$^{(1-(1/n))}$ L $^{(1/n)}$ kg^{-1}) and n^{-1} values confidence intervals were also obtained (as mentioned in table 2.6).

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 for and complexation with natural organic acids. In order 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 2.6).

	Adsorption coefficients		*Freundlich Isotherm Constants*							
			Non-linear form *($q_e = K_f C_e^{(1/n)}$)*				Linear form *($\log q_e = \log K_f + n^{-1} \log C_e$)*			
Coconut Shell AC	Kd (L/g)		K_f (mg$^{(1-(1/n))}$ L$^{(1/n)}$ g^{-1})		1/n		Log K_f (ng$^{(1-(1/n))}$ L$^{(1/n)}$ kg^{-1})		1/n	
	Bare AC	Preloading effect	Bare AC	Preloading effect	Bare AC	Preloading effect	Bare AC	Preloading effect	Bare AC	Preloading effect
2-cbp	12.63	1.39	7.00	0.96	0.34	1.43	7.41	6.76	0.39	0.39
2,2',5,5'-tPCB	16.50	2.96	2.35	2.47	0.44	0.90	7.52	6.86	0.25	0.27
3,3',4,4'-tPCB	9.99	4.12	4.11	10.83	0.61	1.52	4.67	3.72	0.90	0.97
2,2',4,4',5,5'-hPCB	35.99	11.63	4.44	8.27	0.40	0.85	8.00	7.60	0.23	0.22
3,3',4,4',5,5'-hPCB	17.85	12.22	18.75	35.60	1.00	1.37	7.59	7.49	0.27	0.22
Coal based AC										
2,2',5,5'-tPCB	6.34	3.35	5.89	2.11	0.92	0.78	7.56	6.90	0.20	0.28

Table 2.6: Adsorption Coefficients and Freundlich Isotherm Constants obtained for Selected PCB congeners

In this study, based on K_d values, the preloading effect was found to be most significant for 2-chlorobiphenyl with 89% and non-coplanar 2, 2', 5, 5'-tetrachlorobiphenyl with 82% reduction in adsorption affinity. The effect was less dominant in the case of co-planar 3, 3', 4, 4'-tetrachlorobiphenyl with 59 % and non-coplanar 2, 2', 4, 4', 5, 5'-hexachlorobiphenyl with 68% reduction and was least in case of co-planar 3, 3', 4, 4', 5, 5'-hexachlorobiphenyl with 32% reduction. The measure of non-linearity for isotherms was estimated using the Freundlich isotherm coefficient (1/n). Using the non-linear form of Freundlich coefficients, the trend was found to be favorable with 1/n < 1 (table 2.6 – non-linear) for all bare activated carbon isotherms and non-coplanar congeners with preloaded humic acid but in the case of co-planar 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 figure 2.4. Using the linear form of Freundlich coefficients when log Kf values were compared for bare activated carbon with that of preloaded activated carbon, the difference in magnitude ranged from 0.101 to 0.954 again indicating significant affect of preloading with humic acid (table 2.6 - linear).

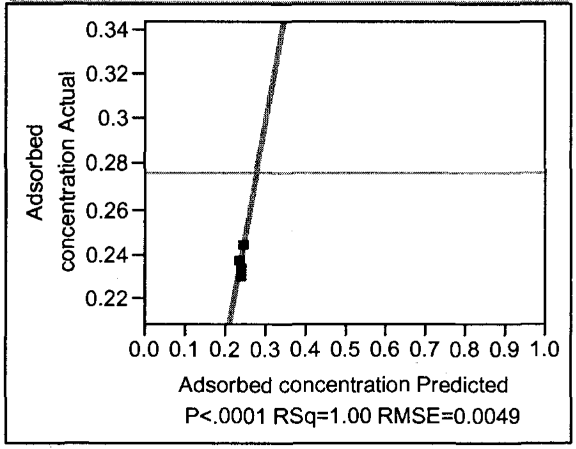
Summary

This study demonstrated the preloading and desorption effect of humic acid on adsorption capacity of coconut shell activated for co-planar and non-coplanar PCBs. The adsorption affinity of bare activated carbon was found to be greater with no desorption effect for highly chlorinated and co-planar congeners compared to lower chlorinated and non-coplanar congeners. Adsorption affinity and capacity of coconut shell activated carbon was found to be significantly affected by preloading with high concentrations of humic acid. The presence of humic acid is a major factor in the design and performance of reactive caps under typical site conditions. The reactive capping mat that will be deployed over the sediment bed will come across 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 effect performance significantly.

Additional Information

Model 1 Details:

Actual by Predicted Plot



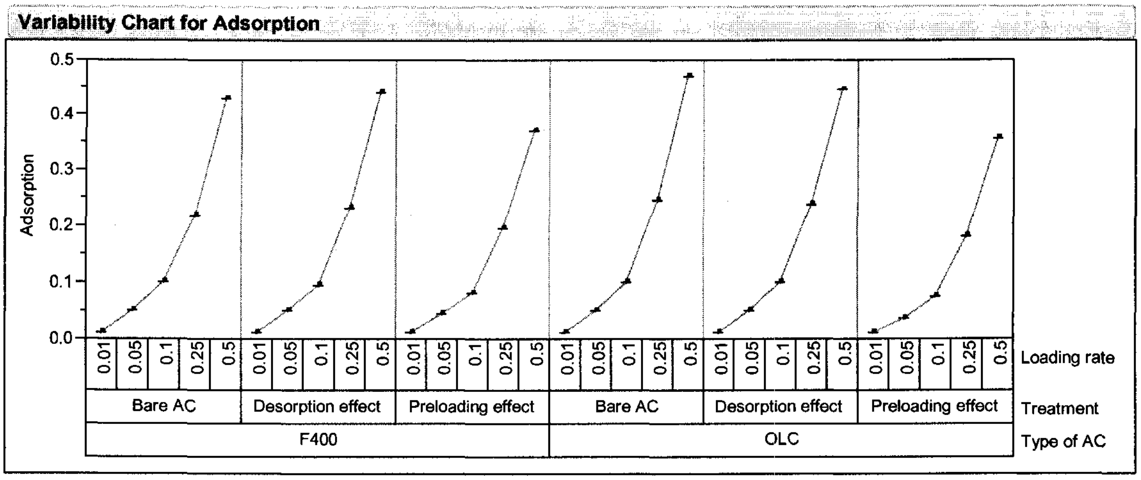
Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	35	5.7685679	0.164816	6822.730
Error	24	0.0005798	0.000024	**Prob > F**
C. Total	59	5.7691476		<.0001*

Effect Tests

Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F
PCB congener	3	3	0.0029605	40.8507	<.0001*
LR	1	1	1.5138861	62668.81	<.0001*
Treatment on AC	2	2	0.0087793	181.7149	<.0001*
PCB congener*Treatment on AC	6	6	0.0033484	23.1017	<.0001*
PCB congener*LR	3	3	0.0042246	58.2939	<.0001*
Treatment on AC*LR	2	2	0.0074106	153.3839	<.0001*
PCB congener*Treatment on AC*LR	6	6	0.0028585	19.7220	<.0001*
LR*LR	1	1	0.0002215	9.1712	0.0058*
LR*LR*PCB congener	3	3	0.0001772	2.4450	0.0885
LR*LR*Treatment on AC	2	2	0.0002977	6.1611	0.0069*
LR*LR*Treatment on AC*PCB congener	6	6	0.0007645	5.2744	0.0014*

Model 2 details:



Variability Chart for Adsorption

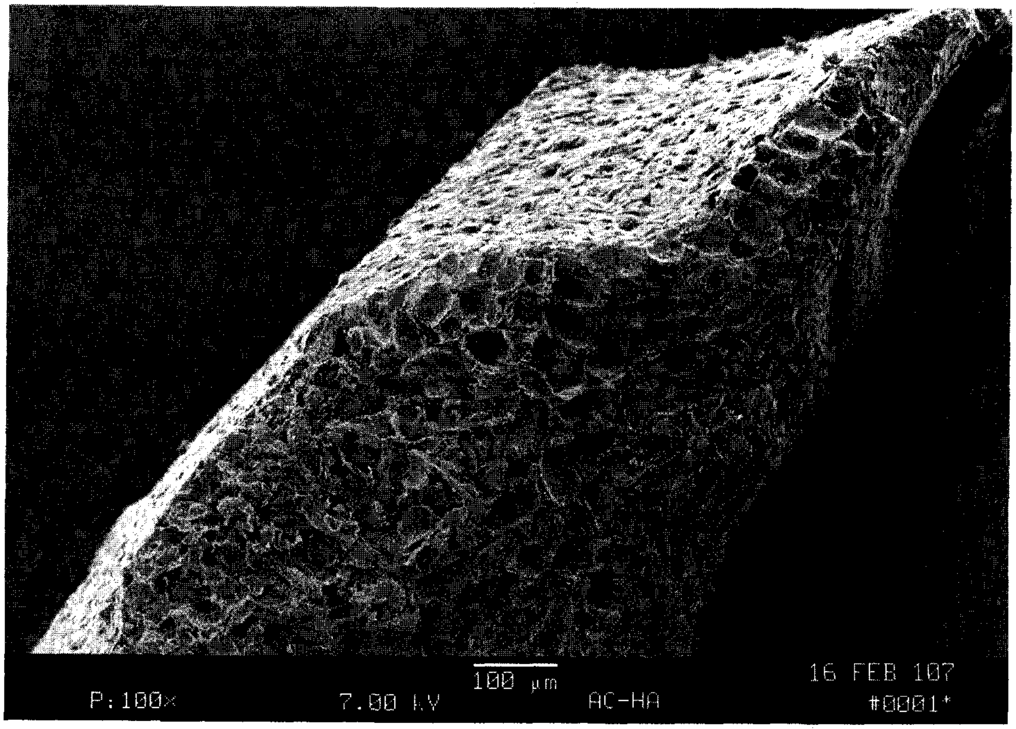
Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	12	0.66843353	0.055703	5233.994
Error	17	0.00018092	0.000011	**Prob > F**
C. Total	29	0.66861446		<.0001*

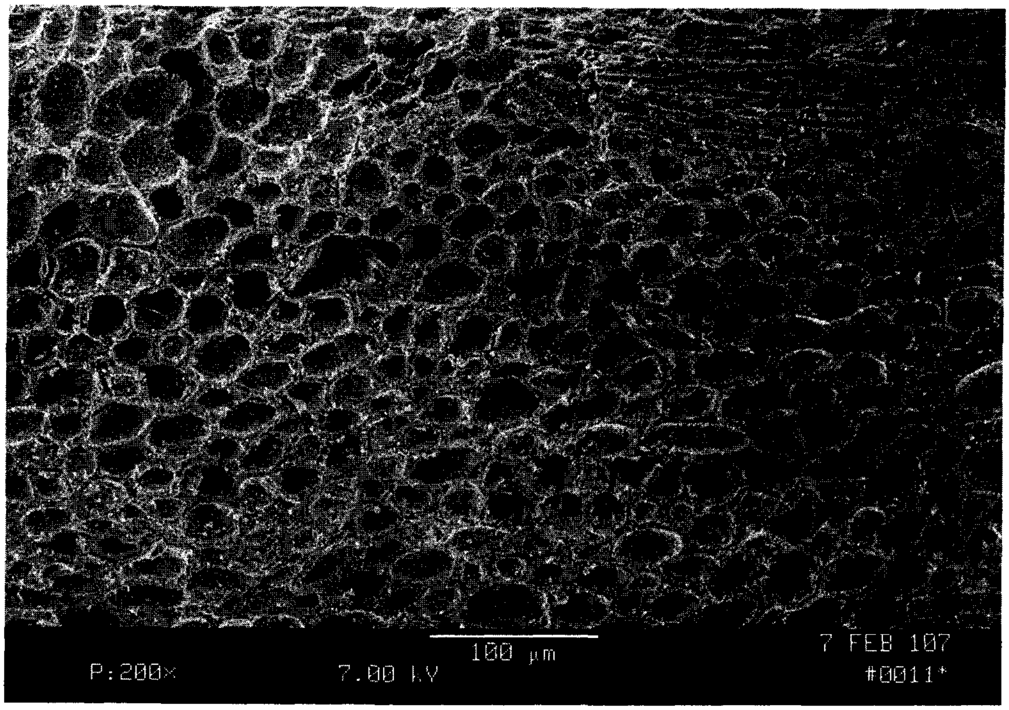
Effect Tests

Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F
Type of AC	1	1	0.00009042	8.4964	0.0097*
Treatment	2	2	0.00666554	313.1567	<.0001*
Type of AC*Treatment	2	2	0.00058111	27.3016	<.0001*
Loading rate	1	1	0.28056137	26362.35	<.0001*
Type of AC*Loading rate	1	1	0.00017908	16.8266	0.0007*
Treatment*Loading rate	2	2	0.00583070	273.9347	<.0001*
Type of AC*Treatment*Loading rate	2	2	0.00060769	28.5500	<.0001*
Loading rate*Loading rate	1	1	0.00026159	24.5794	0.0001*

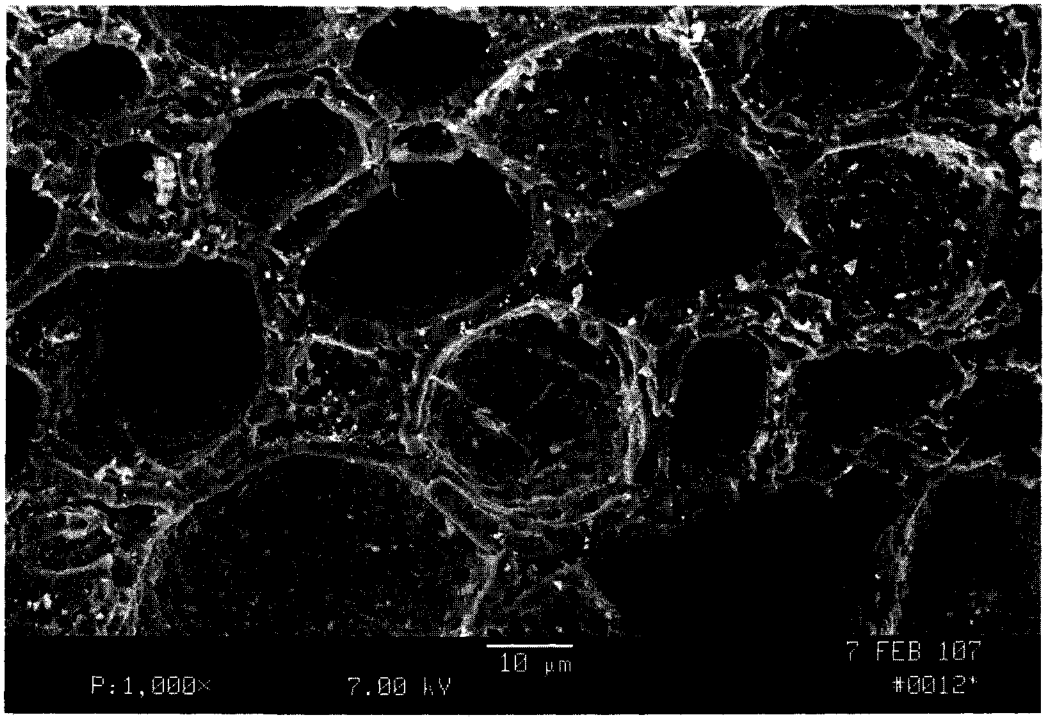
SEM images of activated carbon at different magnifications



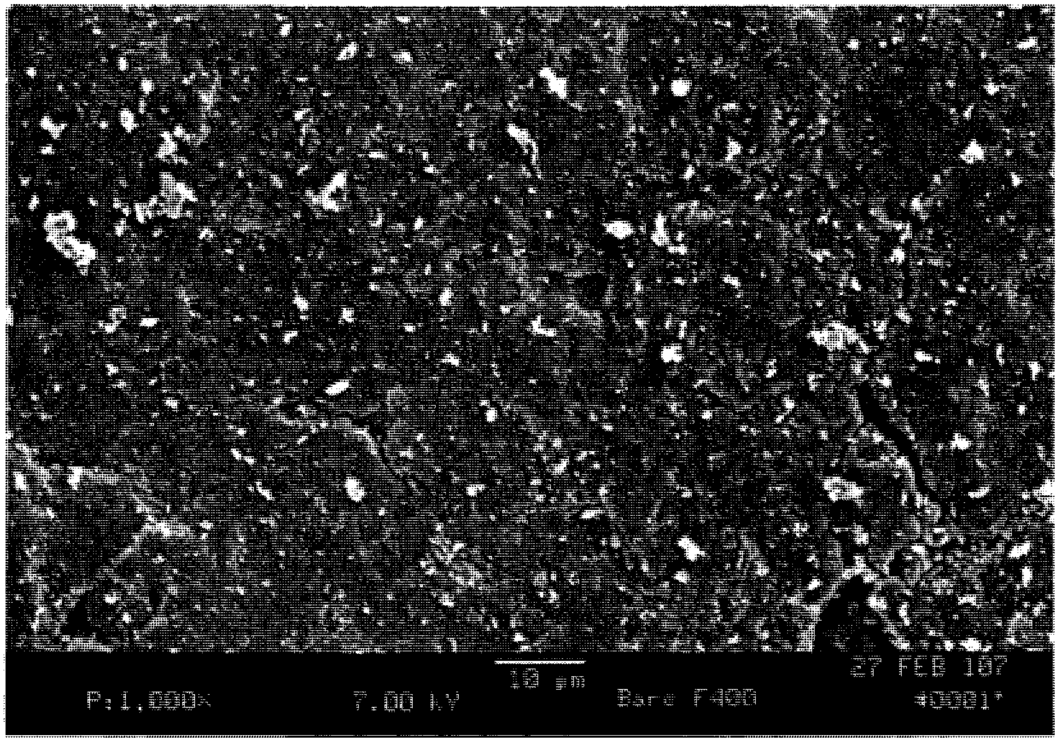
Coconut shell activated carbon: 100 x magnifications



Coconut shell activated carbon: 200 x magnifications



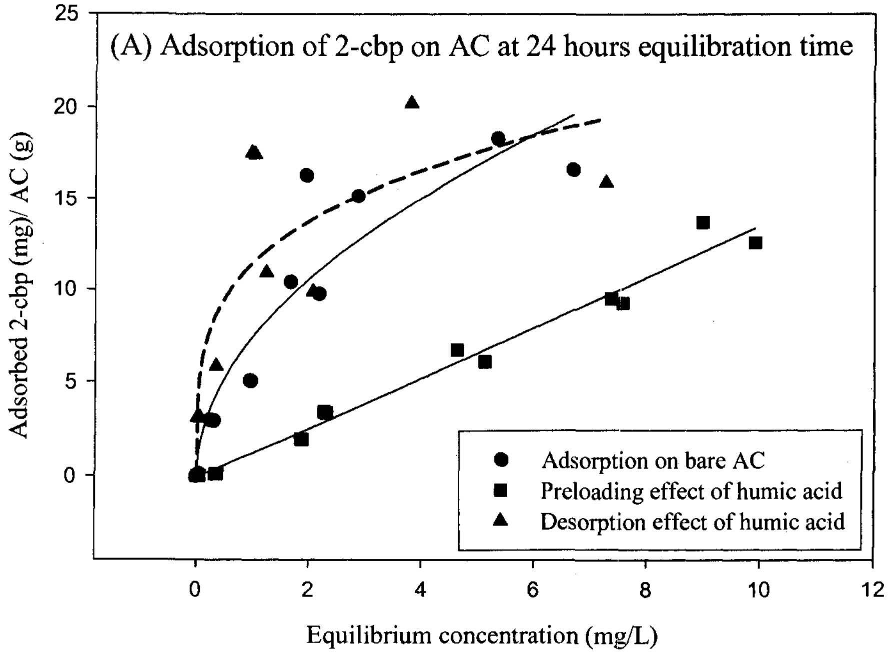
Coconut shell activated carbon: 1000 x magnifications

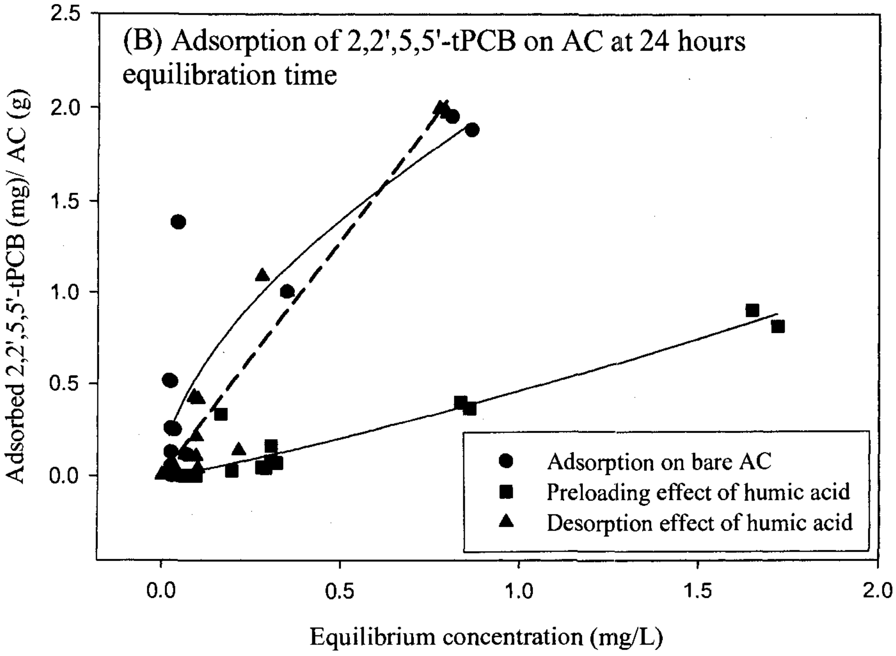


Coal based activated carbon: 1000 x magnifications

Preliminary studies: 24 hours study

Some preliminary studies were conducted to determine the performance of activated carbon for adsorption of mono- and tetra- chlorobiphenyl in the presence and absence of humic acid. These experiments were conducted for 24 hours equilibration time.





Adsorption coefficients for adsorption of selected PCB congeners on coconut shell activated carbon in 24 hours:

	Adsorption coefficients		Freundlich Isotherm Constants			
Coconut Shell AC	Kd (L/g)		K_f ($mg^{(1-(1/n))}$ $L^{(1/n)}$ g^{-1})		1/n	
	Bare AC	Preloading effect	Bare AC	Preloading effect	Bare AC	Preloading effect
2-cbp	2.901	1.360	7.423	1.218	0.570	1.044
2,2',5,5'-tPCB	2.026	0.519	2.092	0.426	0.579	1.187

Results showed significant reducing effects on adsorption capacity of activated carbon in the presence of humic acid. Negligible desorption effects were noticed.

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CHAPTER 3

EFFECT OF HUMIC ACID ON ADSORPTION OF POLYCHLORINATED BIPHENYLS ONTO ORGANOCLAY

Abstract

Organoclay was evaluated as a reactive cap sorbent that can be used for in-situ remediation of contaminated sediments. With this aim, sorption of co-planar and non-coplanar polychlorinated biphenyls including 2-chlorobiphenyl (BZ # 1), 2, 2', 5, 5'-tetrachlorobiphenyl (BZ # 52), 3, 3', 4, 4'- tetrachlorobiphenyl (BZ # 77), 2, 2', 4, 4', 5, 5'-hexachlorobiphenyl (BZ # 153) and 3, 3', 4, 4', 5, 5'- hexachlorobiphenyl (BZ # 169) on organoclays was studied. Three commercially available organoclays were characterized and used for kinetic and equilibrium studies for selected PCB congeners. Kinetic studies were conducted to obtain equilibration time of adsorption of PCBs on organoclay and to determine the effect of humic acid on the kinetics of adsorption. Isotherm studies were conducted to determine the adsorption capacity of organoclays in the presence and absence of humic acid. Studies showed a significant reduction in the performance of organoclays due to preloading with high concentrations of humic acid for all selected PCB congeners. The reduction in sorption capacity due to preloading ranged from 46 % to 96% depending on the congener and the composition of organoclay. Desorption studies that were conducted to simulate the long-term exposure to high humic acid

concentrations in the sediment pore water in typical site conditions also showed reducing effects that were less pronounced compared to preloading effects and varied with the composition of organoclay and PCB congener.

Introduction

Hydrophobic organic contaminants (HOCs) such as polychlorinated biphenyls (PCBs) are of great concern in riverine and marine environments due to their eventual settlement with sediments. PCBs, which are group of 209 congeners, are listed at number five in the CERCLA 2005 priority list of hazardous substances. This listing is based not only on the toxicity of the compounds but also on their frequency of occurrence in national priority list (NPL) sites and their potential of exposure to human beings. The major problem of these contaminants is their continued persistence due to strong sorption on sediments and slow degradation. Highly PCB contaminated sites in riverine and estuarine environments present environmental, economic and technical challenges to meet the clean up goals. Currently, dredging, monitored natural recovery, and in-situ capping are the remediation options for contaminated sediments. Reactive capping, which consists of a geotextile mat impregnated with sorbents, is the subject of this research as an alternative to dredging for in-situ management of contaminated sites.

One of the sorbents that can be used in reactive caps to sequester HOCs effectively is activated carbon. Therefore, in our previous studies the performance of activated carbon was evaluated in the presence and absence of humic acid. Results showed significant reduction in the adsorption capacity of activated carbon due to the pore blockage effect caused by preloading the activated carbon with humic acid. The reduction of adsorption affinity and capacity has significant implications for the design and performance of the reactive mats, and for this reason it was desirable to evaluate additional sorptive media that may perform better in the presence of natural organic matter. Some studies have discussed that sorbents such as organoclays have better performance in the presence of natural organics that can be found in sediments (Zhao and Vance, 1998). Therefore, three commercially available organoclays were selected for this study in order to evaluate PCB sorption and the interference from humic acid.

Natural clays that have electrically charged and hydrophilic surfaces are ineffective in sequestration of HOCs from water (Dental et al., 1998). In natural clays inorganic cations are strongly hydrated in the presence of water and results in hydrophilic surfaces which are ineffective for sequestration of HOCs (Jayens and Boyd, 1991). If the exchangeable inorganic cations from the interlayer space of these clays are replaced by organic cations such as quaternary ammonium compounds, this can significantly improve their capability to remove HOCs (Carmondy at al, 2007; Dental et al., 1998). Due to intercalation of organic cations the interlayer spacing between the silica sheets increases to create an organophilic zone for adsorption of HOCs. These organophilic surfaces created by alkyl chains provide surfactant properties to the clay and these modified clays are known as organoclays. The size of organophilic zone and the hydrophobicity can be measured by determining the dimensions and the structure of organic cation as well as cation exchange capacity (CEC) and geometry of the base clay (Dental et al., 1998). The hydrophobic characteristics can be altered by changing the properties of organic cation such as increasing the length of alkyl chain or varying the number or branches of the alkyl group (Pernyeszi et al., 2006). The lower the amount of organic cation, the greater the compatibility of organoclay with soil and bacteria and the cost of material is also low (Pernyeszi et al., 2006). Also, with higher amounts there can be a concern of desorption of these organic cations which are used to enhance adsorption capacity of clay for organic contaminants. Studies have shown that organic cations are adsorbed by ion-exchange mechanism with organic cation loading up to 70 % of cation exchange capacity (CEC) of clay and hydrophobic sorption starts to occur with ion-exchange when loading is equal or greater to CEC (Sheng et al., 1998). The organic cations that get adsorbed by ion-exchange mechanism are resistant to desorption where as those which are adsorbed by hydrophobic interaction are less resistant to desorption (Sheng et al., 1998).

Organoclays have been studied for soil remediation, groundwater purification, industrial waste water treatment and oil spill remediation using batch systems (Zhao et al., 1998; Dental et al., 1998; Carmondy et al., 2007; Pernyeszi et al., 2006; Ake et al., 2003; Wiles et al., 2005). There are limitations for direct use of organoclay in column systems and flow systems due to their low permeability and wettability (Pernyeszi et al., 2006). Therefore, studies have been conducted by adhering organoclays to sand and activated carbon in order to increase their hydraulic permeability for their use in column systems (Ake et al., 2003; Wiles et al., 2005). Studies have shown good adsorption capacity of organoclays for chlorinated compounds such as trichloroethylene and polychlorophenols (Zhao et al., 1998; Dental et al., 1998; Carmondy et al., 2007; Pernyeszi et al., 2006; Ake et al., 2003; Wiles et al., 2005). There remains a need to determine the sorption capacity of organoclays for PCBs which are persistent organic contaminant of major environmental concern.

Studies have shown that humic substances that are formed by decomposition of plant detritus and microbial degradation are ubiquitous and are distributed throughout the hydro- and lithosphere (Wandruszka, 2000). The affect of humic acid on the sorption capacity depends on the type of clay and organic cations used in preparing the organoclay (Zhao et al., 1998). Therefore, it necessitates determining the interferences that can be caused by humic acids on the adsorption capacity of organoclays that can be used as a reactive cap sorbent for in-situ remediation of contaminated sediments. The two main objectives of this study were to determine the sorption capacity of organoclays for PCBs and to determine the affect of humic acid on the sorption capacity of organoclays for its applicability in contaminated sediment remediation.

Chemicals and materials

For all the experiments ultra high purity chemicals and GC-grade solvents obtained from Fischer Scientific (Agawam, MA, USA) were used. The PCB congeners 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; internal standard

2, 4, 6-trichlorobiphenyl and surrogate standard 2, 4, 5, 6-tetrachloro-m-xylene (TCMX) were purchased from Ultra scientific (North Kingstown, RI, USA) either in neat form or dissolved in hexane. Humic acid sodium salt was obtained from Sigma-Aldrich (St. Louis, MO, USA). Sodium azide that was used to avoid biological growth in the experiments was obtained from EMD Chemicals Inc. (San Diego, CA, USA) and sodium sulfate anhydrous from Fisher Scientific (Morris Plains, NJ, USA)

Organoclays: Three types of organoclays used in this study were obtained as PM 199 from CETCO; PS 86 from Polymer Ventures and Colorsorb 16 x 40 from Biomin Inc. The base clay used in CETCO and Biomin Inc. organoclays was bentonite whereas in Polymer Ventures organoclay attapulgite was used as base clay (Figure 3.1.1 and 3.1.2).

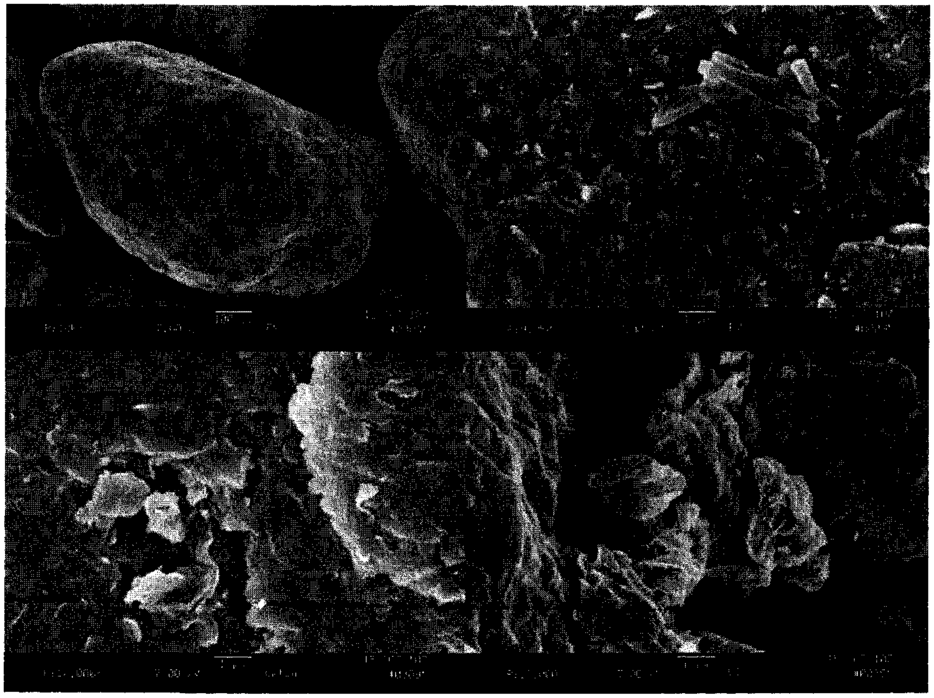
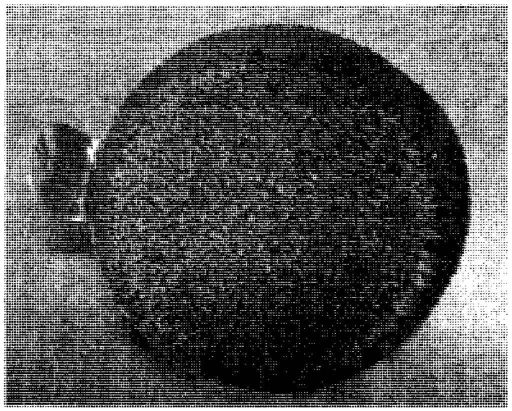
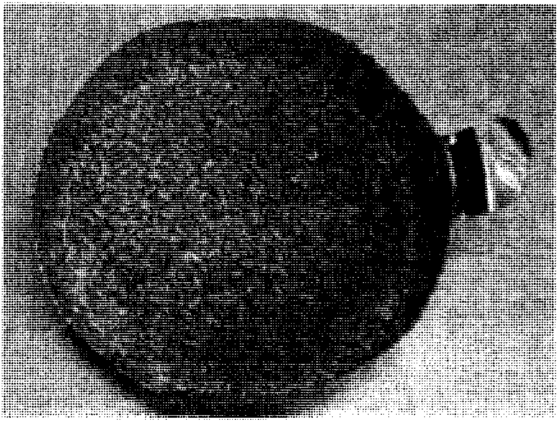


Figure3.1.1: Surface profiles of organoclays: Polymer Ventures (100 x magnification – top left and 10 K x magnification - top right); CETCO (10K x magnification - bottom left) and Biomin Inc. (10K x magnification - bottom right)



Base clay: Bentonite
CETCO organoclay

Base clay: Attapulgite
Polymer Ventures organoclay



Base clay: Bentonite
Biomin Inc. organoclay

Figure3.1.2: Three formulations of organoclay

Characterization of organoclays

X-ray diffraction (XRD): XRD patterns were obtained on small angle X-Ray scattering (SAXS) 2m – 2D area detector using CuK α radiation with a wavelength of 1.5418 A° at the Institute of Technology Characterization Facility, University of Minnesota (Figure 3.1.3). The instrument was operated at 44 KV and 60 mA between 1.3 degree 2θ and 9 degree 2θ at a step size of 0.01 degree 2θ to obtain the interlayer d-spacing of organoclays (table 3.1).

Thermogravimetric analysis (TGA): Differential thermal analysis (DTA) was performed on TA Instruments, model SDTQ600 to obtain % organic content of all three organoclays (table 3.1). Nitrogen flow was maintained at 100 mL min^{-1} with oxygen supply at 242 mL min^{-1} from 28°C to 1000°C with a heating rate of 10°C min^{-1}.

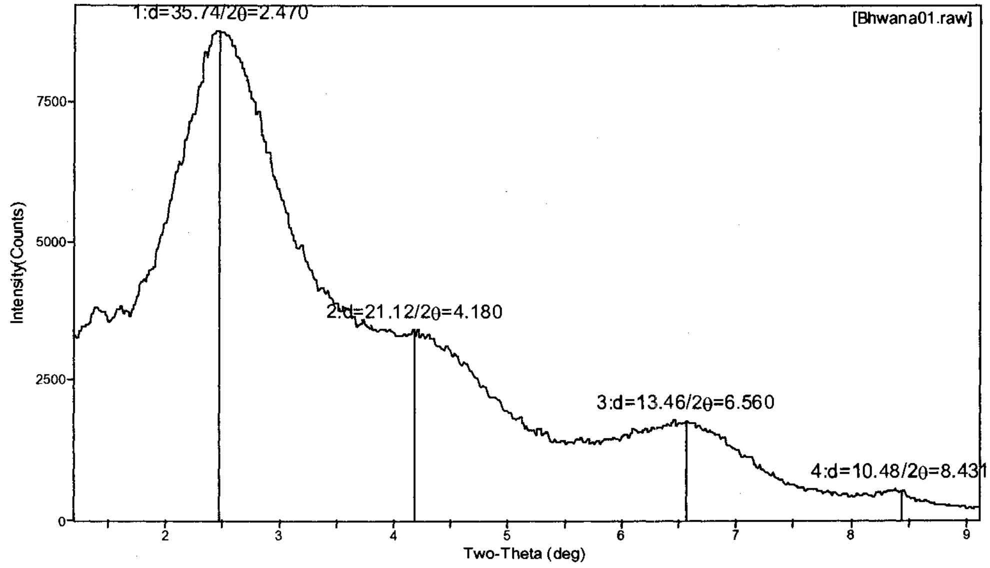


Figure 3.1.3: 2d SAXS scan for determination of d-spacing

Table3.1: Characteristics of Organoclays

	CETCO Organoclay	Polymer Ventures Organoclay	Biomin Inc. Organoclay
Base Clay	Bentonite	Attapulgite	Bentonite
BET surface area (m^2/ g)	0.3225	16.7294	0.1872
Interlayer spacing (d_{001} spacing Å)	35.74 ($2\theta = 2.47$)	35.85 ($2\theta = 2.46$)	37.89 ($2\theta = 2.33$)
% Organic Matter	19.10	10.54	26.95
Inorganic Cations* (ppm)			
Calcium (Ca)	967.2	750.8	682.2
Magnesium (Mg)	175.0	230.0	169.0
Potassium (K)	79.0	337.0	46.0
Phosphorus (P)	1.0	12.0	1.0
Estd. CEC * (meq/ 100g) based on inorganic cations	6.50	6.53	4.94

Overview of experimental protocol

Batch equilibration method was used to for kinetics and isotherm studies of 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. Experiments were conducted in separate batches of 125 ml of either deionized (DI) water or humic acid solution (prepared in DI water) for pure system and humic acid system, respectively. PCBs were spiked in the system at fixed concentration for kinetics experiment and at different concentration for isotherm studies depending on the loading rate. For spiking, stock solution of PCBs was prepared in ultra-high purity methanol because it has been shown to have no measurable effect on sorption capacity of organoclay (Lee et al., 2005). Organoclays were either used as obtained from companies or preloaded with humic acid for the system in which effect of humic acid was determined.

Preloading of organoclay with humic acid: For preloading of organoclays, stock solution of 1g L^{-1} humic acid was prepared using de-ionized (DI) water and sodium salt of humic acid as obtained from Sigma Aldrich. To avoid biological growth in the system 10% sodium azide was added to the stock solution. Separate batches were prepared with fixed amount of organoclay and 125 ml of humic acid stock solution in Erlenmeyer flask. All the samples were thoroughly mixed at 150 rpm on a rotary shaker for 48 hours and were used as such for the experiments.

In summary, two types of systems were used for all experiments in 125 ml batches were: a pure system having bare organoclay and PCBs spiked in DI water and a humic acid system having organoclay preloaded with humic acid and PCBs spiked in the humic acid solution. All the methods used for preparing stock solution of PCBs and humic acid, preloading of organoclays and preparation of each batch for pure system and humic acid system were consistent throughout the complete experimentation to maintain the accuracy of the results. All the glassware used was of pyrex to avoid any loss of PCBs on the walls of the flask. The controls were also prepared with each set of experiment to account any loss of PCBs other than sorption on organoclays.

Kinetic experiments

The kinetics of 2-chlorobiphenyl sorption on organoclays was obtained using CETCO (organo-bentonite) and Polymer Ventures (organo-attapulgite) organoclay. Experiments were conducted with 4 mg L^{-1} concentration of 2-chlorobiphenyl for the duration of 15 days in the presence and absence of humic acid. For each kinetic study, the numbers of samples with pure system were equal to that of humic acid system and were sampled at the same time. All the samples were continuously mixed for the length of the experiment prior to sampling at 150 rpm on a rotary shaker.

Sorption Isotherms

Sorption isotherms for all selected PCB congeners were obtained at the equilibration time of 48 hours. The equilibration time was selected on the basis of sorption kinetics of bare organoclay while also considering the retention time of contaminants in a thin reactive cap. Experiments were conducted in the presence and absence of humic acid to determine the effect of humic acid on sorption capacity of organoclays. In all the batches the amount of organoclay was constant with varying concentrations of PCBs depending on the loading rates (table 3.2). The loading rates ranged from concentrations less than and equal to water solubility of each compound and the highest loading was slightly higher than the solubility limit. The second highest loading was equal to the solubility limit of compound in water and was duplicated to check the accuracy of the complete experiment. The effect of humic acid was determined by preloading with humic acid and desorption upon spiking with humic acid. The preloading effect was determined by preloading the organoclays prior to the sorption of PCBs as mentioned previously. Desorption effects were determined by adding humic acid to the pure system after PCB adsorption for 48 hours. The concentration of humic acid to determine desorption effects was kept the same (1g L^{-1}) as it was in humic acid system to determine the preloading effect. Desorption studies were also conducted for the equilibration time of 48 hours similar to the studies conducted to determine the sorption capacity of organoclay and preloading effect of humic acid.

Table 3.2: Details of selected PCB congeners used in the study

PCB congener	† Solubility Limit in water (ppm)	† Log K_{OW}	Log K_{DOC}	Isotherm Studies Concentration Range (mg/L)
2-cbp	4.0	4.7	3.63*	0.01 – 8
2,2',5,5'- tPCB	0.26	5.9	4.6 **	0.008 – 0.4
3,3',4,4'- tPCB	0.26	5.9	-	0.008 – 0.5
2,2',4,4',5,5'- hPCB	0.038	6.7	5.3**	0.008 – 0.04
3,3',4,4',5,5'- hPCB	0.038	6.7	-	0.008 – 0.04

* Butcher et al., 2004, ** Poerschmann et al., 1999, † Erickson, 1997

Sample analysis

Sample extraction: The vial liquid-liquid extraction method was used for the extraction of supernatant of each sample into hexane with TCMX as a surrogate standard. Ten ml of surrogate solvent (prepared in hexane) with twenty ml of sample was taken into a 40 ml vial sealed with Teflon® lined screw caps. All the samples were extracted in duplicates to determine the variation in extraction procedure. The vials were shaken vigorously for 30 seconds three times at intervals of 30 seconds each and then stored for at least for 24 hours at 4° C to allow proper extraction. The extracts were passed through sodium sulfate to remove any chemically bound water to avoid any contamination in GC columns. GC vials were then prepared with filtered extracts and addition of 2, 4, 6-trichlorobiphenyl as an internal standard.

Gas Chromatography/ Mass Spectrometry: All the extracts were analyzed using internal standard method on 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-5ms), 30 m long, 0.25 mm ID and 0.5 μm 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 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 held time of 2 minutes. The surrogate recoveries were achieved to be in the range of 70 – 120% using this internal standard method.

Results and discussions

Kinetics:

The kinetics experiments were conducted to estimate the equilibration time for adsorption of 2-chlorobiphenyl on two compositions of organoclays having different base clays (CETCO and Polymer Ventures organoclays). The result showed approximately the same time was required to reach equilibrium for both types of organoclays (Figure 3.2). The sorption kinetics of 2-chlorobiphenyl was obtained in the presence and absence of humic acid. For this purpose both types of organoclays were preloaded with humic acid prior to the spiking of 2-chlorobiphenyl in the system.

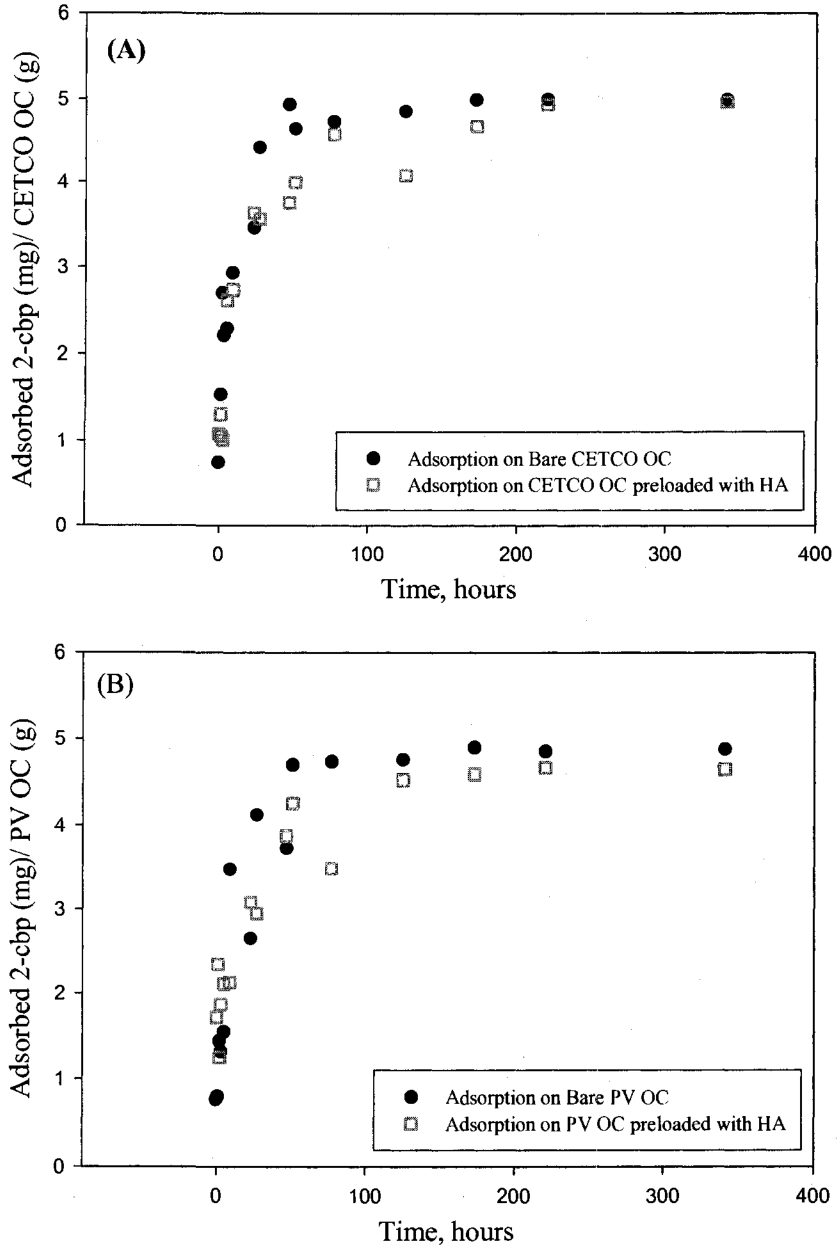


Figure 3.2: Kinetics of sorption of 2-chlorobiphenyl on organoclays: (A) CETCO organoclay (B) Polymer Ventures organoclay

The equilibrium was reached at around 48 hours for bare organoclays, but the presence of humic acid has been found to slow the sorption kinetics. This may be due to the slow diffusivity of 2-chlorobiphenyl into the interlayer spacing of organoclays in the presence of humic acid molecules that can block the path of the contaminants due to hydrophobic interactions with organophilic outer layers of organoclays.

Isotherms:

The sorption capacity of all the three organoclays was evaluated in the presence and absence of humic acid. PCBs selected for this study 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. The selection was done on the basis of their co-planarity to represent the whole range of congeners from lower chlorinated to highly chlorinated ones with different hydrophobicities. The effect of humic acid was evaluated by preloading organoclay with humic acid prior to PCB spiking and desorption effect by spiking humic acid in the system after PCB adsorption on organoclay. Preloading effect was estimated to simulate the typical site conditions where sorbents might come across very high concentrations of natural organics that can affect the sorption capacity of sorbents for target organic contaminants. Desorption studies simulated the long term exposure of these sorbents to organic acids after adsorption of contaminants as well as to determine the reversibility of the system.

Adsorption capacity of the sorbents was evaluated by using linear fit and Freundlich fit for the data (table 3.3). The linear fit was used to obtain the partition coefficient (K_d) to estimate the sorption affinities of organoclays. The Freundlich model used is described as:

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

where, q_e is the amount of contaminant adsorbed on the sorbent (mg/g), K_F is the Freundlich isotherm constant, C_e is the equilibrium concentration (mg/L) and $1/n$ is the dimensionless Freundlich exponent. The value of the Freundlich exponent was used to understand the nature of adsorption of PCBs on organoclays. The non-linearity of isotherms was estimated based on (1/n) values; the trend is considered to be favorable for $(1/n) < 1$ and unfavorable for $(1/n) > 1$ (Figure 3.3 – 3.7).

Sorption of 2-chlorobiphenyl was evaluated for all the three organoclays including CETCO organoclay, Polymer Ventures organoclay and Biomin Inc. organoclay (Figure 3.3 A-C). Figure 3.3 shows significant reduction effect of preloading with humic acid on all the three organoclays for sorption of 2-chlorobiphenyl where as no desorption was noticed for CETCO and Biomin Inc. organoclay and slight desorption was noticed in the case of Polymer Ventures organoclay, when humic acid was introduced in the system once 2-chlorobiphenyl was adsorbed. The adsorption coefficients (K_d) based on a linear fit of the data showed greater affinity in the case of bare CETCO organoclay as compared to the other two compositions, but the sorption capacity of all organoclays for 2-chlorobiphenyl was found to be less as compared to coconut shell activated carbon as evaluated in the previous studies (table 3.3). About 78% reduction in the sorption capacity (Kd values) of CETCO organoclay was noticed due to preloading with humic acid (table 3.3). The reduction was noticed to be about 60% for Polymer Ventures organoclay and about 45% in the case of Biomin Inc. organoclay for 2-chlorobiphenyl sorption.

	Adsorption Isotherm Constants		Freundlich Isotherm Constants			
	Kd (L g^{-1})		K_f (mg$^{[1-(1/n)]}$ L$^{(1/n)}$ g^{-1})		1/n	
CETCO OC	Adsorption on bare OC	Preloading effect	Adsorption on bare OC	Preloading effect	Adsorption on bare OC	Preloading effect
2-cbp	7.8	1.7	7.6	1.2	1.6	1.3
2,2',5,5'-tPCB	11.5	2.7	7	2.1	0.8	0.9
3,3',4,4'-tPCB	7.9	0.5	126057.6	0.4	4.6	0.7
2,2',4,4',5,5'-hPCB	228.2	30.5	20.2	7.3	0.6	0.6
3,3',4,4',5,5'-hPCB	150	9.2	1.3	880	0.3	2.2
PV OC						
2-cbp	4.3	1.7	5.6	1.7	0.6	1
2,2',5,5'-tPCB	53.7	2.1	107604.9	1.8	2.6	0.9
BI OC						
2-cbp	1.9	1	4.9	3	0.3	0.3
Coconut shell AC						
2-cbp	12.6	1.4	7	1	0.3	1.4
2,2',5,5'-tPCB	16.5	3	2.3	2.5	0.4	0.9
3,3',4,4'-tPCB	10.5	3.9	6.6	11.7	0.8	1.6
2,2',4,4',5,5'-hPCB	36	11.6	4.4	8.3	0.4	0.9
3,3',4,4',5,5'-hPCB	18.2	12.2	18.8	35.6	1	1.4
Coal based AC						
2,2',5,5'-tPCB	6.3	3.4	5.9	2.1	0.9	0.8

Table 3.3: Adsorption Isotherm Coefficients (K_d) and Freundlich Isotherm Constants (K_f and 1/n) for different types of sorbents for selected PCB congeners

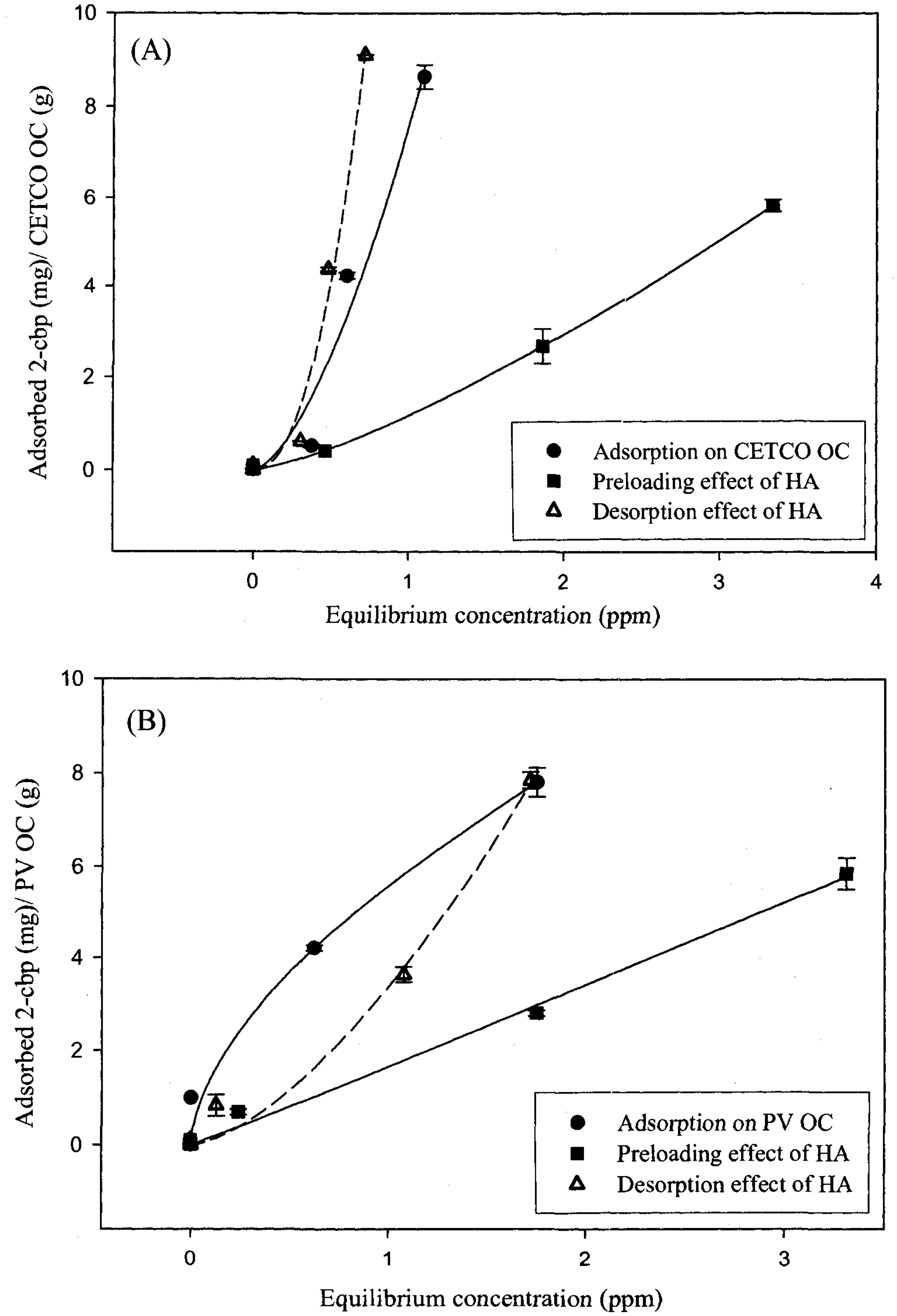


Figure 3.3 A-B: Freundlich adsorption isotherms for 2-chlorobiphenyl in presence and of humic acid (A) CETCO organoclay (B) Polymer Ventures organoclay

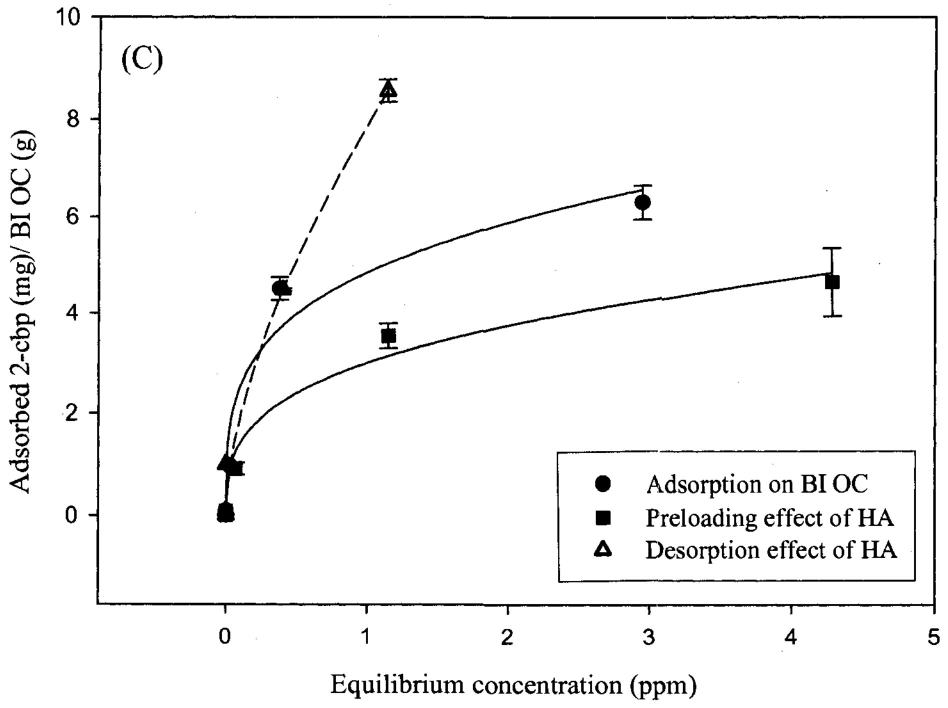


Figure 3.3C: Freundlich adsorption isotherms for 2-chlorobiphenyl in presence and of humic acid: Biomin Inc. organoclay

The statistical analysis was done to evaluate the performance of the three compositions of organoclays for sorption of 2-chlorobiphenyl. The model 1 was developed on the Fit model platform using software JMP® 7 (table 3.4). The hypothesis of this model was that there was difference in the performance of three organoclays for 2-chlorobiphenyl sorption in the presence and absence of humic acid. The three factors considered in this model were: type of organoclay, loading rate of 2-chlorobiphenyl and treatment effects (preloading/ desorption) on organoclay. The regression analysis was done using full factorial design with these three factors.

Table 3.4: Specifications for Statistical Model 1

Model 1 specifications:
Type of OC
Treatment on OC
Type of OC *Treatment on OC
Loading rate
Type of OC *Loading rate
Treatment on OC*Loading rate
Type of OC *Treatment on OC*Loading rate

According to analysis of variance (ANOVA) the p-value was < 0.0001, therefore, the hypothesis of the model was found to be significant (details in additional information). The F-test was performed on each term including main effects and interaction terms of the model to determine the significance of the factors based on the p-value < 0.05. The least square means of adsorbed concentration of 2-chlorobiphenyl on all organoclays were plotted against the treatment effects (preloading/ desorption effect) (Figure 3.4). There was no substantial difference in the performance of bare CETCO and Polymer Ventures organoclays but the sorption capacity of Biomin Inc. organoclay was less. The preloading of organoclays with humic acid significantly reduced their sorption capacity (Figure 3.4). No desorption was found in case of CETCO and Biomin Inc. organoclay but significant desorption was observed in the case of Polymer Ventures organoclay that had different base clay as compared to CETCO and Biomin Inc. that had same base clays (Figure 3.4).

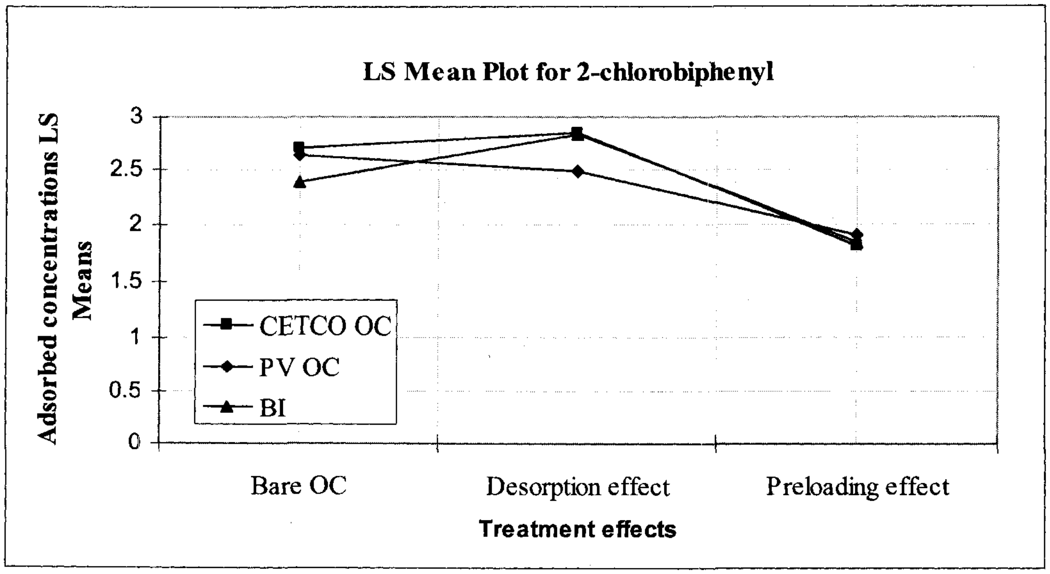


Figure 3.4: Least square means plot for adsorption of 2-chlorobiphenyl on all the three organoclays

For 2, 2', 5, 5'-tetrachlorobiphenyl sorption isotherms were obtained using CETCO and Polymer Ventures organoclay (Figure 3.5 A-B). Based on the Kd values (table 3.3) it was noticed that the sorption capacity of Polymer Ventures organoclay was higher than CETCO organoclay but preloading with humic acid significantly reduced the sorption capacity of both types of organoclays.

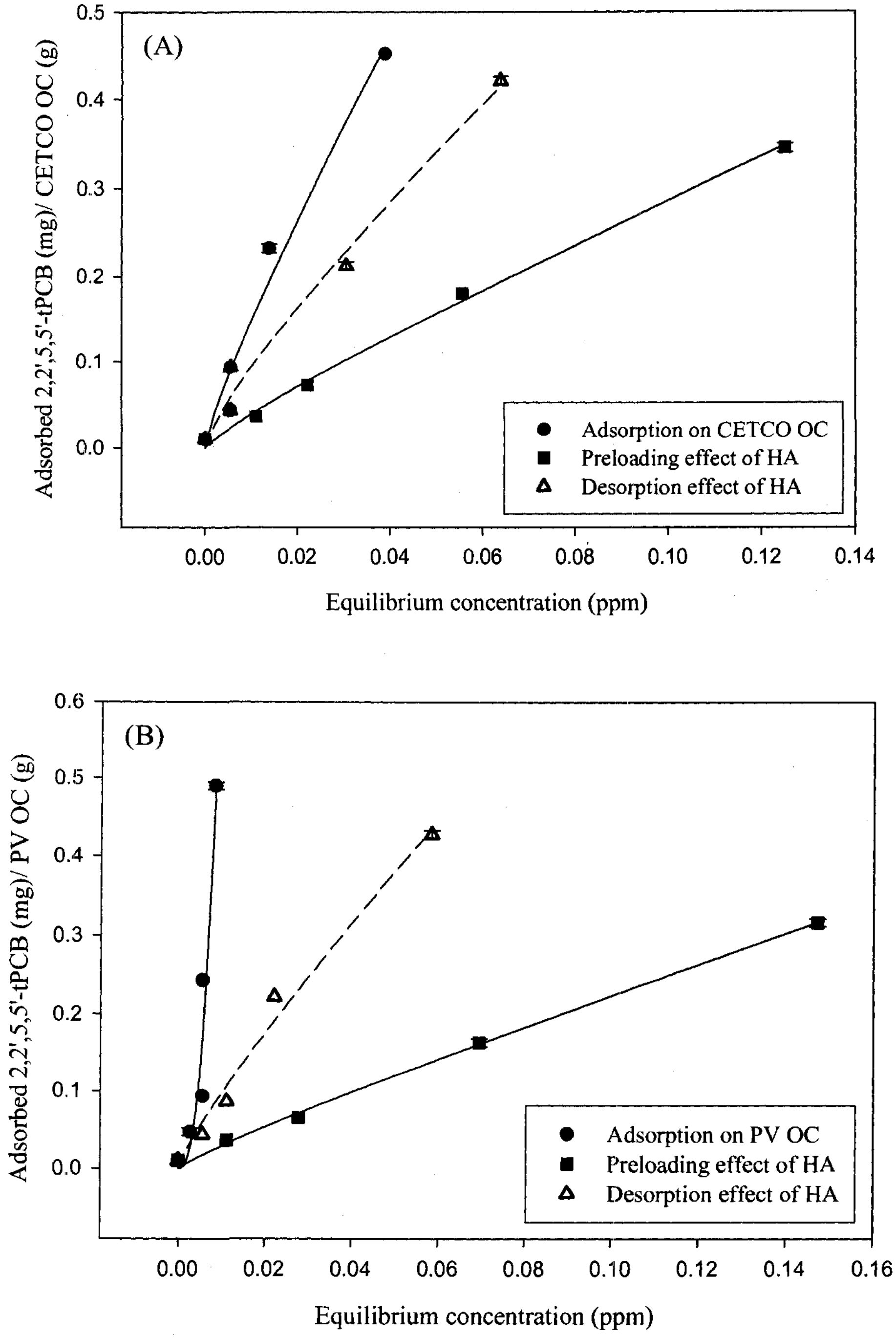


Figure 3.5 A-B: Freundlich adsorption isotherms for adsorption of tetrachlorobiphenyl in presence and absence of humic acid (A) 2, 2', 5, 5'- tPCB adsorption on CETCO organoclay (B) 2, 2', 5, 5'- tPCB adsorption on Polymer ventures organoclay

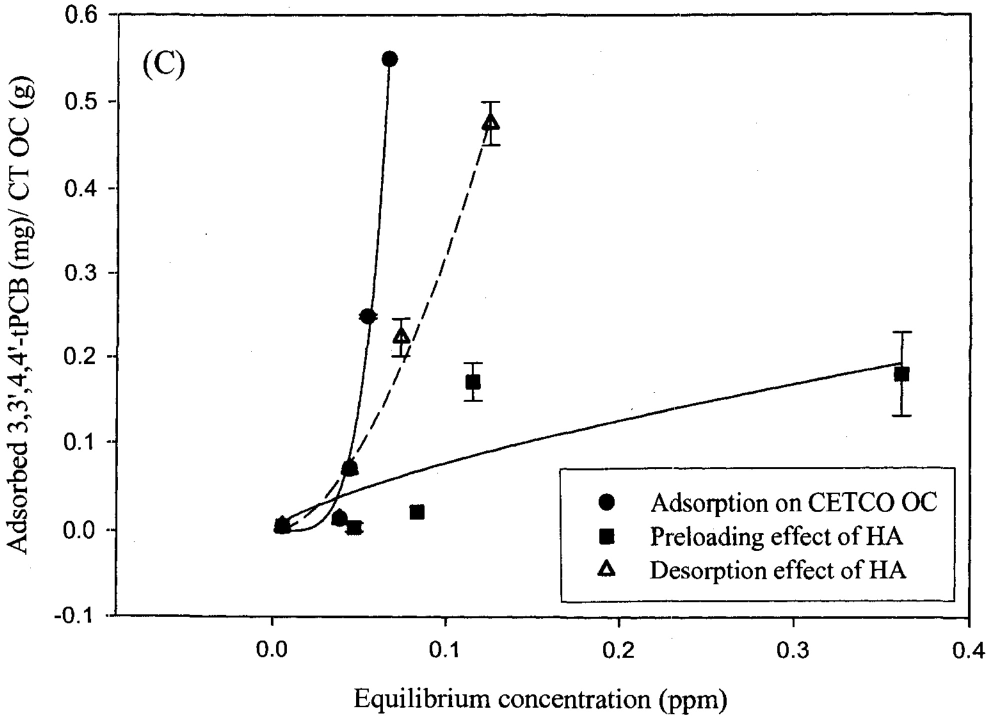


Figure 3.5C: Freundlich adsorption isotherms for adsorption of tetrachlorobiphenyl in presence and absence of humic acid: 3, 3', 4, 4'- tPCB adsorption on CETCO organoclay

The reduction was found to be about 76% for CETCO organoclay and about 96% in the case of Polymer Ventures organoclay (table 3.3). The performance of these two organoclays for sorption of 2, 2', 5, 5'-tetrachlorobipheny was also analyzed statistically using a Fit model platform in JMP® 7. The model 2 was developed based on the hypothesis that the performance of CETCO and Polymer Ventures organoclays are different for 2, 2', 5, 5'-tetrachlorobiphenyl sorption (table 3.5). In this model three factors taken into consideration were: type of organoclay, treatment on organoclay and loading rate of 2, 2', 5, 5'-tetrachlorobiphenyl. The full factorial design was developed with all the three factors and the quadratic term for loading rate.

Table 3.5: Specifications for Statistical Model 2

Model 2 specifications:
Type of OC
Treatment on OC
Type of OC*Treatment on OC
Loading rate
Type of OC*Loading rate
Treatment on OC*Loading rate
Type of OC*Treatment on OC*Loading rate
Loading rate*Loading rate
Loading rate*Loading rate*Type of OC

According to ANOVA the p-value obtained was < 0.0001, therefore, the hypothesis of the model was found to be significant (details in additional information). The Student's t obtained at $\alpha = 0.05$ to determine the effects of humic acid on performance of both type of organoclays showed the performance of bare Polymer Ventures organoclay to be better than that of CETCO organoclay. The preloading effect of humic acid was found to be more significant in the case of Polymer Ventures organoclay but desorption effects were found to be similar in both the cases (table 3.6). This shows CETCO organoclay performed better than Polymer Ventures organoclay in the presence of humic acid.

Table 3.6: LS Means Differences Student's t at $\alpha = 0.050$ and $t = 2.11991$ for comparing performance of CETCO and Polymer Ventures organoclays in presence of humic acid

Level*						Least Sq Mean
PV, Bare OC	A					0.177
CETCO, Bare OC		B				0.168
PV, Desorption effect			C			0.158
CETCO, Desorption effect			C			0.158
CETCO, Preloading effect				D		0.131
PV, Preloading effect					E	0.119

The sorption capacity of CETCO organoclay was further evaluated for co-planar 3, 3', 4, 4'- tetrachlorobiphenyl and two of the hexa-chloro-congeners. The performance of CETCO organoclay was compared for non-coplanar and co-planar tetra- and hexa-chlorobiphenyls (Figure 3.5A, 3.5C and 3.6). Adsorption coefficients (Kd) of non-coplanar congener were found to be higher compared to their co-planar isomers for both tetra- and hexa- chlorobiphenyls (table 3.3).

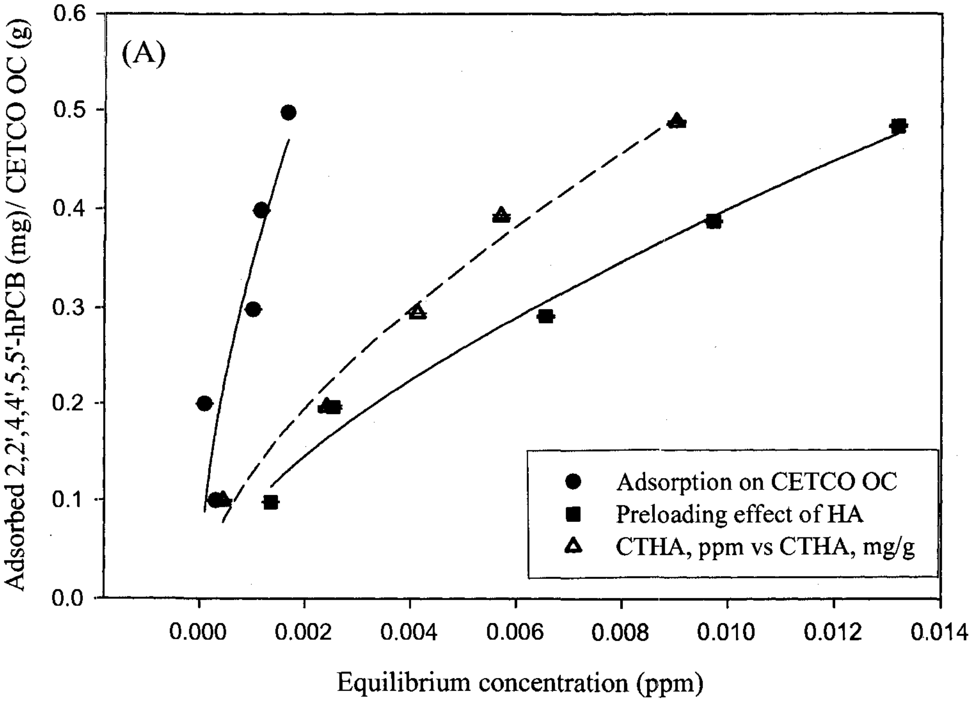


Figure 3.6 A: Freundlich adsorption isotherms for adsorption of hexachlorobiphenyl on CETCO organoclay in presence and absence of humic acid: 2, 2', 4, 4', 5, 5'-hPCB

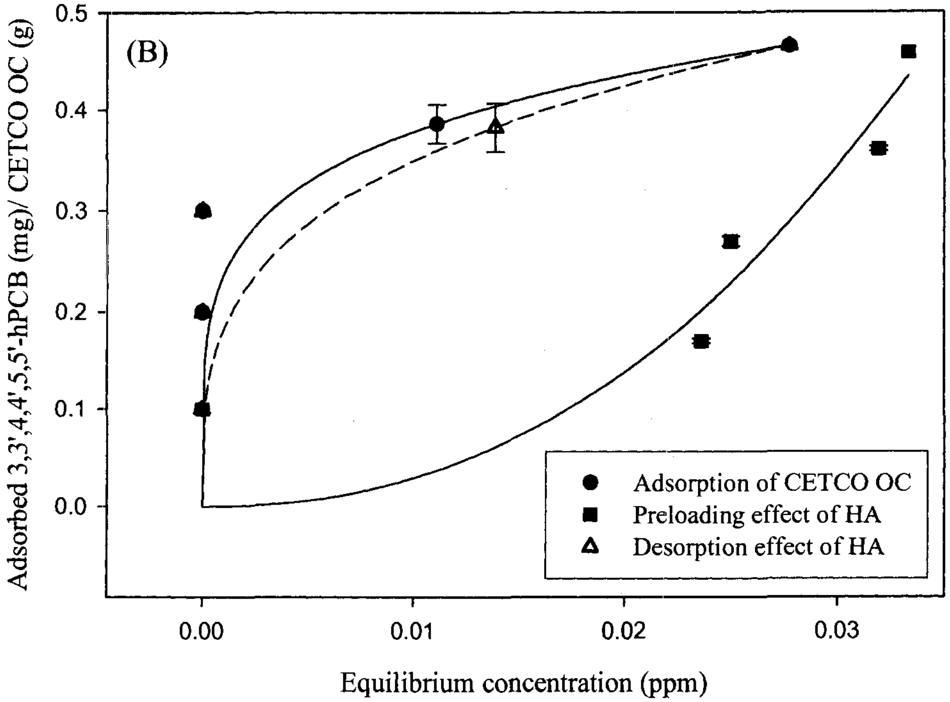


Figure 3.6B: Freundlich adsorption isotherms for adsorption of hexachlorobiphenyl on CETCO organoclay in presence and absence of humic acid: 3, 3', 4, 4', 5, 5'-hPCB

The reduction effect of preloading was found to be more pronounced for co-planar congener but desorption was found to be almost same for both non-coplanar and co-planar congeners. There was about 93% reduction in performance of CETCO organoclay for 3, 3', 4, 4'-tetrachlorobiphenyl, 86% for 2, 2', 4, 4', 5, 5'-hexachlorobiphenyl and 93% for 3, 3', 4, 4', 5, 5'-hexachlorobiphenyl. It is interesting to note that in previous studies, the reduction in performance of activated carbon was noticed to be more for non-coplanar congeners where as in case of CETCO organoclay it has been observed for co-planar congeners. The sorption capacity of CETCO organoclay was also found to be highest for highly chlorinated congeners and the order was: hexa-chlorobiphenyl > tetra-chlorobiphenyl ≥ mono-chlorobiphenyl, which is similar to activated carbon (table 3.3).

The statistical analysis was done on JMP$^{®}$ 7 and a model 3 was developed to evaluate the performance of CETCO organoclay for tetra- and hexa- chlorobiphenyl based on the number of chlorine atoms as well as co-planarity of the congeners in presence and absence of humic acid (table 3.7). The hypothesis of this model was that number of chlorine atoms in PCBs and their co-planarity affect the sorption capacity of CETCO organoclay. The full factorial design was developed for regression analysis of the model with the entire three factors and the quadratic term for loading rate.

Table 3.7: Specifications for Statistical Model 3

Model 3 specification:
PCB congener
Treatment on OC
PCB congener*Treatment on OC
Loading Rate
PCB congener*Loading Rate
Treatment on OC*Loading Rate
PCB congener*Treatment on OC*Loading Rate
Loading Rate*Loading Rate
Loading Rate*Loading Rate*Treatment on OC

The p-value obtained was < 0.0001 in ANOVA, therefore, the hypothesis of this model was significant (details in additional information). The least square means plot was obtained by plotting least square means of adsorbed concentration of all PCB congeners against the treatment effects (preloading/ desorption effect) on CETCO organoclay (Figure 3.7). The preloading effect was found to more pronounced in case of co-planar congeners as compared to their non-coplanar isomers and desorption effects were not substantial in any case (table 3.8). It was also observed that the adsorption affinity of CETCO organoclay was higher for hexa-chlorobiphenyls than for tetra-chlorobiphenyls for all the treatment effects.

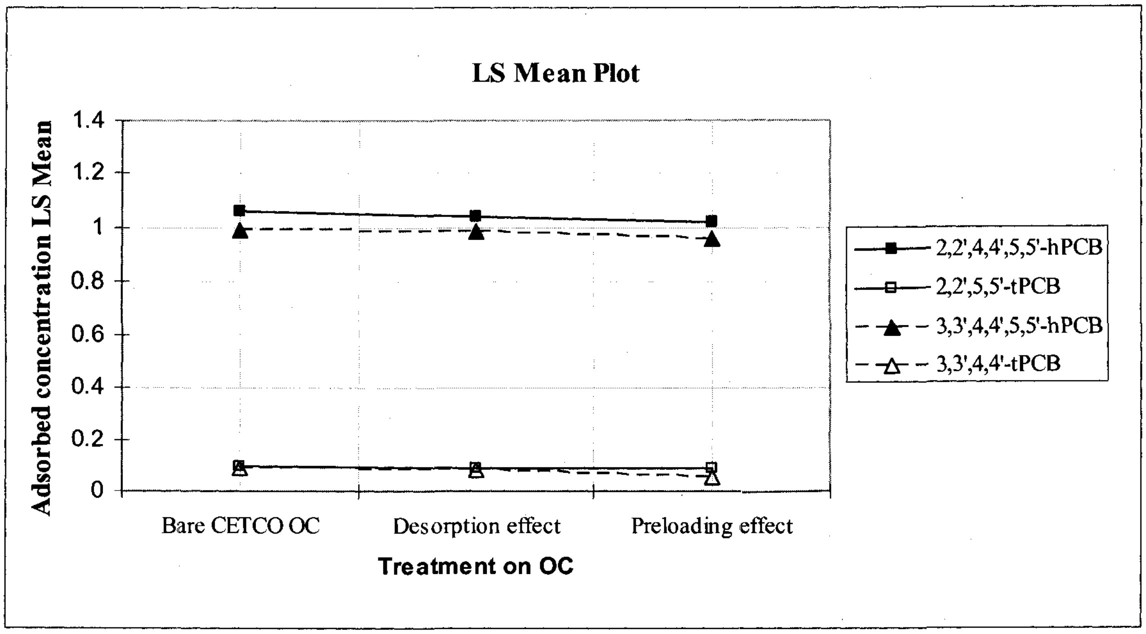
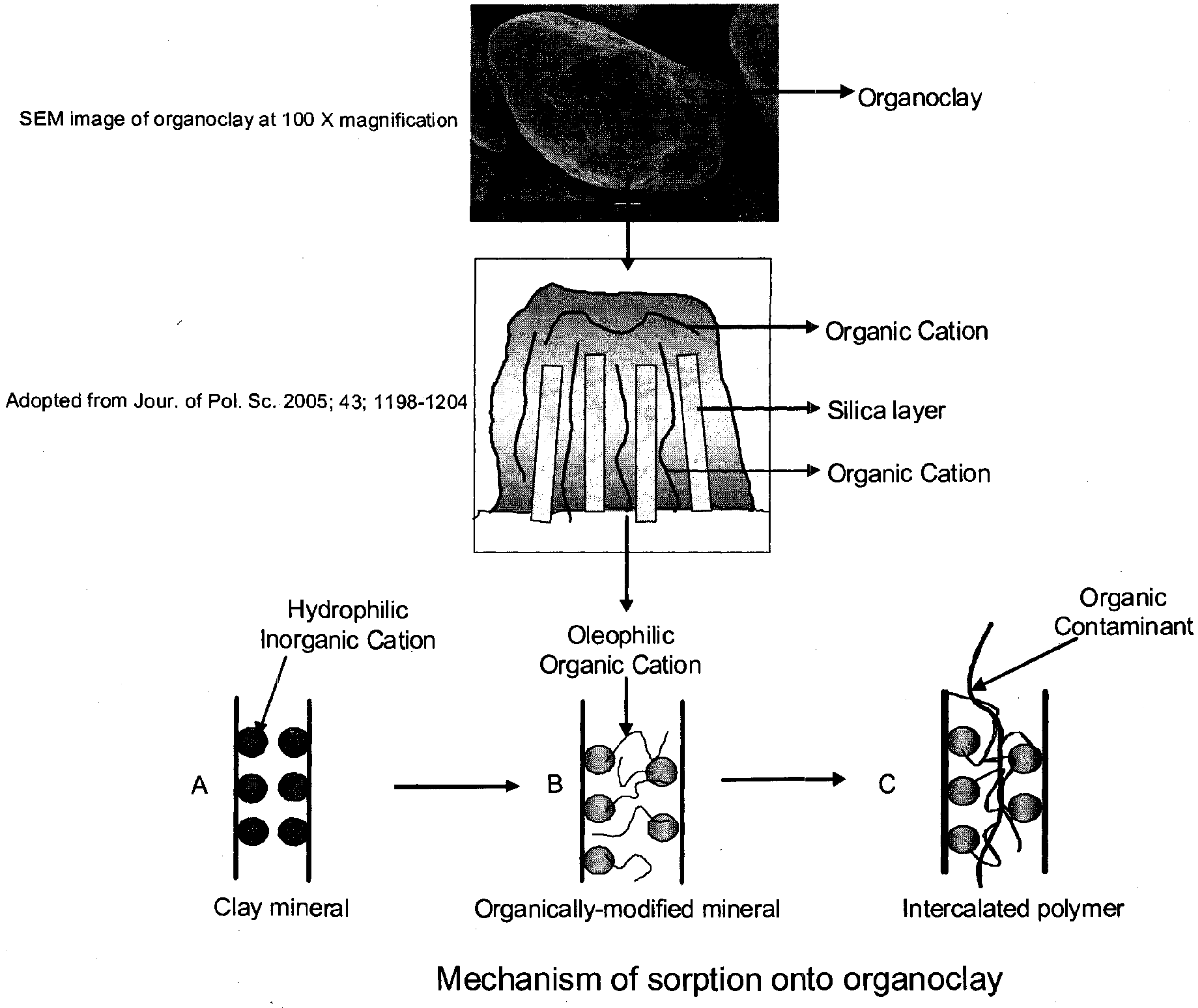


Figure 3.7: Least square means plot for adsorption of tetra- and hexa- chlorinated congeners on CETCO organoclay

Table 3.8: LSMeans Differences Student's t at α=0.050 and t=2.03 for performance of CETCO organoclay for tetra- and hexa- chlorobiphenyl

Level					Least Sq Mean
2,2',4,4',5,5'-hPCB,Bare AC	A				1.056
2,2',4,4',5,5'-hPCB,Desorption effect	A	B			1.036
2,2',4,4',5,5'-hPCB,Preloading effect	A	B			1.019
3,3',4,4',5,5'-hPCB,Bare AC	A	B			0.988
3,3',4,4',5,5'-hPCB,Desorption effect	A	B			0.984
3,3',4,4',5,5'-hPCB,Preloading effect		B			0.957
2,2',5,5'-tPCB,Bare AC			C		0.095
2,2',5,5'-tPCB,Desorption effect			C		0.091
3,3',4,4'-tPCB,Bare AC			C		0.088
2,2',5,5'-tPCB,Preloading effect			C		0.085
3,3',4,4'-tPCB,Desorption effect			C		0.082
3,3',4,4'-tPCB,Preloading effect				D	0.054

The mechanism of sorption of organic contaminants onto organoclay can be explained on the basis of surfactant behavior of the organic cations. The organic contaminants are adsorbed on the oleophilic surface of organoclays due to hydrophobic interactions. The organic cations that are placed in between silica layers of the clay are capable of making micelles and thereby holding organic contaminants in that zone. If humic acid is present in the system then it competes with the target organic contaminant for available sites. Thurman et al. (1982) have reported the radius of gyration of aquatic humic substance to be 4.7- 33 Å corresponding to their molecular weight of 500 to > 10,000. Studies have also shown that depending on pH of the system the building units of humic acid of radial size ≤ 25 Å can be aggregated to make clusters with average radius of 400-500 Å (Oesterberg et al., 1992). While preloading, the larger humic acid molecules that come in contact with the surface of organoclays first get adsorbed to it by hydrophobic interaction with organic cations in the oleophilic zone.



Adopted from Jour. of Pol. Sc. 2005; 43; 1198-1204

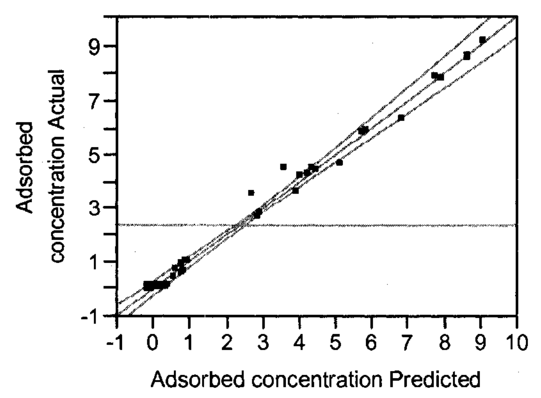
Figure 3.8: Mechanism of sorption of organoclay

These giant humic acid molecules and their aggregates then interfere with the sorption of PCBs by blocking their way to the surfactant moieties. These PCB molecules can adsorb to the humic acid molecules that are already attached to the organoclay surface depending on their partition coefficients (K_{DOC}) as mentioned in table 3.2. In desorption studies 2-chlorobiphenyl did not show any affect from humic acid added in the system after its adsorption but there was some effect in the case of tetra- and hexachlorinated congeners. This fact can be supported by lower K_{DOC} of 2-chlorobiphenyl as compared to that of higher chlorinated congeners that allows its preferable sorption onto organoclay surface.

Additional Information

Model 1 detail:

Actual by Predicted Plot



P<.0001 RSq=0.99 RMSE=0.3259

Analysis of Variance

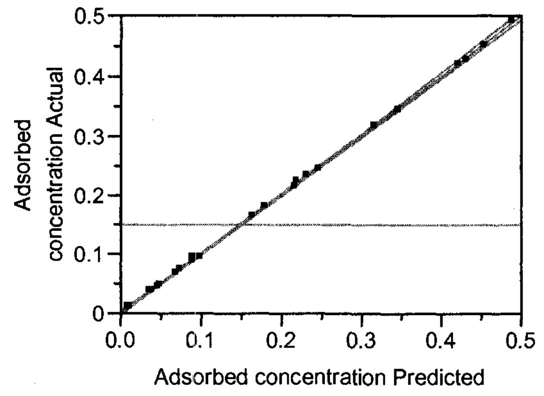
Source	DF	Sum of Squares	Mean Square	F Ratio
Model	17	367.85563	21.6386	203.7433
Error	27	2.86754	0.1062	**Prob > F**
C. Total	44	370.72317		<.0001*

Effect Tests

Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F
OC	2	2	0.10911	0.5137	0.6040
Treatment on OC	2	2	6.54440	30.8102	<.0001*
OC*Treatment on OC	4	4	0.59693	1.4051	0.2589
Loading rate	1	1	346.56433	3263.163	<.0001*
OC*Loading rate	2	2	1.79056	8.4297	0.0014*
Treatment on OC*Loading rate	2	2	11.03097	51.9324	<.0001*
OC*Treatment on OC*Loading rate	4	4	1.21933	2.8702	0.0421*

Model 2 detail:

Actual by Predicted Plot



P<.0001 RSq=1.00 RMSE=0.0029

Analysis of Variance

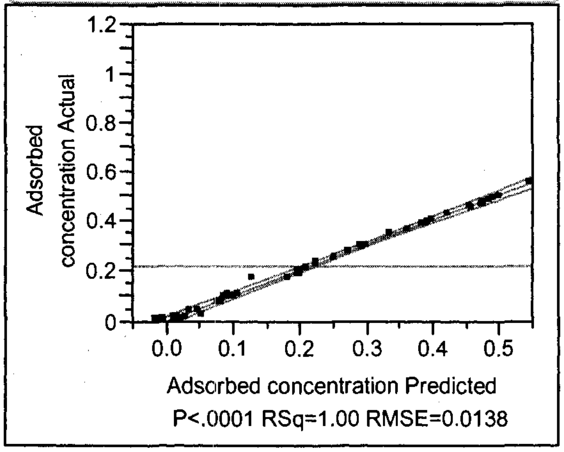
Source	**DF**	**Sum of Squares**	**Mean Square**	**F Ratio**
Model	13	0.66207551	0.050929	5981.288
Error	16	0.00013624	8.515e-6	**Prob > F**
C. Total	29	0.66221174		<.0001*

Effect Tests

Source	**Nparm**	**DF**	**Sum of Squares**	**F Ratio**	**Prob > F**
Type of OC	1	1	0.00000255	0.2992	0.5920
Treatment on OC	2	2	0.01206597	708.5376	<.0001*
Type of OC*Treatment on OC	2	2	0.00054977	32.2835	<.0001*
Loading rate	1	1	0.26588132	31226.15	<.0001*
Type of OC*Loading rate	1	1	0.00000273	0.3203	0.5793
Treatment on OC*Loading rate	2	2	0.01374250	806.9868	<.0001*
Type of OC*Treatment on OC*Loading rate	2	2	0.00075619	44.4048	<.0001*
Loading rate*Loading rate	1	1	0.00006313	7.4141	0.0150*
Loading rate*Loading rate*Type of OC	1	1	0.00001106	1.2992	0.2711

Model 3 detail:

Actual by Predicted Plot



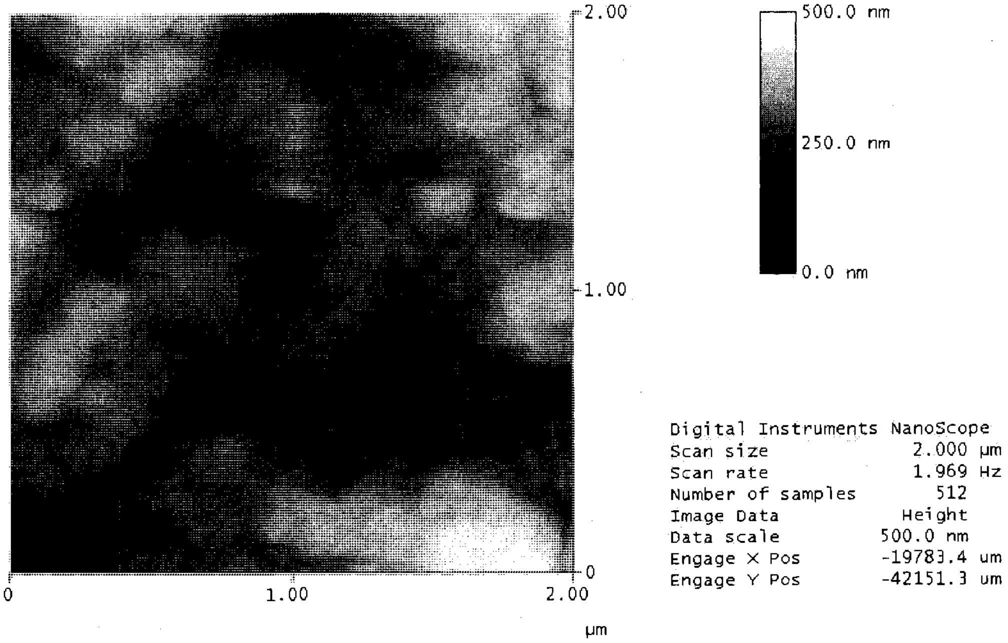
Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	26	1.6004990	0.061558	324.7787
Error	33	0.0062547	0.000190	**Prob > F**
C. Total	59	1.6067538		<.0001*

Effect Tests

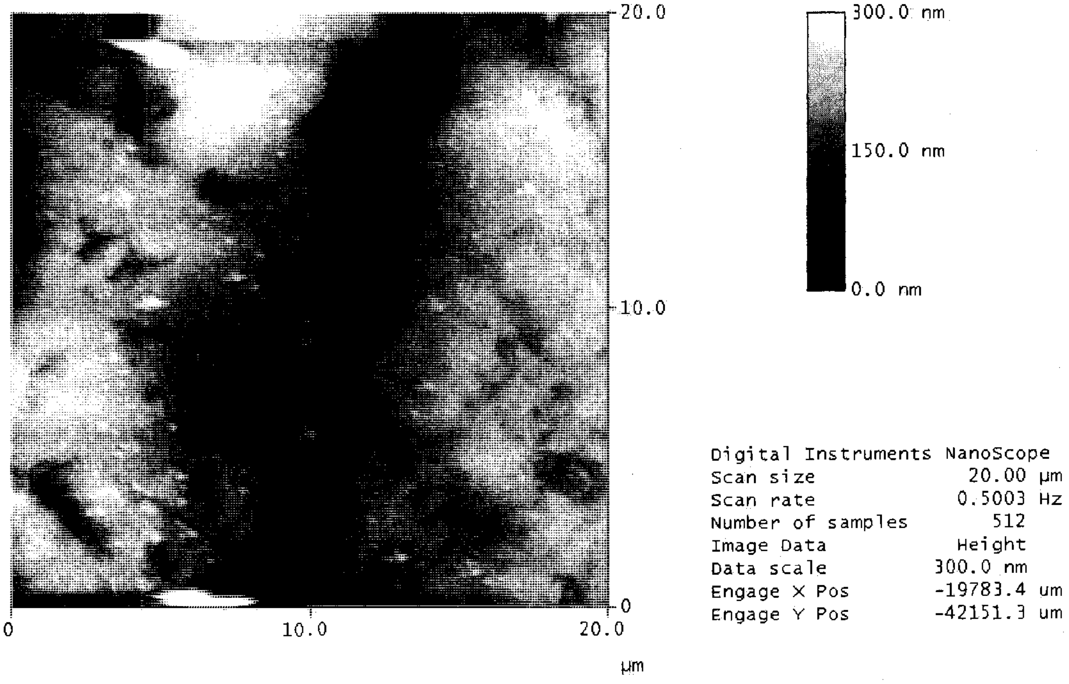
Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F
PCB congener	3	3	0.80704529	1419.326	<.0001*
Treatment on OC	2	2	0.00052366	1.3814	0.2654
PCB congener*Treatment on OC	6	6	0.00078664	0.6917	0.6578
Loading Rate	1	1	0.62613166	3303.476	<.0001*
PCB congener*Loading Rate	3	3	0.40555736	713.2413	<.0001*
Treatment on OC*Loading Rate	2	2	0.00033598	0.8863	0.4218
PCB congener*Treatment on OC*Loading Rate	6	6	0.01206138	10.6060	<.0001*
Loading Rate*Loading Rate	1	1	0.00025379	1.3390	0.2555
Loading Rate*Loading Rate*Treatment on OC	2	2	0.00188635	4.9762	0.0129*

Atomic Force Micrographs produced to demonstrate the topography of organoclays



Digital Instruments NanoScope	
Scan size	2.000 µm
Scan rate	1.969 Hz
Number of samples	512
Image Data	Height
Data scale	500.0 nm
Engage X Pos	-19783.4 um
Engage Y Pos	-42151.3 um

AFM image of CETCO organoclay



Digital Instruments NanoScope	
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Image Data	Height
Data scale	300.0 nm
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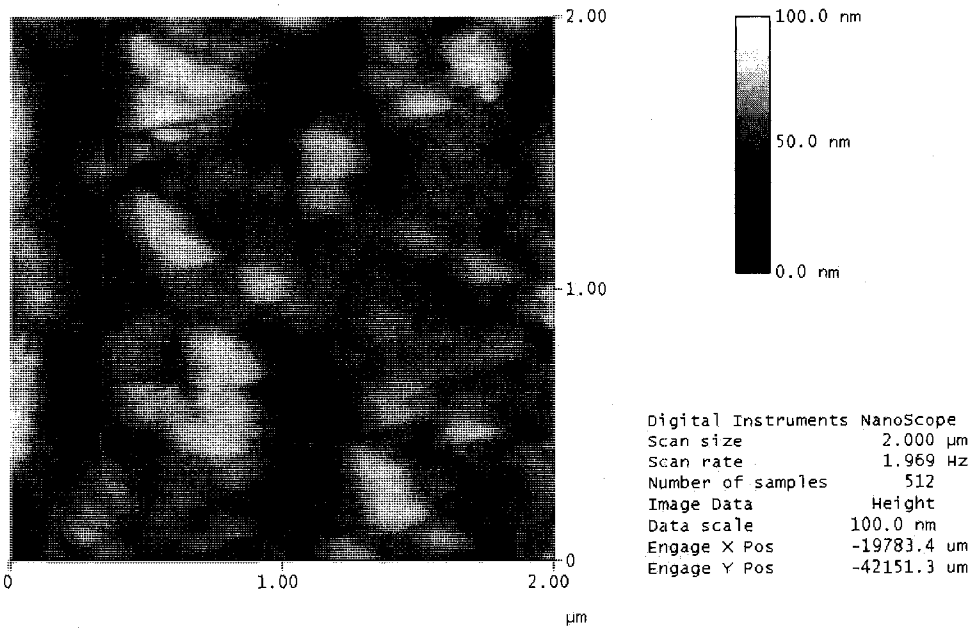
Engage Y Pos	-42151.3 um

AFM image of Polymer Ventures organoclay



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Digital Instruments NanoScope
Scan size              2.000 µm
Scan rate              1.969 Hz
Number of samples       512
Image Data            Height
Data scale          100.0 nm
Engage X Pos      -19783.4 um
Engage Y Pos      -42151.3 um
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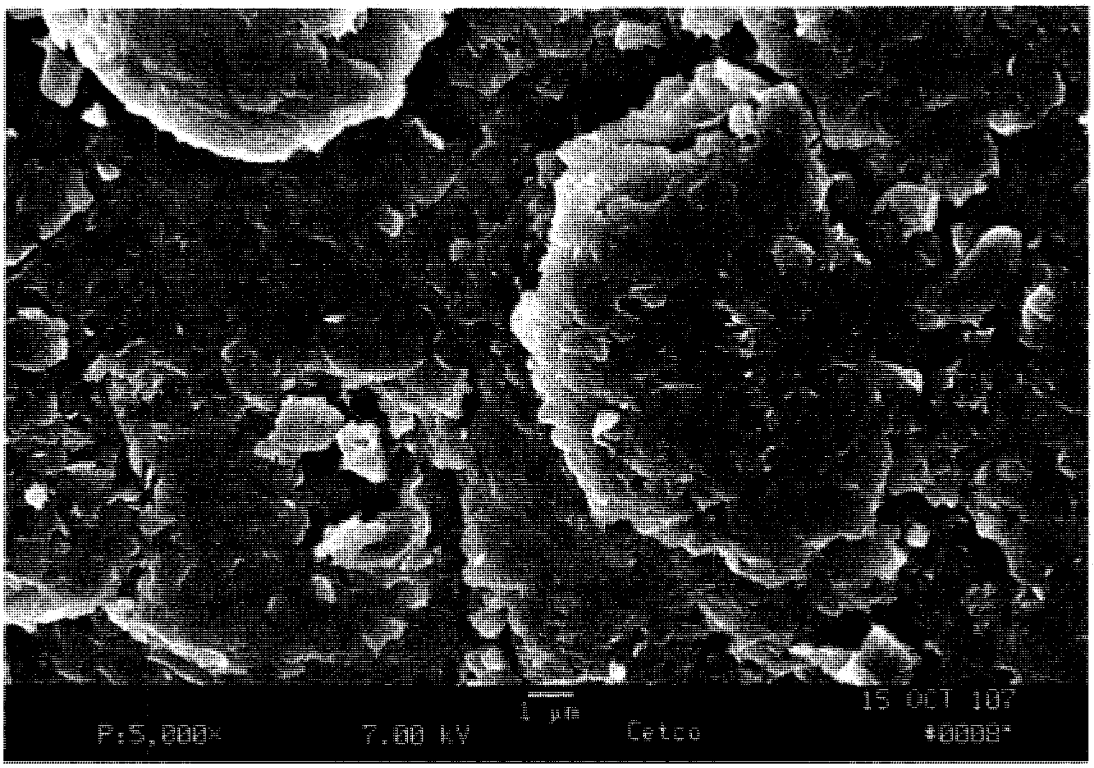
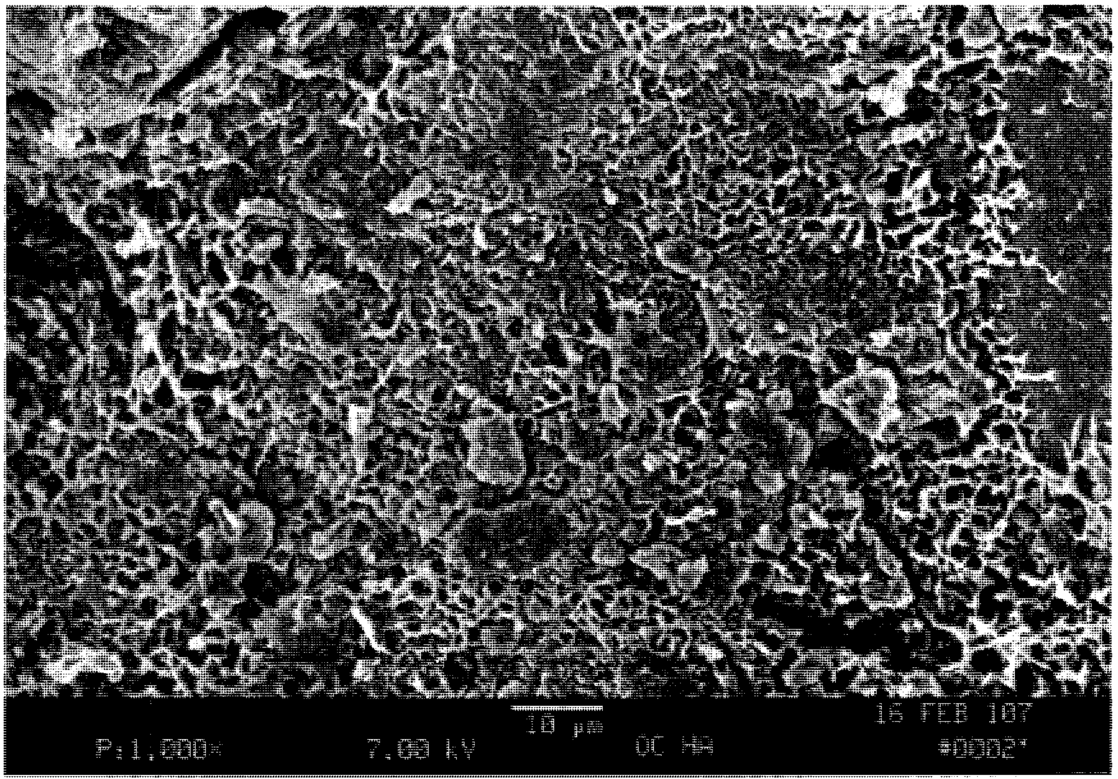
AFM image of Biomin Inc. organoclay

This part of analysis was done in Mechanical Engineering with help of Dr. Todd Gross, Professor and Chair, Dept. of Mechanical Engineering, University of New Hampshire.



SEM of bare CETCO organoclay



SEM of CETCO organoclay preloaded with 1g/L humic acid solution

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CHAPTER 4

COMPARISON OF PERFORMANCE OF ACTIVATED CARBON AND ORGANOCLAY AS REACTIVE CAP SORBENTS FOR ADSORPTION OF PAH IN PRESENCE OF HUMIC ACID

Abstract

Coconut shell activated carbon and bentonite based organoclay were compared as reactive cap sorbents that can be used for sequestration of Polycyclic Aromatic Hydrocarbon (PAH) in riverine and marine environment. The presence of natural organic matter (NOM) plays an important role in the fate and transport of organic contaminants in sediments. Therefore, research was conducted to determine the adsorption capacities of sorbents in the presence and absence of humic acid that constitutes an important fraction of NOM. PAHs selected for this study were naphthalene, phenanthrene and pyrene that are readily diffusible in sediment pore waters. Kinetic experiments were conducted to determine the equilibration time required for adsorption of pyrene and phenanthrene onto selected sorbents and to estimate the effects of humic acid. Based on the equilibration time isotherm studies were conducted to determine the adsorption capacities of sorbents for naphthalene, phenanthrene and pyrene. Effect of humic acid was determined in two ways: (i) by preloading the sorbents with humic acid prior to the spiking of PAHs and (ii) desorption caused by humic acid on already adsorbed PAHs. Preloading effects were used to simulate the typical site

conditions and desorption to simulate the long term exposure to NOM present in the system.

Introduction

Polycyclic Aromatic Hydrocarbons (PAHs) are a class of ubiquitous, non-polar organic contaminants that are of major environmental concern because of their toxicity and potential carcinogenity. The concentrations of PAHs in soil and sediments have been found to be increasing with increasing urbanization in the last 20-40 years (Van Metre et al. 2000). The sorption of PAHs to soil and sediment is highly controlled by the presence of organic matter that plays an important role in the fate and transport of PAHs (Means et al. 1980; Liang et al. 2006). The tendency of PAHs to interact with soil and sediment causes slow release of these contaminants into sediment pore water (McGroddy et al. 1995; Maruya et al. 1996). This partitioning behavior of PAHs to solid matrices and their reduced availability to the pore water depend on the presence of organic carbon matrices (such as soot particles) that enhance binding and source of PAHs (pyrogenic/ surface run off) (Maruya et al. 1996). The availability of PAHs in pore water is reliant not only on the solid matrices of sediments but also on the size of the PAH molecules. PAH molecules larger than 10 Å or adsorbed on suspended particles are not easily available for uptake as compared to the small ringed PAHs (including naphthalene, phenanthrene and pyrene) that can diffuse easily in sediment pore water (Williamson et al. 2002). Therefore, this study is focused on adsorption of easily diffusible PAHs including naphthalene, phenanthrene and pyrene on to activated carbon and organoclay in the presence of humic acid. Humic acid, which is complex, heterogeneous and refractory in nature, constitutes a major part of soil and sediment organic matter (Liang et al. 2006).

Sediments contaminated with hydrophobic organic contaminants (HOCs) such as PAHs can be treated using ex-situ treatment methods such as dredging and disposal or by in-situ treatment methods such as monitored natural recovery (MNR) or capping (reactive/ non-reactive) technology. The most common and in-use technologies are dredging followed by treatment and disposal and MNR. In-situ treatment methods such as reactive capping technologies are under intense research for their effective potential use. Reactive capping can be established by direct mixing of reactive material in the sediments by placement of loose granular material or by introducing reactive core mat consisting of a geotextile impregnated with reactive material in the riverine or marine environment. This research is mainly focused on evaluating sorbents that can be used in the reactive core mat for in-situ management of contaminated sediments.

Studies conducted by Zimmerman et al. (2004) added 3.4 wt % coal - based activated carbon to sediments as in-situ treatment method and showed 84% reduction in aqueous concentration of PAHs. Cornelissen et al. (2006) evaluated the effectiveness of activated carbon amendments and found that 2 wt % of activated carbon can significantly reduce the pore water concentrations of PAHs in strongly sorbing sediments that are rich in carbonaceous geosorbents. However, there can be reduction in the performance of activated carbon in the presence of natural organics such as humic and fulvic acids. The building unit of a humic acid molecules can be ≤ 25 Å and can form aggregates of average radii of 400-500 Å (Osterberg et al. 1992). These humic molecules that are larger than a target organic contaminants cannot enter the pore structure of activated carbon and may block the way of the target organic contaminants to the internal pore structure (Li et al. 2003; Quinlivan et al. 2005; Pignatello et al. 2006). Besides porosity another factor that plays an important role in adsorption of HOCs is surface chemistry of activated carbon. Based on these two properties (high porosity and hydrophobic surfaces) coconut shell activated carbon was selected for this research.

Another sorbent that was evaluated in this study is bentonite based organoclay. Organoclays are organically modified clays in which inorganic cationic counter ions are replaced by organic cations by an ion exchange process (Jayens and Boyd, 1991). These organic cations increase the interlayer spacing between the silica plates as well as create an oleophilic zone for sorption of organic contaminants (Carmondy at al, 2007; Dental et al., 1998). These organic cations behave like a surfactant and trap organic contaminants into their miceller structure. Studies conducted to use organoclay in soil remediation, groundwater purification, industrial waste water treatment and oil spills have shown good adsorption capacity of organoclays for chlorinated compounds and aromatic hydrocarbons (Zhao et al., 1998; Dental et al., 1998; Carmondy et al., 2007; Pernyeszi et al., 2006; Ake et al., 2003; Wiles et al., 2005). Zhao et al. (1998) have shown that organoclay can perform better than activated carbon in the presence of humic acids depending on its composition. Therefore, in this research organoclay was selected as an alternative or amendment to be used alone or in combination with activated carbon for reactive capping of sediments. For its applicability in treatment of sediment porewater it was necessary to evaluate its performance in the presence of natural organics such as humic acids. Therefore, the sorption capacity of organoclay was evaluated for PAHs in the presence and absence of humic acid.

With the main objective of developing a reactive capping mat that contains a sorbent amendment mixture capable of sequestering persistent organic contaminants, this research is focused on evaluation of sorbents that can be used in this mat for its effective implementation. For this purpose the sorption affinity and capacity of coconut shell activated carbon was compared with that of bentonite based organoclay for PAHs in the presence and absence of humic acid.

Materials and Methods

Chemicals

PAHs selected for this study were naphthalene, obtained from Accustandard Inc. (New Haven, CT, USA), phenanthrene and pyrene, both of which were obtained from Ultra Scientific (North Kingstown, RI, USA) in neat form or dissolved in methylene chloride. Acenaphthene d-10 used as internal standard and 2-fluorobiphenyl used as surrogate standard were also purchased from Ultra scientific (North Kingstown, RI, USA). Humic acid was obtained from Sigma-Aldrich (St. Louis, MO, USA) in the form of sodium salt. Sodium azide used in the experiments to avoid biological contamination was purchased from EMD Chemicals Inc. (San Diego, CA, USA). Sodium sulfate anhydrous used in sample preparation to remove chemically bound water prior to GC/MS analysis was obtained from Fisher Scientific (Morris Plains, NJ, USA). Ultra high purity chemicals and GC-grade solvents used throughout experimentation were obtained from Fischer Scientific (Agawam, MA, USA).

Sorbent material

Activated carbon: OLC 12 x 40 a coconut shell based activated carbon used in this research, was obtained from Calgon Carbon Corporation (Pittsburg, PA, USA). Coconut shell activated carbon was selected because of its high microporosity and wider use in trace organics removal.

Organoclay: PM 199 bentonite based organically modified clay was obtained from CETCO (Arlington Heights, IL, USA). Hydrogenated tallow based quaternary amines have been used to increase the inter-layer spacing of bentonite clay which was found to be about 35.74 Å with about 19% organic content. Because of its high hydrophobicity, PM 199 was used in the experiments as obtained from CETCO with no modification.

Experimental Procedures

All the experiments including kinetic and isotherm studies were conducted in separate batches of 125 ml in the presence and absence of humic acid. The stock solutions of naphthalene, phenanthrene and pyrene were prepared separately in methanol because there is no measurable effect of methanol on sorption capacity of organoclay (Lee et al., 2005) and activated carbon (Dowaidar et al., 2007). This stock solution was used for spiking the samples prepared with deionized (DI) water or humic acid solution. In kinetic experiments humic acid interferences were determined by preloading the sorbents with humic acid. In isotherm studies the effect of humic acid was determined by preloading the sorbents with humic acid prior to the spiking of PAHs and desorption of contaminants (once adsorbed) was determined by spiking the humic acid in the system after PAHs were allowed to adsorb on sorbent for selected equilibration time.

Preloading sorbents: The preloading of sorbents including organoclay and activated carbon was done by 1g L^{-1} humic acid stock solution having 10% sodium azide to avoid biological growth. The preloading was done in separate batches having 0.1 g of sorbent in 125 ml flask. Sorbents were soaked in the humic acid solution and kept on continuous mixing for 48 hours on rotary shaker at 150 rpm. After preloading the same flask containing preloaded sorbent and humic acid solution was used as such for further experimentation.

Kinetics experiments:

The kinetic studies were conducted to estimate the equilibration time required for adsorption of phenanthrene and pyrene onto activated carbon and organoclay in the presence and absence of humic acid. The experiments were conducted with bare sorbents in de-ionized water and preloaded samples in humic acid solution for 15 days.

The concentration used for phenanthrene was 1.6 mg L^{-1} and 0.16 mg L^{-1} for pyrene. The amount of sorbent was kept constant at 0.1 g. Separate batches were prepared for phenanthrene and pyrene for bare sorbents (organoclay and activated carbon) and preloaded sorbents. All the samples were kept on continuous mixing at 150 rpm until sampling was done.

Isotherm experiments:

Isotherm experiments were conducted at different loadings of selected PAHs including naphthalene, phenanthrene and pyrene for organoclay and activated carbon in the presence and absence of humic acid. These experiments were conducted separately for each PAH for both the sorbents for equilibration time as obtained from pyrene kinetics with continuous mixing at 150 rpm on rotary shaker. Pyrene was the biggest (4-ringed structure) compound among three selected PAHs and had a longer equilibration time than phenanthrene in the presence of humic acid therefore equilibration time was selected on the basis of pyrene kinetics in the presence of humic acid. The effect of humic acid was determined by preloading the sorbents or by spiking humic acid after adsorption of PAHs. For determination of sorbent adsorption capacities, experiments were conducted with bare sorbents in de-ionized water spiked with different concentrations of PAHs (table 4.1). To determine the effect of preloading sorbents were preloaded with humic acid prior to the spiking of PAHs and were kept in the same humic acid solution used for preloading. After equilibration sampling was done for both bare sorbents and preloaded sorbent samples. After sampling, bare sorbent samples were spiked with humic acid to obtain the same concentration of humic acid as used for preloading (1 g L^{-1}) to determine the desorption effects. The samples were again kept for continuous mixing for the same equilibration time.

Isotherm studies for bare activated carbon: Due to very high adsorption capacity of activated carbon for all selected PAHs it was difficult to determine the actual behavior of activated carbon at low concentrations of PAHs while maintaining the spiked concentrations below the water solubility limits. To estimate the adsorption capacity of activated carbon it was necessary to load the activated carbon with sufficiently high concentrations of PAHs. Therefore, separate systems were prepared having 0.1 g bare activated carbon in de-ionized water and spiked with five different concentrations of PAHs within the solubility limit as done before. These experiments were also conducted separately for each PAH (naphthalene, phenanthrene and pyrene) but spiking was done three times at every 72 hours duration using same concentrations each time in order to obtain the final spike concentration to be thrice as used in the first set of isotherm studies (table 4.1). After third spiking all the samples were kept on continuous mixing on rotary shaker at 150 rpm for equilibration time of 10 days.

Sample Extraction and Analysis:

All the samples were extracted with surrogate solvent having 2-fbp as surrogate standard in methylene chloride. The ratio of sample volume to surrogate solvent (1:2) was kept the same for all the samples. From each batch two sub-samples were extracted in order to estimate any kind of deviation in the extraction method. All the samples were mixed thoroughly with surrogate solvent for 30 seconds three times at duration of 30 seconds each and then stored at 4° C for at least 24 hours. The surrogate recoveries obtained were high in the range of 70 – 130% using this extraction method. The extracted samples solvent was then restored and passed through sodium sulfate prior to GC vial preparation to avoid presence of water in any form. The filtered samples were then taken into GC vials and mixed with internal standard Acenaphthene-d10 followed by GC/MS analysis.

GC/ MS analysis: All the extracted samples were analyzed using internal standard method on 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-5ms), 30 m long, 0.25 mm ID and 0.5 µm thick. The ion-trap was operated in selected scan mode (MS/MS) for each selected PAH. The column temperature was programmed at 80° C with hold time of 2 min followed by a temperature ramp up to 315 ° C at the rate of 15° C - 30° C with final held time of 2 minutes depending on the PAH.

Results and Discussions

Kinetic studies:

Figure 4.1 shows the adsorption kinetics of phenanthrene and pyrene adsorption on organoclay and activated carbon in the presence and absence of humic acid. Figure 4.1A-B represents the kinetics of phenanthrene adsorption on organoclay and activated carbon, respectively. In the case of organoclay the effect of humic acid was found to be less significant and reduced with time as compared to that of activated carbon. For both type of sorbents equilibration time for phenanthrene adsorption was found to be around 72 hours which was approximately the same for organoclay preloaded with humic acid but it was approximately 120 hours for activated carbon preloaded with humic acid.

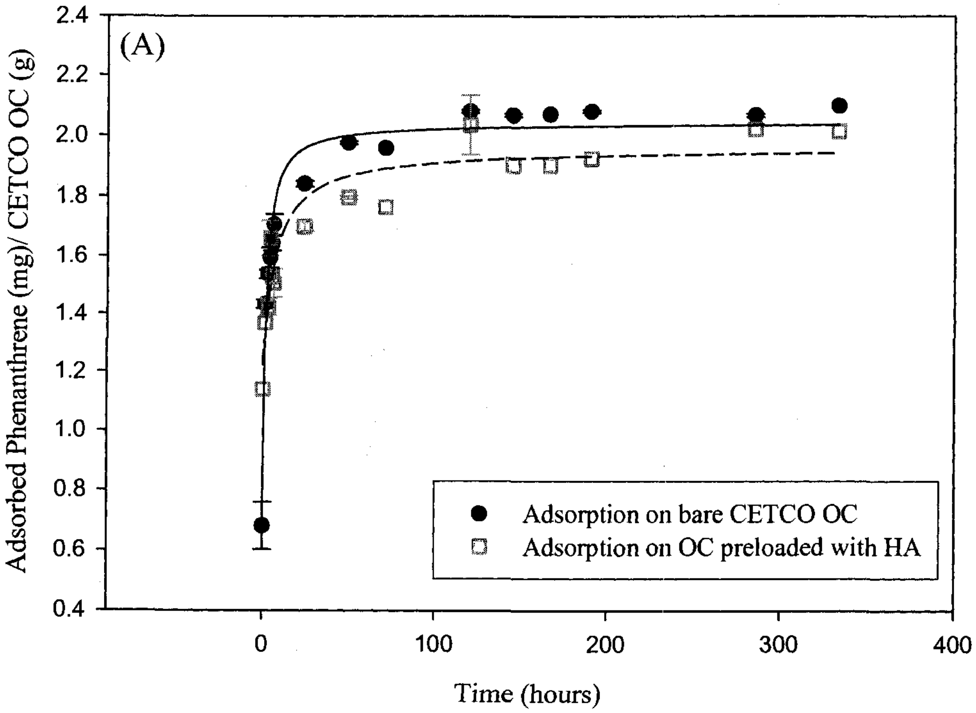
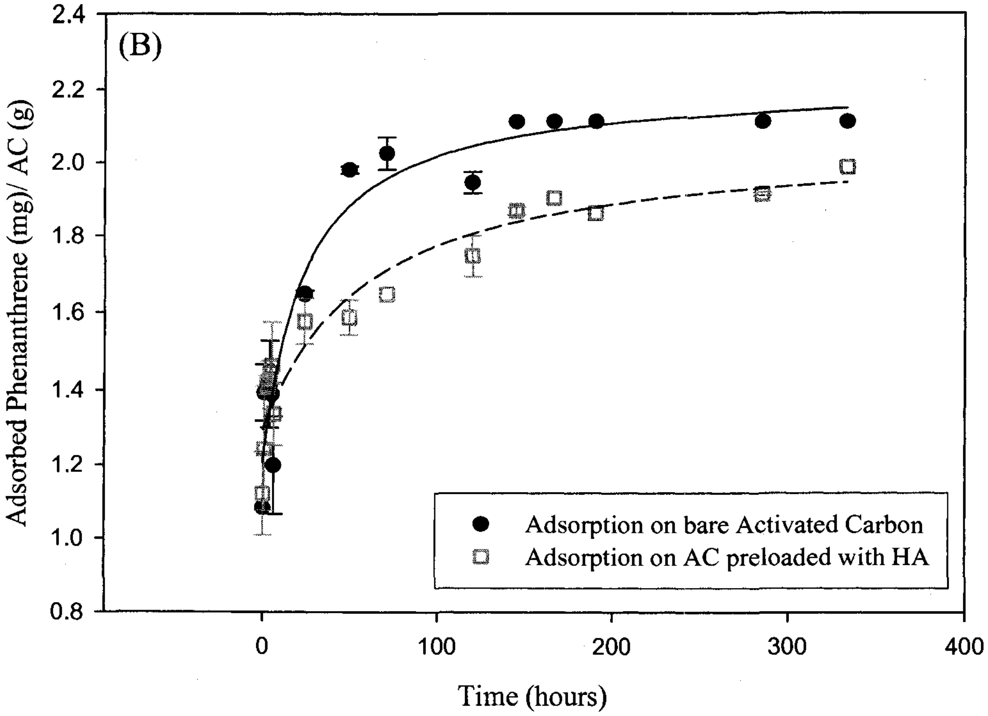


Figure4.1A: Kinetics: Phenanthrene adsorption on organoclay



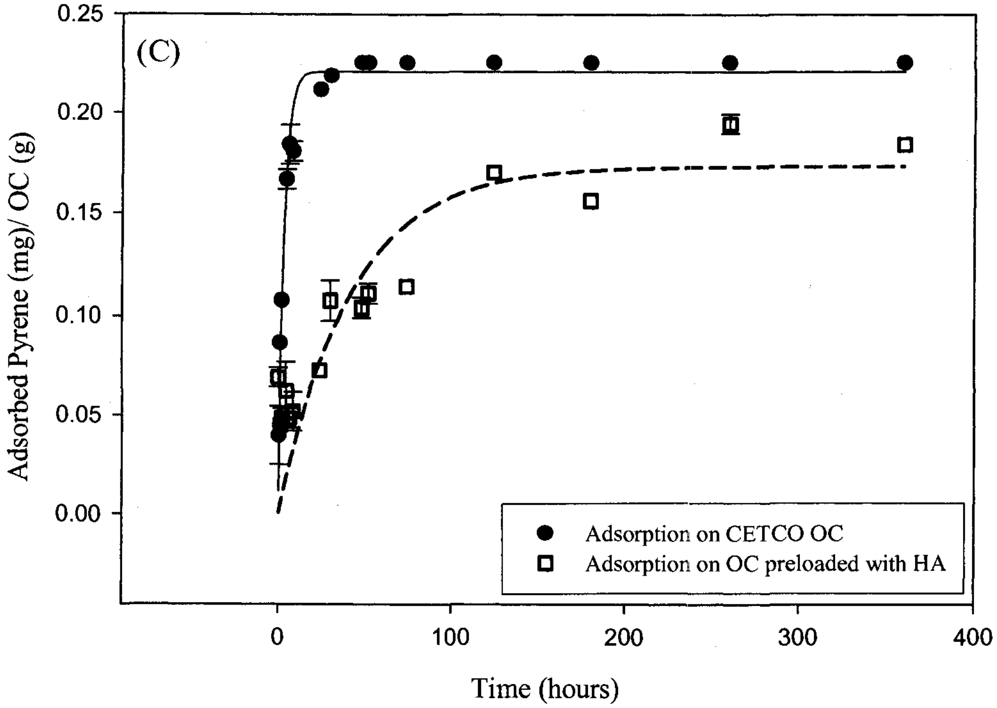


Figure4.1B-C: Kinetics of adsorption: (B) Phenanthrene adsorption on activated carbon (C) Pyrene adsorption on organoclay

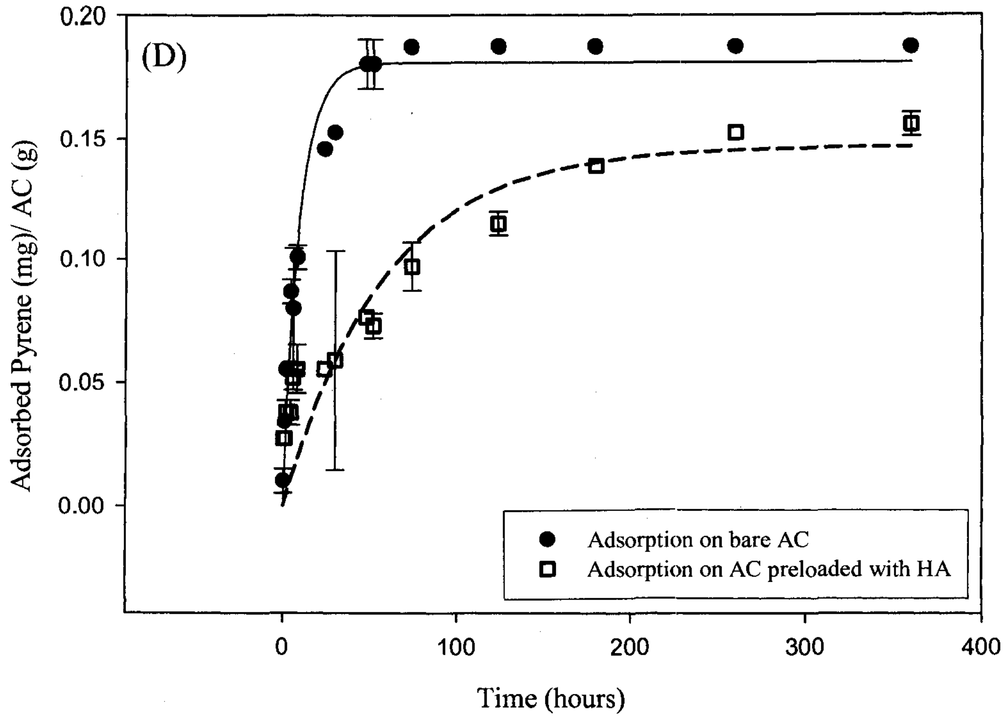


Figure4.1 D: Kinetics: Pyrene adsorption on activated carbon

Figure 4.1 C-D shows kinetics of pyrene adsorption on organoclay and activated carbon, respectively. In the case of pyrene adsorption capacity of organoclay was found to be higher than that of activated carbon and the effect of preloading was also found to be significant in the case of activated carbon. In the case of pyrene also, equilibrium for bare sorbents was achieved around 72 hours but in the presence of humic acid equilibration time was found to be around 100 hours for organoclay and around 200 hours for activated carbon. Therefore, an equilibration time of 5 days was selected for isotherm studies of organoclay for all selected PAHs and 9 days for activated carbon. The delaying effect of preloading the sorbents with humic acid can be attributed to the pore blockage effect on activated carbon and blocking of interlayer spacing of organoclay due to the high loading of humic acid. The humic acid molecule that are ≤ 25

Å and are capable of making bigger aggregates of about 400 – 500 Å (Osterberg et al. 1992) can block porous structure of activated carbon (<4-250 Å given by Henning and Schafer) and 35.74 Å interlayer spacing between the silica layers of organoclay making internal pore structure of activated carbon and hydrophobic zone of organoclay less available to the target compounds. The target compounds then diffuse slowly through a reduced pore area into the available adsorption sites depending on their diffusivity, availability of sites and partition coefficients for humic acid (table 4.1).

PAH	† Minimal box dimension (A°)			††Molecular Diffusion Coefficient 10^5 D/(cm2 s-1) at 40° C	†††Log K_{OW}	††† Log K_{DOC} for humic acid	Isotherm Studies Concentration Range After Single Spiking (mg L^{-1})	Concentration Range After Triple Spiking (mg L^{-1})
	Length (L)	Breadth (B)	Depth (D)					
Naphthalene	8.9	7.2	3.1	1.06	3.3	3.05	0.8 - 40	2.4 - 120
Phenanthrene	11.5	7.7	3.1	0.495	4.44	3.85	0.08 - 2	0.24 - 6
Pyrene	11.4	9.5	3.1	0.49	5.19	4.46	0.008 – 0.2	0.024 – 0.6

† Williamson et al. (2002); †† Gustafson et al. (1994); ††† Poerschmann et al. (1999)

Table 4.1: Details and Concentration of PAH compounds used in the study

Isotherm studies:

The adsorption capacity of activated carbon and organoclay for naphthalene, phenanthrene and pyrene was determined in the presence and absence of humic acid. The effect of humic acid was determined as preloading effect and desorption effect. As mentioned earlier, in the case of preloading both the sorbents were exposed to the high loadings of humic acid prior to the selected PAH adsorption. In the desorption study the selected PAHs were allowed to adsorb on sorbent surfaces followed by introduction of humic acid in the system to determine if PAHs, once adsorbed on sorbent surfaces, are prone to desorption. The adsorption capacities of both the sorbents and the preloading effect of humic acid on the adsorption capacities of both the sorbents were evaluated on the basis of K_d values (table 4.2) that were obtained as slopes by plotting aqueous equilibrium concentration on x-axis against adsorbed concentration on Y-axis. The adsorption capacities of the sorbents were also determined by using the Freundlich model in its non-linear form:

$$q_e = K_f\,(C_e^{1/n})$$

Here, qe is adsorbed concentration (mg g^{-1}), Kf is Freundlich Isotherm constant, Ce is equilibrium concentration (mg L^{-1}) and 1/n is the Freundlich exponent which is dimensionless. Figure 4.2 shows Freundlich isotherms and actual trends of the adsorption isotherm curves for naphthalene, phenanthrene and pyrene adsorption on activated carbon and organoclay. In the case of activated carbon (Figure 4.2A, 4.2C and 4.2E) the data points obtained from both the isotherm studies were merged to obtain the trend of isotherm behavior for bare activated carbon over a wide range of concentrations.

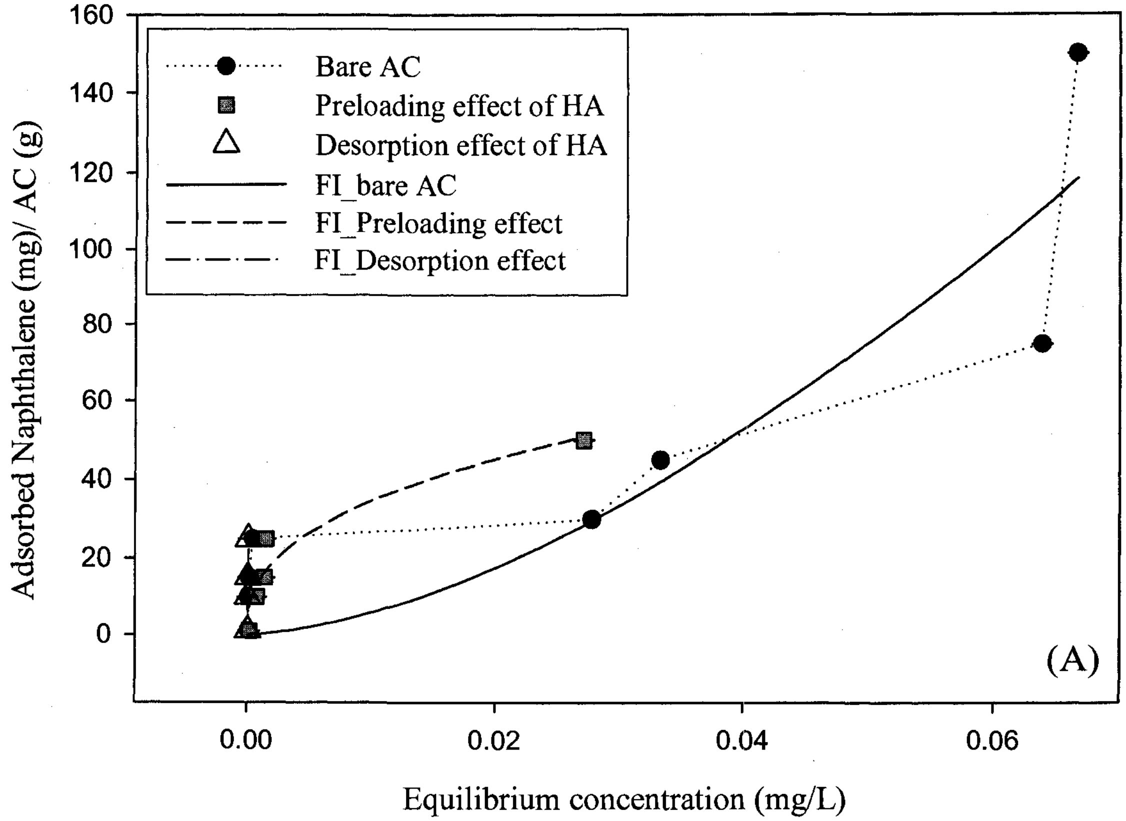
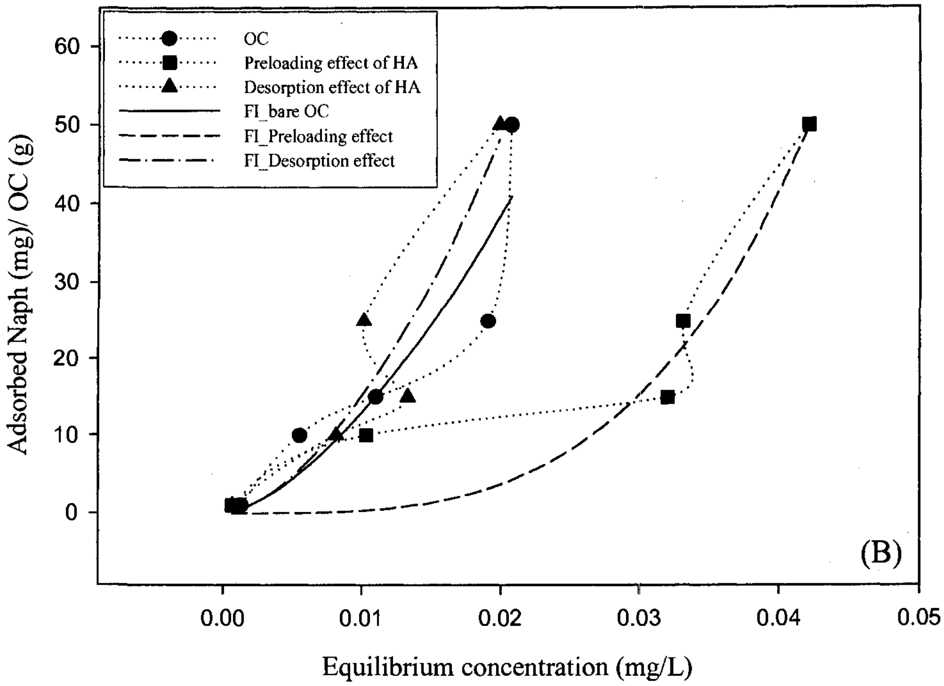


Figure 4.2 A: Freundlich Isotherms and actual trend of curves for adsorption on bare sorbents and preloading and desorption effect of humic acid: Naphthalene adsorption on activated carbon



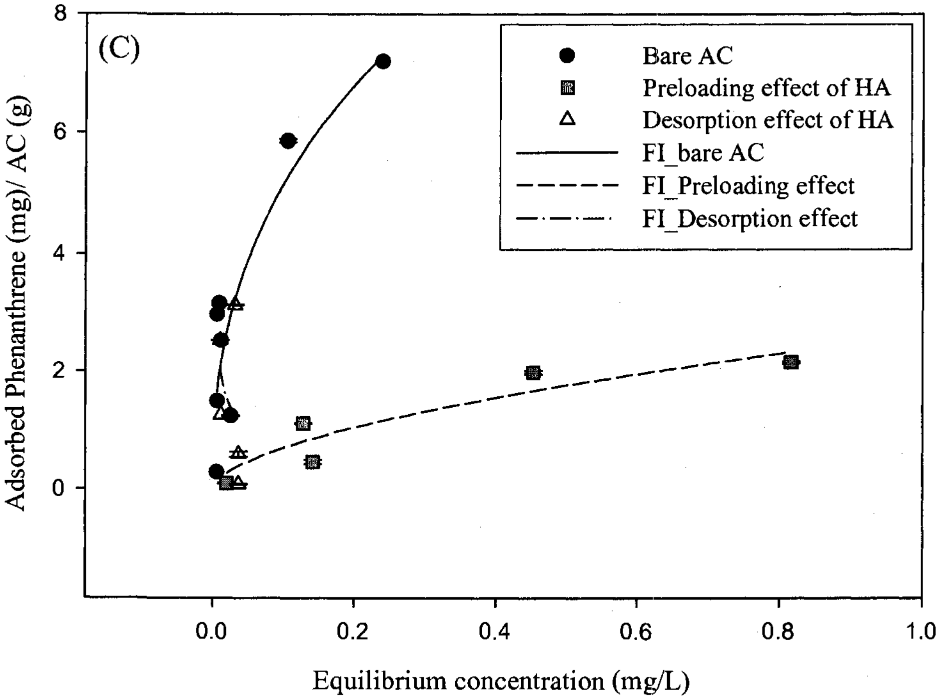


Figure 4.2 B-C: Freundlich Isotherms and actual trend of curves for adsorption on bare sorbents and preloading and desorption effect of humic acid: (b) Naphthalene adsorption on organoclay (c) Phenanthrene adsorption on activated carbon

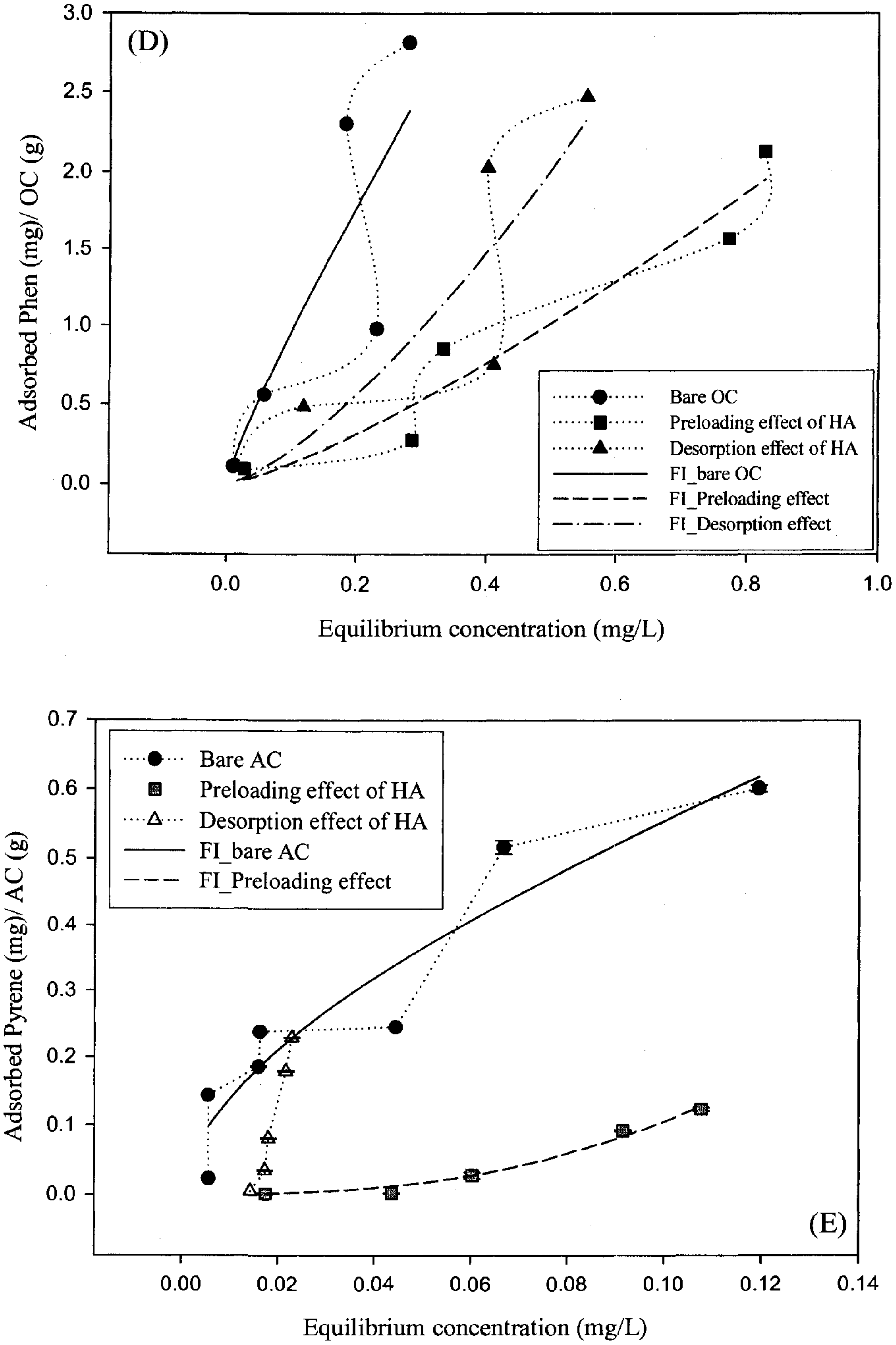


Figure 4.2 D-E: Freundlich Isotherms and actual trend of curves for adsorption on bare sorbents and preloading and desorption effect of humic acid: (d) Phenanthrene adsorption on organoclay (e) Pyrene adsorption on activated carbon

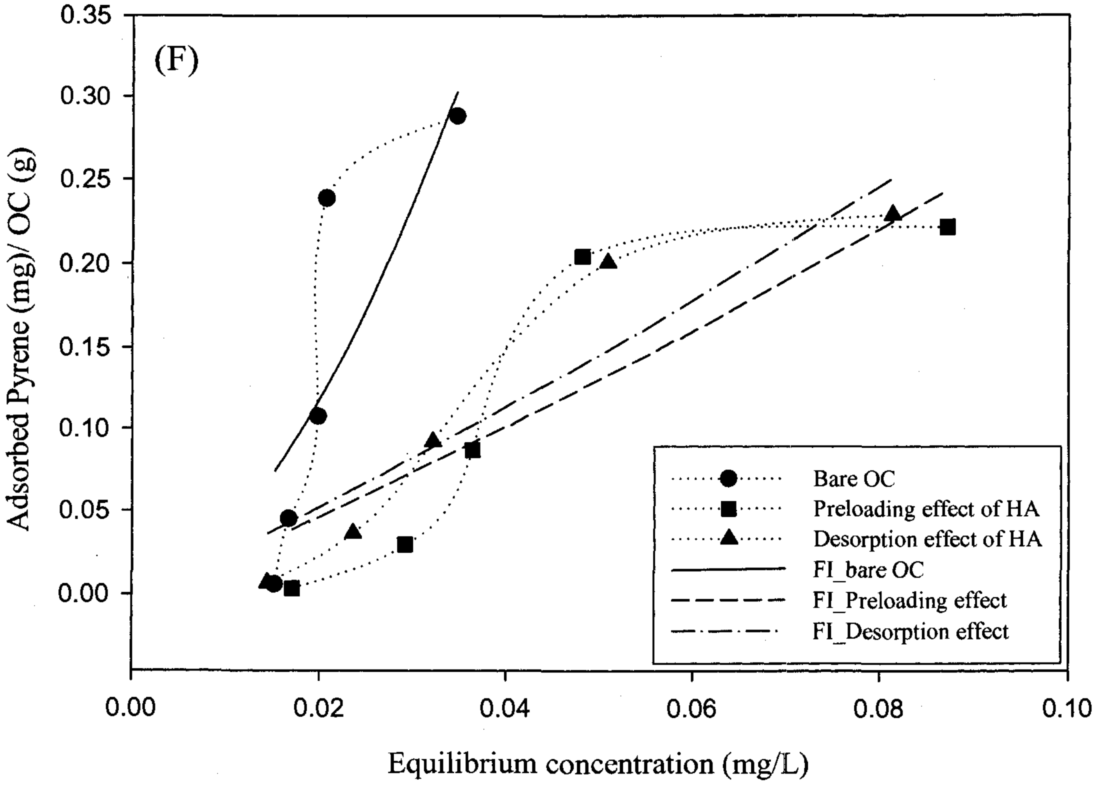


Figure 4.2 F: Pyrene adsorption on organoclay

The adsorption capacity of both the sorbents was found to be very high for naphthalene (table 4.2). The desorption effect of humic acid was not significant for both the sorbents but preloading effect was significant for organoclay (Figure 4.2 A-B). The preloading effect was not found to be as significant for naphthalene adsorption on activated carbon with only 3.4% reduction in comparison to organoclay that had 52.1% reduction in adsorption affinity.

	Adsorption Isotherm Constants		Freundlich Isotherm Constants			
	Kd (L g^{-1})		K_f ($mg^{[1-(1/n)]}$ $L^{(1/n)}$ g^{-1})		1/n	
CETCO OC	Adsorption on bare OC/ AC	Preloading effect	Adsorption on bare OC/ AC	Preloading effect	Adsorption on bare OC/ AC	Preloading effect
Naphthalene	2015.10	964.50	18230.11	3178855.65	1.57	3.49
Phenanthrene	10.58	2.43	7.26	2.49	0.88	1.30
Pyrene	13.42	3.29	93.98	3.75	1.71	1.12
Coconut shell AC						
Naphthalene	1503.30	1452.00	8691.36	203.68	1.59	0.38
Phenanthrene	24.59	2.51	12.84	2.62	0.39	0.57
Pyrene	4.59	1.46	2.22	44.53	0.60	2.63

Table 4.2: Adsorption Isotherm and Freundlich Isotherm Constants for adsorption of Naphthalene, Phenanthrene and Pyrene on Organoclay and Activated Carbon

Based on the K_d values the adsorption capacity was found to be higher for organoclay but the performance of both the sorbents was also compared statistically using JMP® 7 software. The variability chart was developed to indicate the trend of isotherms (linear/ non-linear) to select the factors for the model (details in additional information). The experimental factors considered in the model were the type of sorbent, treatment of sorbent (Bare Sorbent; Preloading and Desorption effects) and the loading rate (table 4.3). Due to the non-linear behavior of the isotherm curves in the variability chart, the quadratic term of loading rate was also included in the model.

Table 4.3: Specifications for statistical model 1

Model 1 specification:
Sorbent
Treatment
Sorbent*Treatment
Loading Rate
Sorbent*Loading Rate
Treatment*Loading Rate
Sorbent*Treatment*Loading Rate
Loading Rate*Loading Rate

The p-value in analysis of variance (ANOVA) was obtained to be < 0.0001 that indicated the selected model was significant (details in additional information). The F-test was also performed to determine the significance of each term selected in the model. The least square means plots of adsorbed concentrations were obtained to determine the difference in adsorption capacities of both sorbents and to determine the preloading and desorption effects on their performance. Statistically, the adsorption capacity of organoclay was found to be slightly higher than that of activated carbon. No desorption was noticed for both the sorbents but reduction in adsorption capacity of organoclay was noticed due to preloading with humic acid (figure 4.3A).

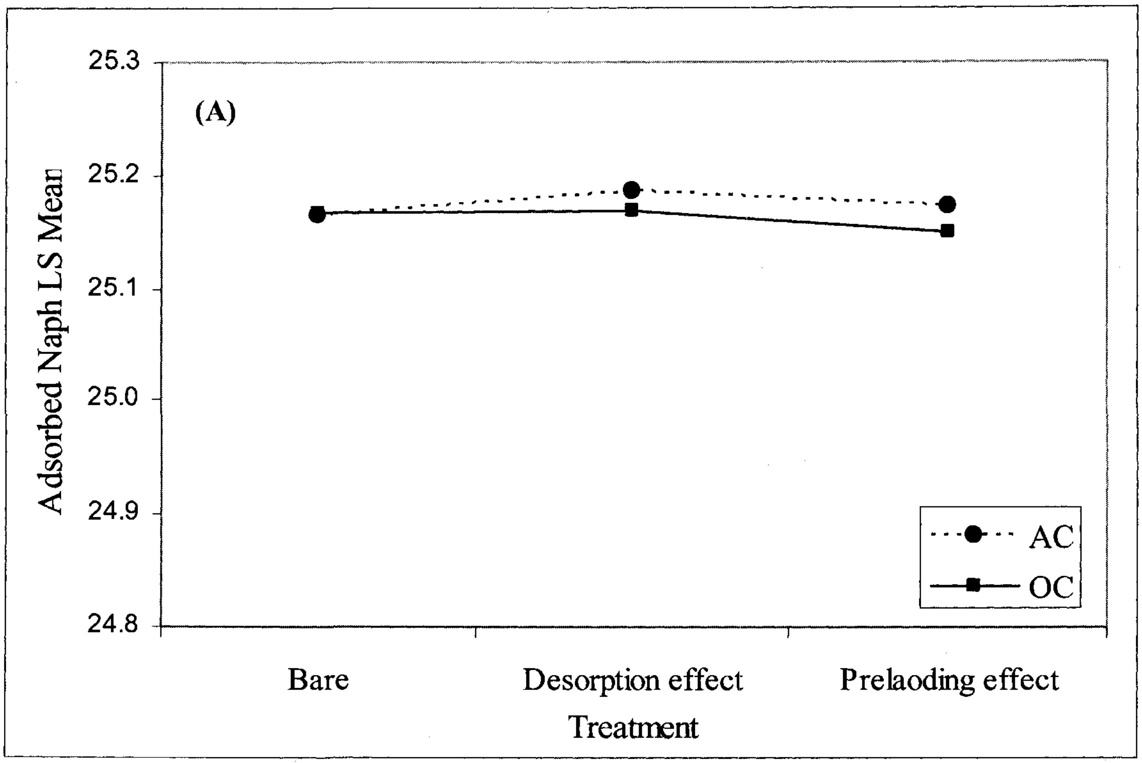


Figure 4.3 A: Least square means plot for comparison of performance of organoclay and activated carbon for adsorption of naphthalene

Figure 4.2C-D shows phenanthrene adsorption on activated carbon and organoclay respectively in the presence and absence of humic acid. The adsorption capacity of activated carbon was found to be higher than that of organoclay based on K_d values (table 4.2). The effect of preloading the sorbents with humic acid was significant for both activated carbon and organoclay. There was a 90 % reduction in adsorption capacity of activated carbon due to preloading with humic acid and a 77 % reduction for organoclay. There was no desorption in the case of activated carbon but slight desorption was noticed in the case of organoclay. The statistical analysis was also done to compare the performance of both the sorbents for phenanthrene adsorption. The model 2 was developed for phenanthrene as shown in table 4.4 (details in additional information).

Table 4.4: Specifications for statistical model 2

Model 2 specification:
Sorbent
Treatment
Sorbent*Treatment
Loading rate
Sorbent* Loading rate
Treatment* Loading rate
Sorbent*Treatment* Loading rate
Loading rate * Loading rate

The results showed higher adsorption capacity of activated carbon for phenanthrene as compared to that of organoclay (figure4.3B). The preloading effect of humic acid was found to be significant for both the sorbents. There was no desorption in the case of activated carbon but slight desorption was noticed in the case of organoclay.

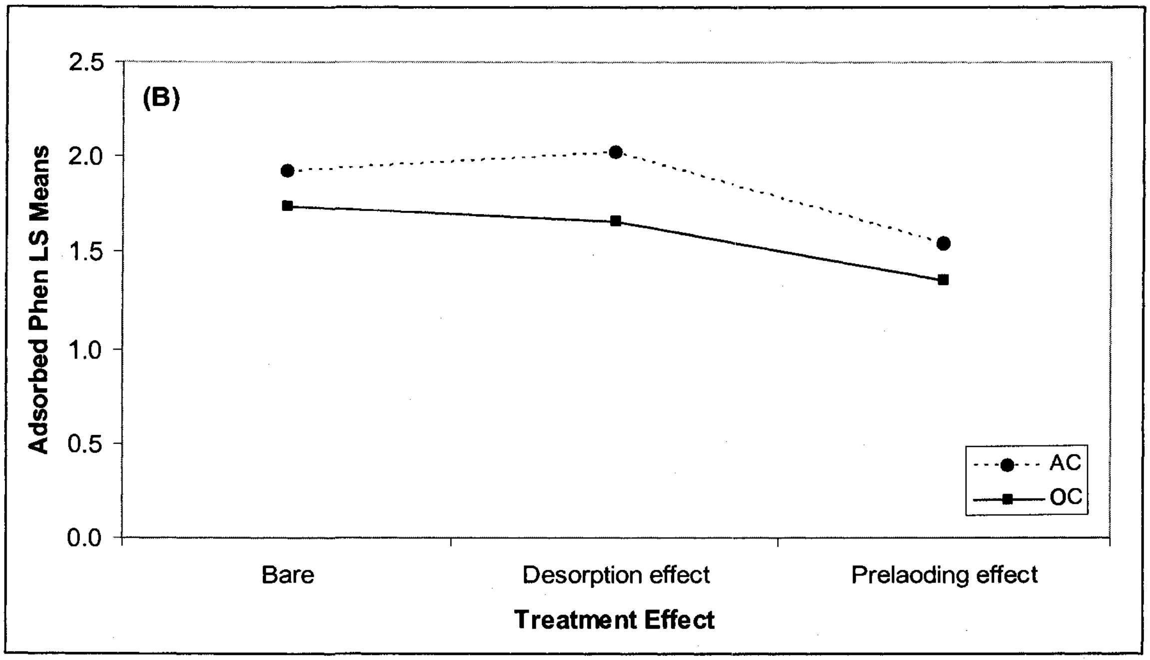


Figure 4.3 B: Least square means plot for comparison of performance of organoclay and activated carbon for adsorption of phenanthrene

Figure 4.2 E-F shows results for pyrene adsorption on activated carbon and organoclay with preloading and desorption effect of humic acid. The adsorption capacity of organoclay was found to be higher than that of activated carbon for pyrene based on the K_d values (table 4.2). The preloading effect was found to be significant for both the sorbents with 76% reduction in adsorption capacity of organoclay and 68% reduction in the adsorption capacity of activated carbon. The desorption effect was found to less in case of activated carbon as compared to organoclay. These results were also analyzed statistically (in the same way as for naphthalene and pyrene) by developing a full factorial model with main factors: the type of sorbent, treatment of sorbent (Bare Sorbent; Preloading and Desorption effects) and the loading rate (table 4.5). Due to non-linear trend of isotherms, quadratic term of loading rate was also considered in the model.

Table 4.5: Specifications for statistical model 3

Model 3 specifications:
Sorbent
Treatment
Sorbent*Treatment
Loading rate
Sorbent* Loading rate
Treatment* Loading rate
Sorbent*Treatment* Loading rate
Loading rate * Loading rate

The adsorption capacity of organoclay was found to be higher than that of activated carbon (figure 4.3C). The preloading effect was found to be significant for both the sorbents and the desorption effect was not significant for activated carbon as it was for organoclay.

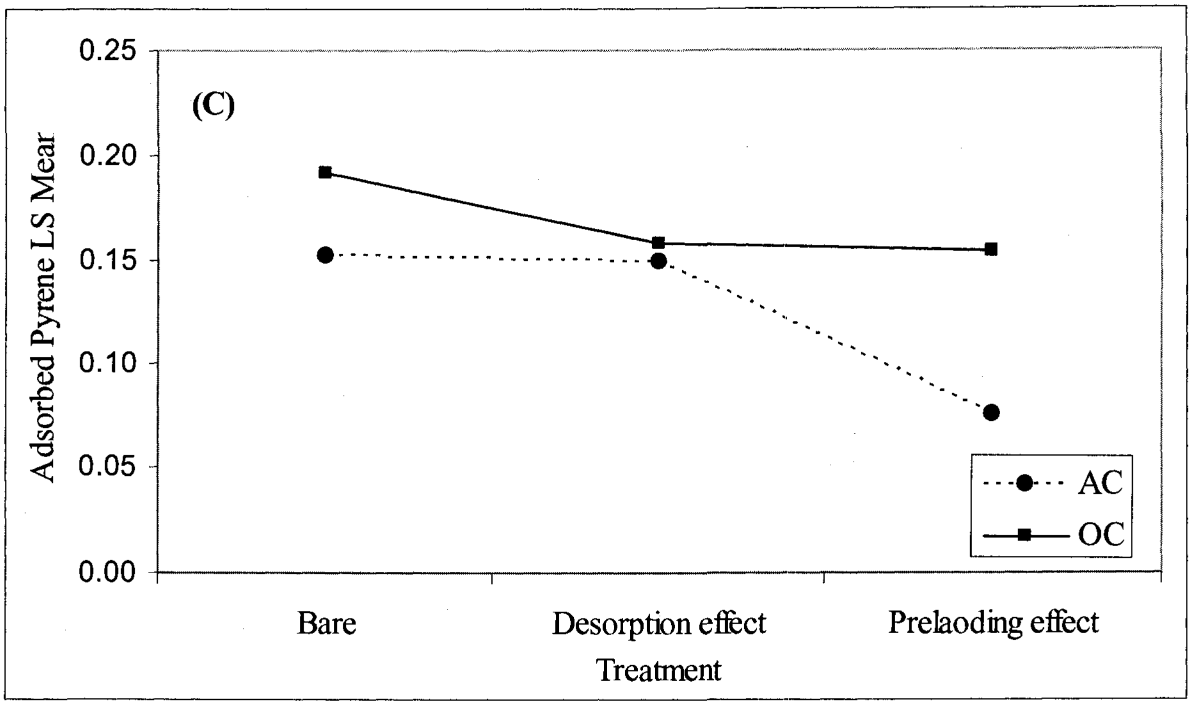


Figure 4.3 C: Least square means plot for comparison of performance of organoclay and activated carbon for adsorption: Pyrene

In isotherm studies, the adsorption capacity of activated carbon was greatest for naphthalene followed by phenanthrene and then for pyrene. For organoclay the maximum adsorption was found for naphthalene but it was very similar for phenanthrene and pyrene (table 4.2). Williamson et al. (2002) reported the minimal box dimensions (table 4.1) for all three PAHs used in this study showed that the length and breadth of naphthalene was smaller than that of phenanthrene and pyrene (which have similar length and slightly different breadth). This shows that highest adsorption of naphthalene on both the sorbents can be attributed to its smaller structure compared to phenanthrene and pyrene.

In the case of organoclay, the S-shape of the curve was apparent (figure 4.2B, D and F). According to El Nahhal et al (2004) S-shape of the isotherms shows low affinity for PAH at lower concentration and more adsorption at higher concentration. Initially, adsorption occurs for single molecular unit of PAH and then, due to intermolecular interaction, PAH molecules vertically stack together. This is followed by competition between molecules present in the solution for adsorption sites giving the characteristic S-shape to the curve.

Humic Acid Effects: The effect of preloading the sorbent with humic acid significantly reduced the adsorption of phenanthrene and pyrene on activated carbon and reduced adsorption of all the three PAHs on organoclay. This reduction in adsorption can be attributed to the pore blockage of activated carbon and blocking of interlayer spacing of organoclay. In desorption studies, it was noticed that the desorption was negligible for naphthalene adsorption on both the sorbents but it was higher for phenanthrene and highest in case of pyrene adsorption on organoclay corresponding to the increase in K_{DOC} values for humic acid. The negligible desorption of naphthalene can be attributed to the highest affinity of both the sorbents and lowest K_{DOC} for naphthalene. The desorption pattern that was observable for phenanthrene and pyrene can be explained on the basis of the nature of adsorption of these compounds on sorbents (especially on organoclay) and their partition coefficients for humic acid. The molecules of phenanthrene and pyrene that stack together due to intermolecular interaction on the organoclay surface at higher concentrations are prone to migrate back to the humic acid solution due to high partition coefficients for humic acid (K_{DOC} values as reported by Poerschmann et al., 1999) (table4.1).

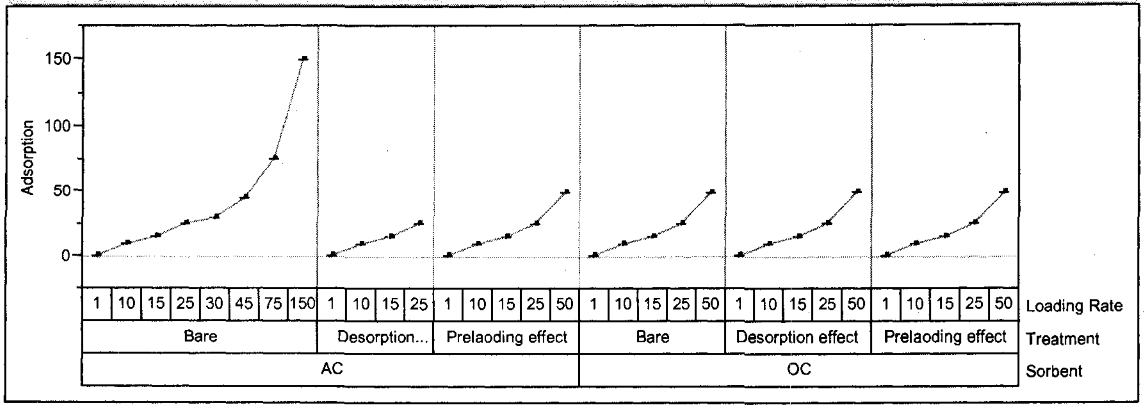
Conclusion

The adsorption capacity of activated carbon was found to be the highest for naphthalene followed by phenanthrene and pyrene. For organoclay also, the maximum adsorption was seen for naphthalene but it was almost identical for phenanthrene and pyrene that have a slight difference in their box dimensions and have similar diffusivity. The performance of bare organoclay was found to be better for naphthalene and pyrene compared to activated carbon. The preloading effect was found to be significant for both the sorbents for phenanthrene and pyrene though there was negligible effect on naphthalene adsorption. Desorption effects were not found to be significant for naphthalene for both the sorbents but it was statistically significant for phenanthrene and pyrene adsorption on organoclay. This shows that if these sorbents are exposed to very high concentrations of natural organics such as 1g L^{-1} (as in the case of this study) then it can affect the performance of the reactive core mat. Also, long term exposure of organoclay to natural organic matter might affect the performance by desorption depending on the sorption pattern of target compounds and their partition coefficients for humic acid.

Additional Information

Model 1: Naphthalene

Variability Chart for Adsorption



Analysis of Variance

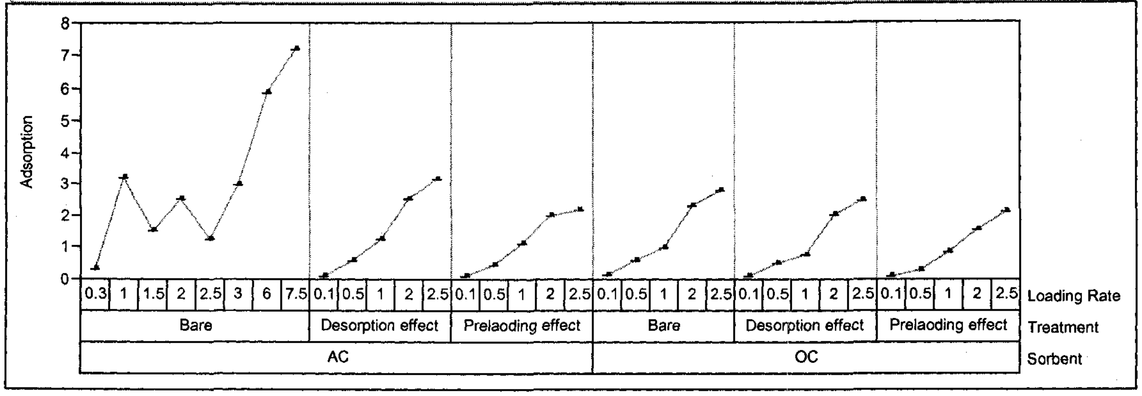
Source	DF	Sum of Squares	Mean Square	F Ratio
Model	12	26419.956	2201.66	27560975
Error	19	0.00151778	7.988e-5	**Prob > F**
C. Total	31	26419.957		<.0001*

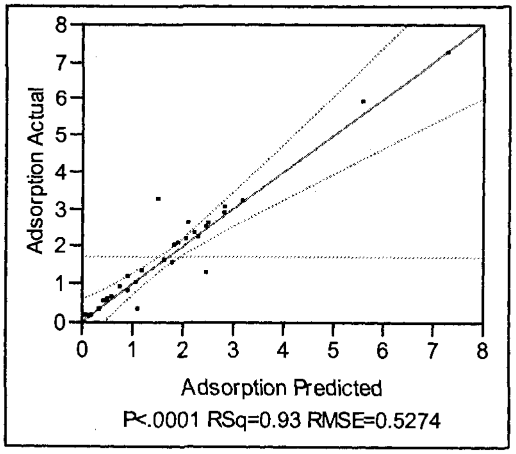
Effect Tests

Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F
Sorbent	1	1	0.00083846	10.4961	0.0043*
Treatment	2	2	0.00076508	4.7887	0.0207*
Sorbent*Treatment	2	2	0.00085911	5.3773	0.0141*
Loading Rate	1	1	5544.6311	69409096	<.0001*
Sorbent*Loading Rate	1	1	2.32853e-6	0.0291	0.8662
Treatment*Loading Rate	2	2	0.00046325	2.8995	0.0796
Sorbent*Treatment*Loading Rate	2	2	0.00059497	3.7240	0.0432*
Loading Rate*Loading Rate	1	1	0.0012	14.5595	0.0012*

Model 2: Phenanthrene

Variability Chart for Adsorption





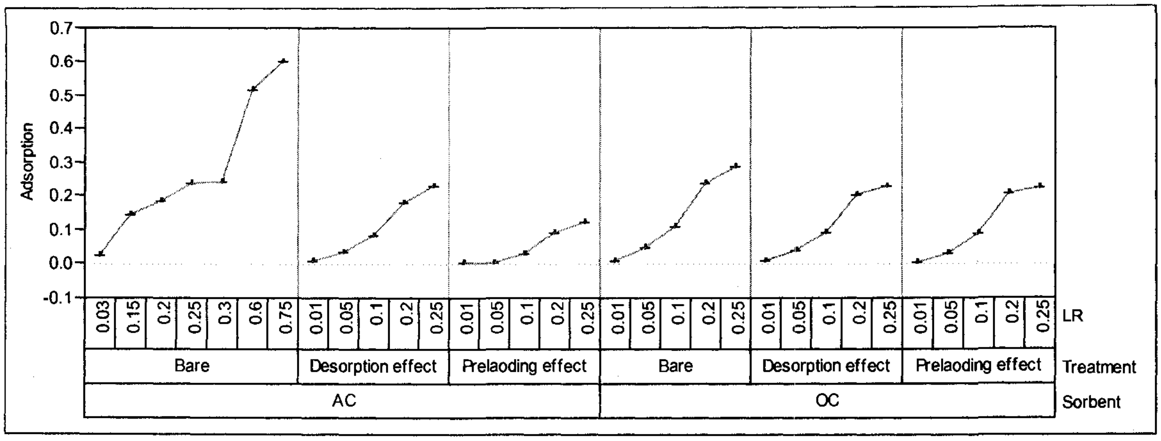
Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	12	77.553175	6.46276	23.2332
Error	20	5.563385	0.27817	**Prob > F**
C. Total	32	83.116560		<.0001*

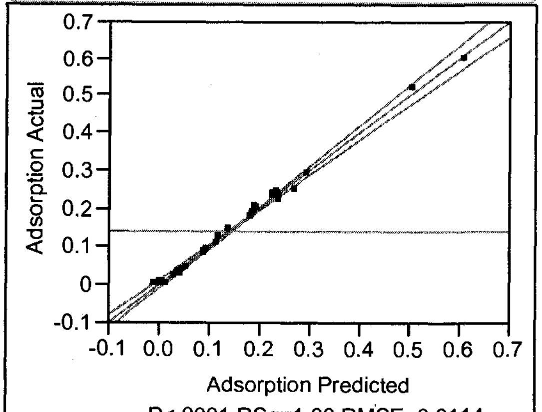
Effect Tests

Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F
Sorbent	1	1	0.433281	1.5576	0.2264
Treatment	2	2	0.993129	1.7851	0.1935
Sorbent*Treatment	2	2	0.164848	0.2963	0.7468
Loading Rate	1	1	28.253551	101.5696	<.0001*
Sorbent*Loading Rate	1	1	0.036112	0.1298	0.7224
Treatment*Loading Rate	2	2	0.417283	0.7501	0.4852
Sorbent*Treatment*Loading Rate	2	2	0.762388	1.3704	0.2769
Loading Rate*Loading Rate	1	1	0.390341	1.4033	0.2501

Model 3: Pyrene



Actual by Predicted Plot



P<.0001 RSq=1.00 RMSE=0.0114

Analysis of Variance

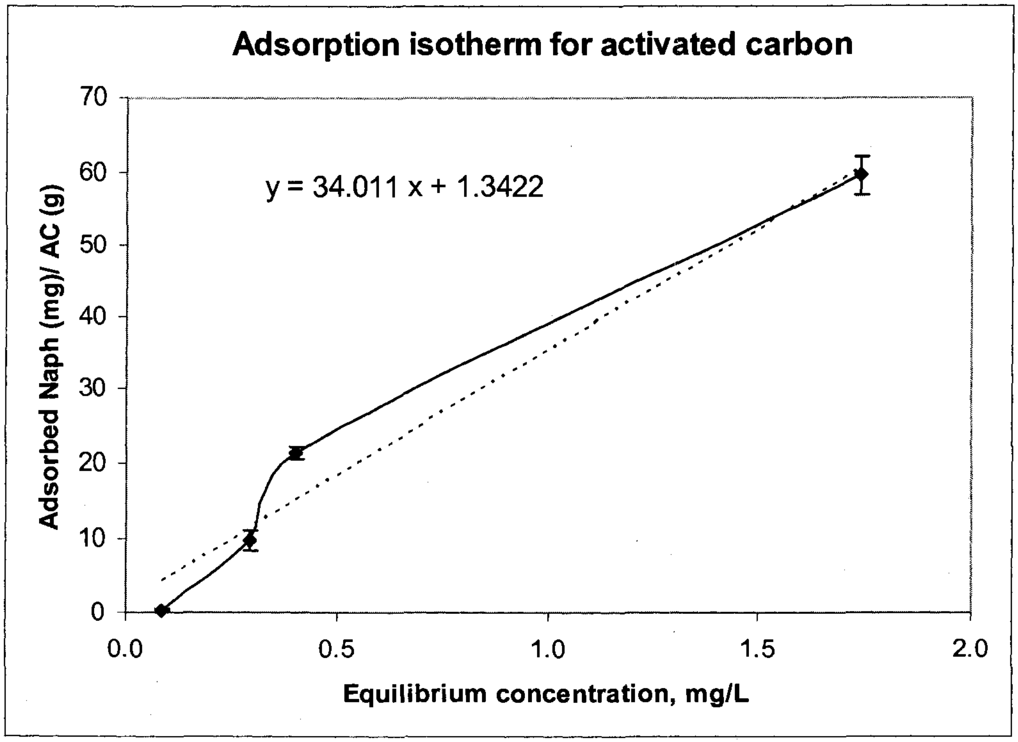
Source	**DF**	**Sum of Squares**	**Mean Square**	**F Ratio**
Model	12	0.63052876	0.052544	407.5217
Error	19	0.00244978	0.000129	**Prob > F**
C. Total	31	0.63297854		<.0001*

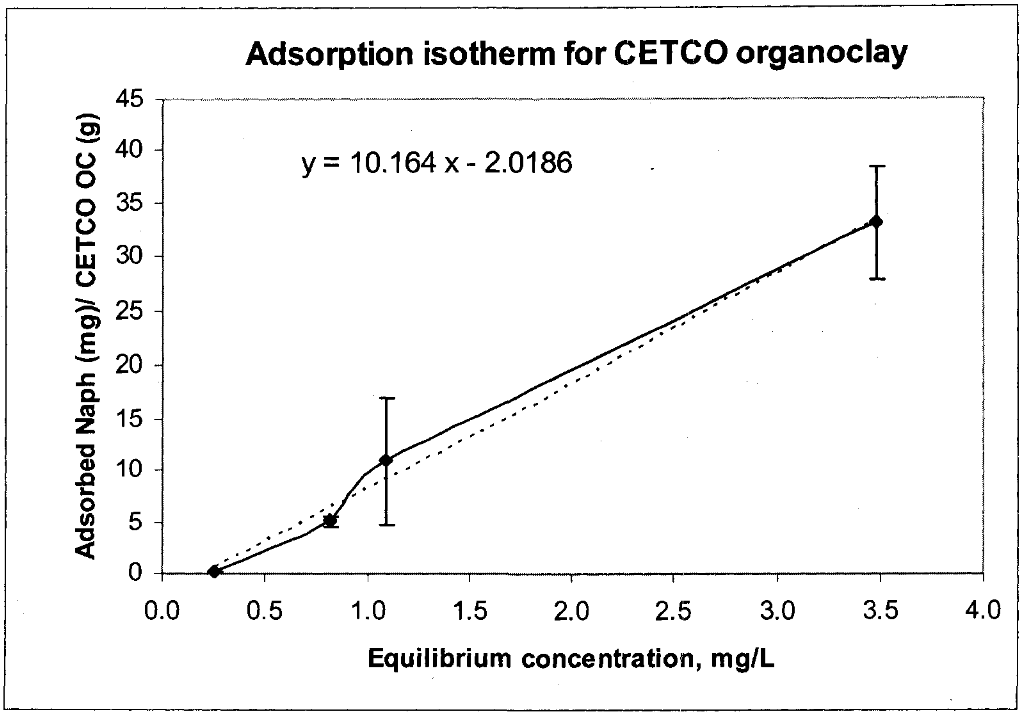
Effect Tests

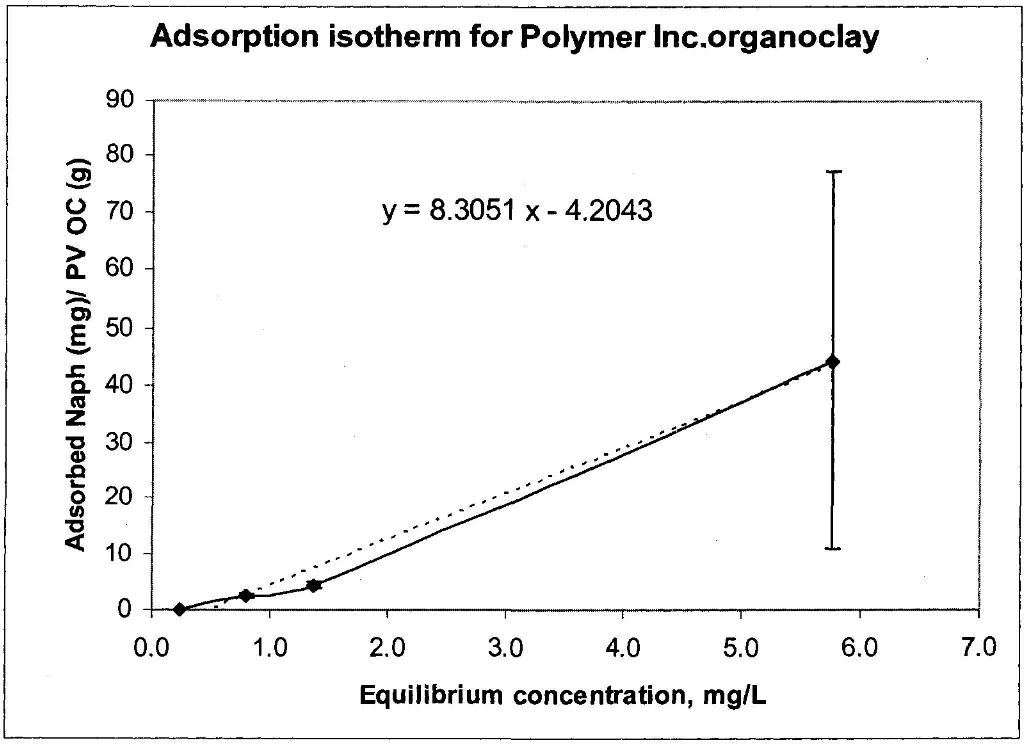
Source	**Nparm**	**DF**	**Sum of Squares**	**F Ratio**	**Prob > F**
Sorbent	1	1	0.01152574	89.3914	<.0001*
Treatment	2	2	0.01448755	56.1813	<.0001*
Sorbent*Treatment	2	2	0.00510109	19.7815	<.0001*
LR	1	1	0.23735722	1840.897	<.0001*
Sorbent*LR	1	1	0.00405245	31.4301	<.0001*
Treatment*LR	2	2	0.00377659	14.6452	0.0001*
Sorbent*Treatment*LR	2	2	0.00178366	6.9169	0.0055*
LR*LR	1	1	0.00059024	4.5778	0.0456*

Preliminary Study

Some preliminary studies were conducted to determine the performance of activated carbon and organoclays for adsorption of naphthalene (representative PAH). These experiments were conducted for the duration of 24 hours. Results showed maximum adsorption capacity of activated carbon for naphthalene followed by CETCO organoclay, Polymer Ventures Organoclay and Biomin Inc. Organoclay.

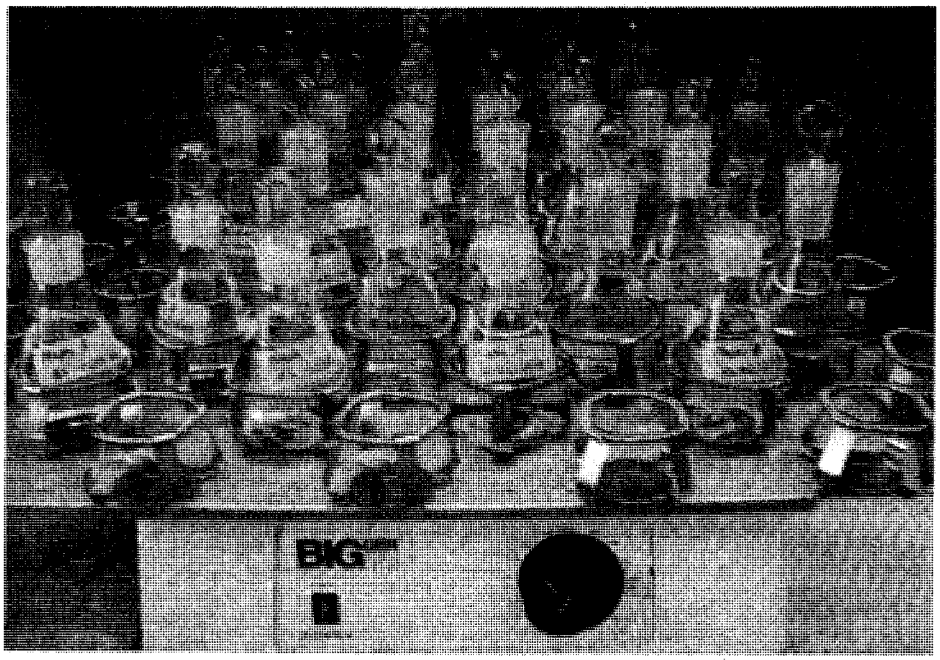



Adsorption isotherm for CETCO organoclay
y = 10.164 x - 2.0186
Adsorbed Naph (mg)/ CETCO OC (g)
45
40
35
30
25
20
15
10
5
0
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
Equilibrium concentration, mg/L

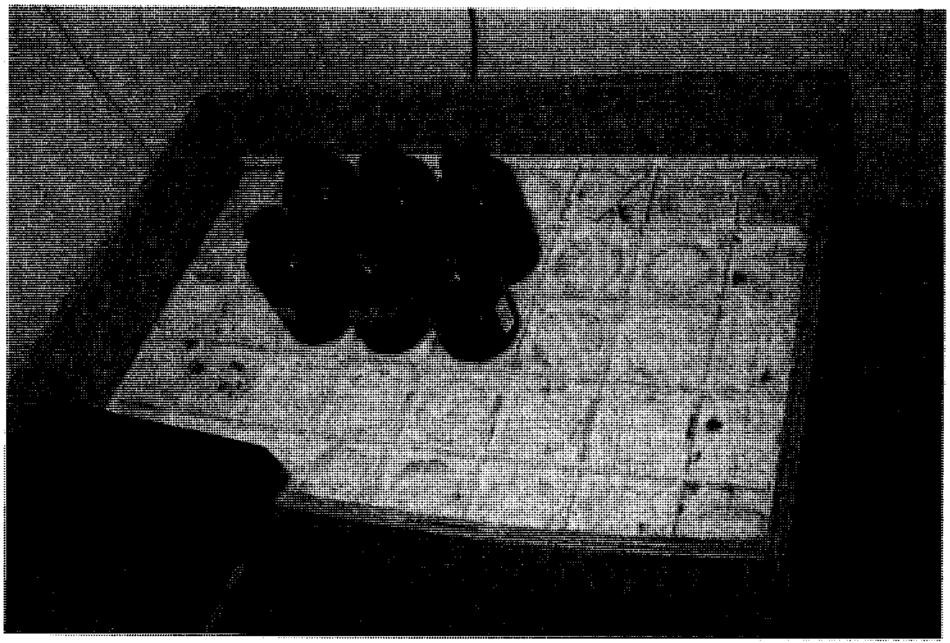

Adsorption isotherm for Polymer Inc.organoclay
y = 8.3051 x - 4.2043
Adsorbed Naph (mg)/ PV OC (g)
90
80
70
60
50
40
30
20
10
0
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
Equilibrium concentration, mg/L

Triple vs. Single Spike experiments:

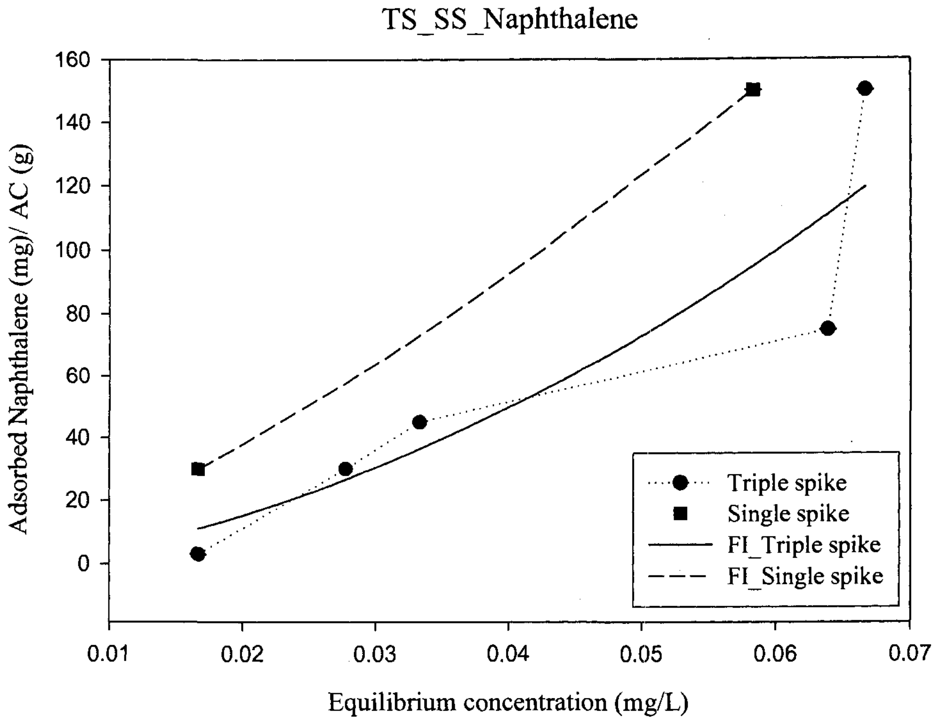
Experiments conducted to compare triple spiking vs. single spiking of PAHs

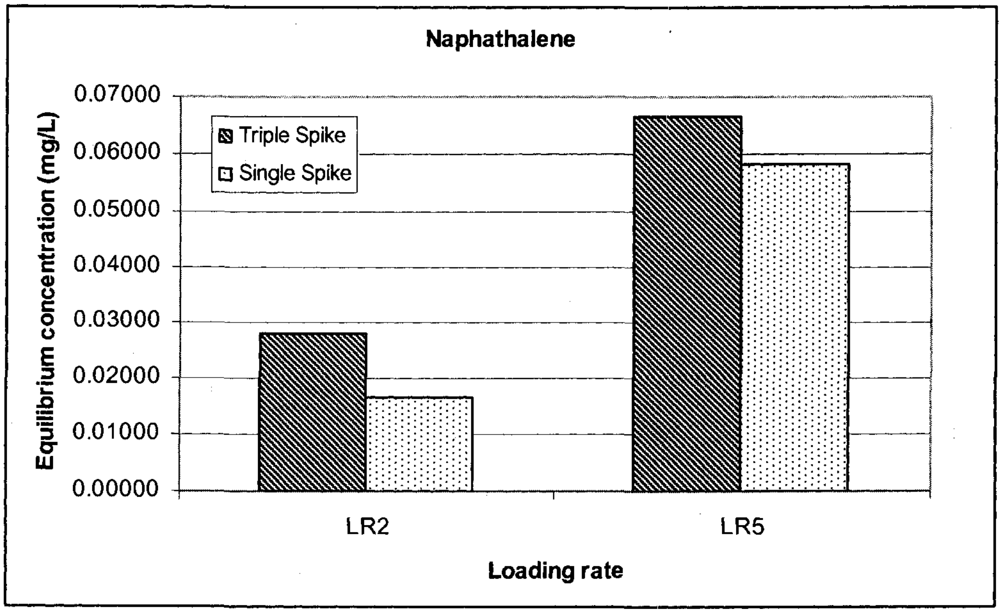


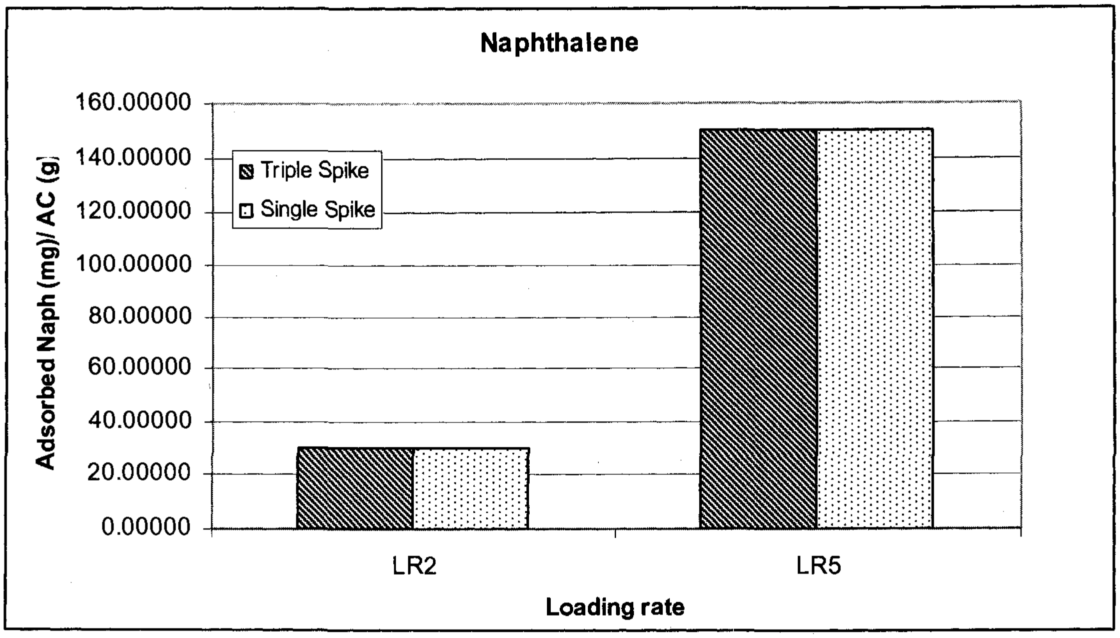
Triple Spike Experiment Set up

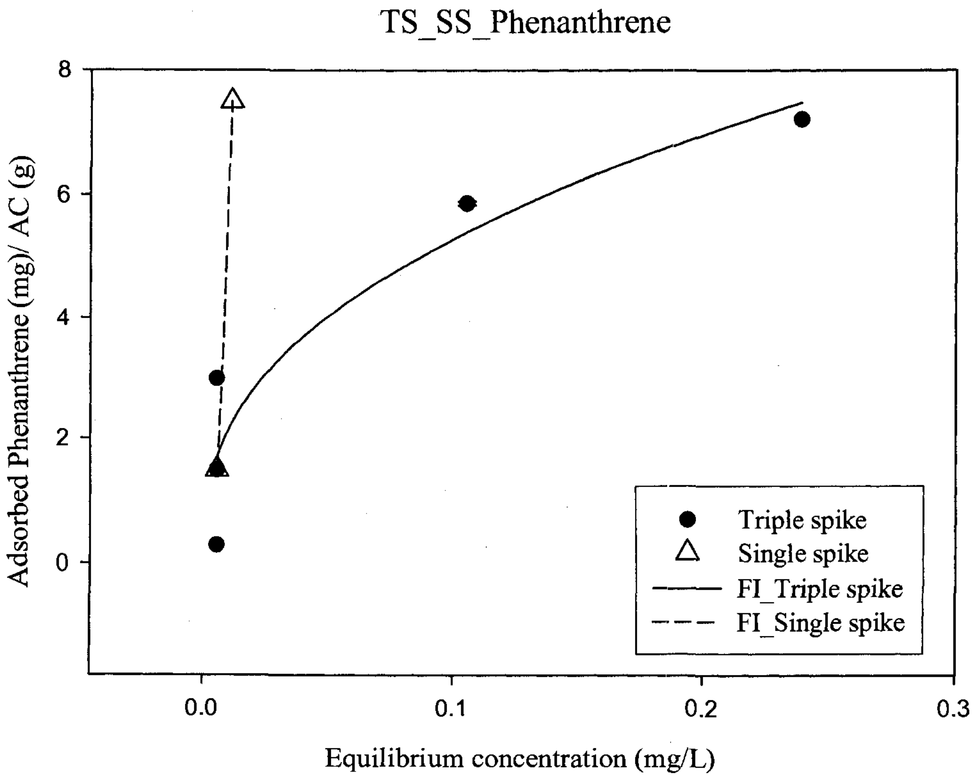


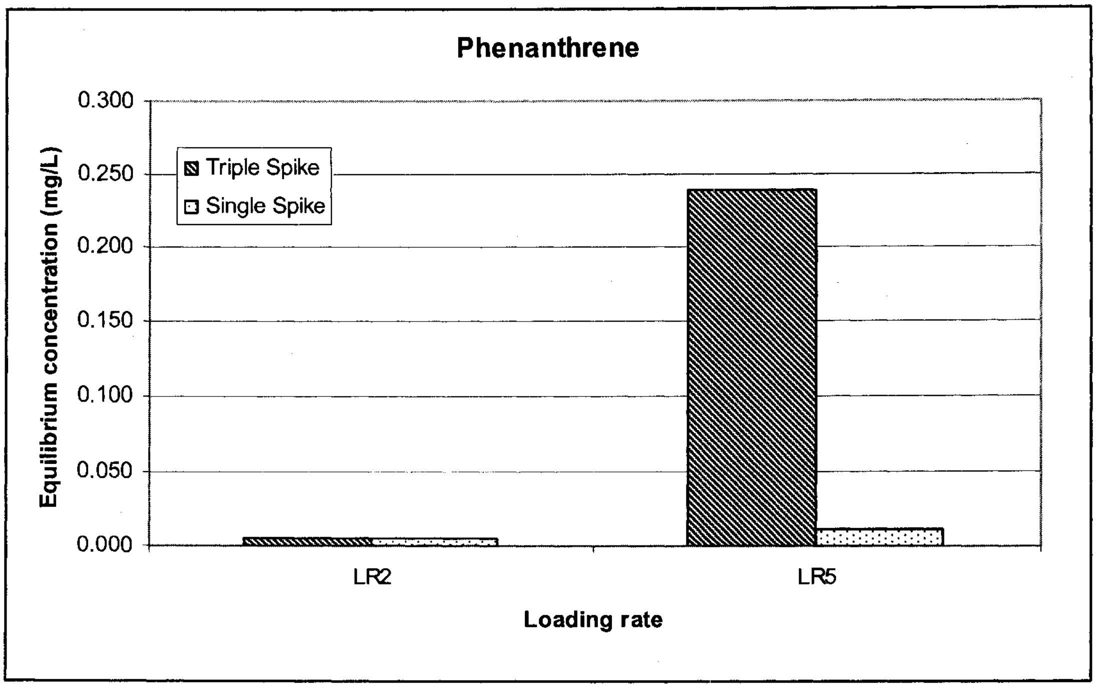
Single Spike Experiment Set up

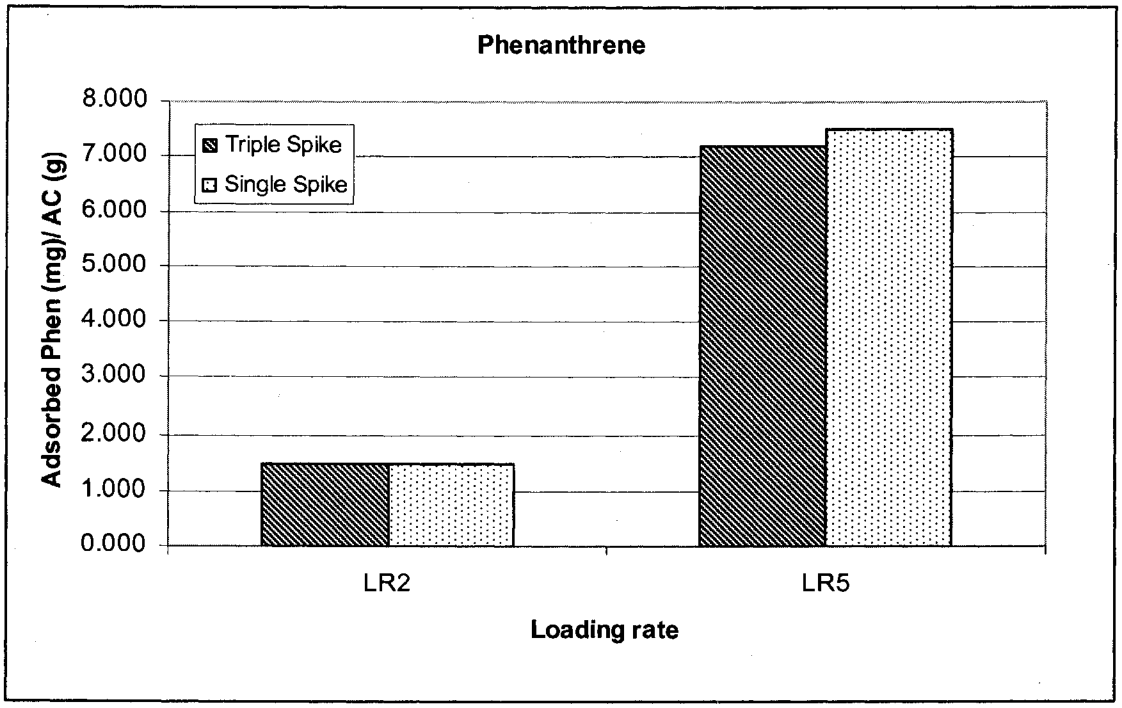

TS_SS_Naphthalene
Adsorbed Naphthalene (mg)/ AC (g)
160
140
120
100
80
60
40
20
0
0.01
0.02
0.03
0.04
0.05
0.06
0.07
Equilibrium concentration (mg/L)
Triple spike
Single spike
FI_Triple spike
FI_Single spike

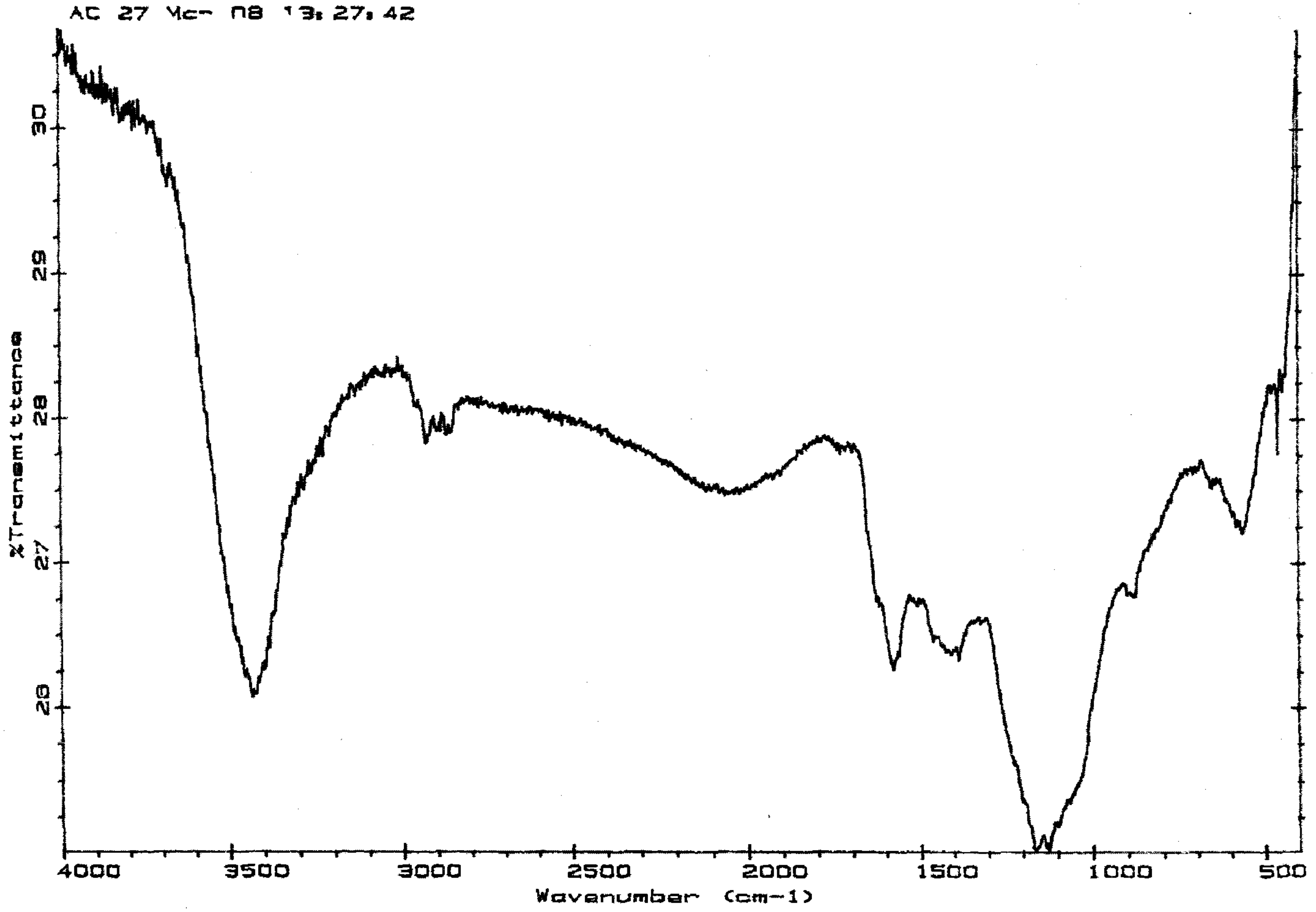

Naphathalene
Equilibrium concentration (mg/L)
0.07000
0.06000
0.05000
0.04000
0.03000
0.02000
0.01000
0.00000
Triple Spike
Single Spike
LR2
LR5
Loading rate


Naphthalene
Adsorbed Naph (mg)/ AC (g)
160.00000
140.00000
120.00000
100.00000
80.00000
60.00000
40.00000
20.00000
0.00000
▨ Triple Spike
☐ Single Spike
LR2
LR5
Loading rate

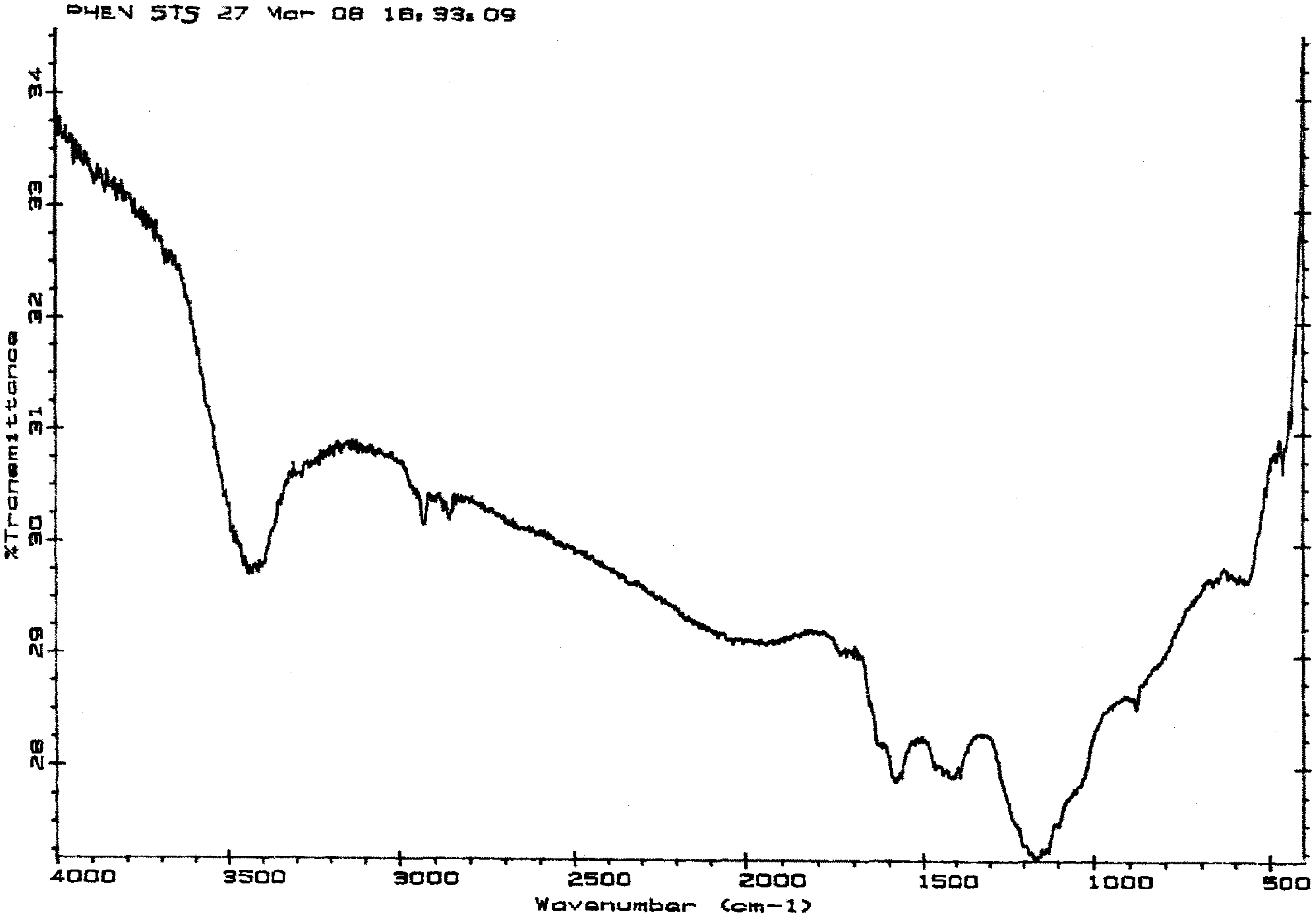

TS_SS_Phenanthrene
Adsorbed Phenanthrene (mg)/ AC (g)
8
6
4
2
0
0.0
0.1
0.2
0.3
Equilibrium concentration (mg/L)
● Triple spike
△ Single spike
FI_Triple spike
FI_Single spike


Phenanthrene
Equilibrium concentration (mg/L)
0.300
0.250
0.200
0.150
0.100
0.050
0.000
▧ Triple Spike
⊡ Single Spike
LR2
LR5
Loading rate

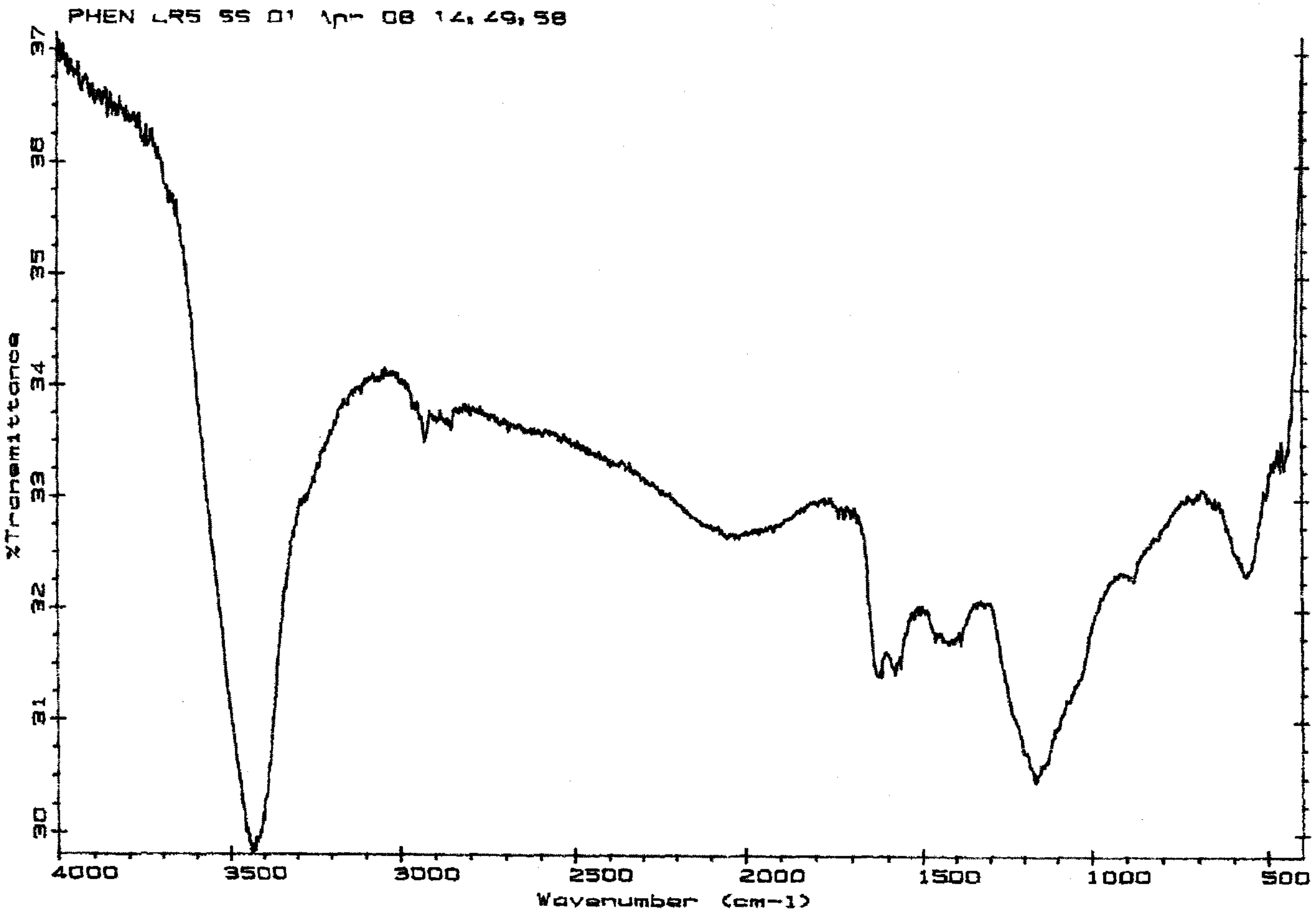

Phenanthrene
Adsorbed Phen (mg)/ AC (g)
8.000
7.000
6.000
5.000
4.000
3.000
2.000
1.000
0.000
▧ Triple Spike
⊡ Single Spike
LR2
LR5
Loading rate



FTIR of bare coconut shell activated carbon

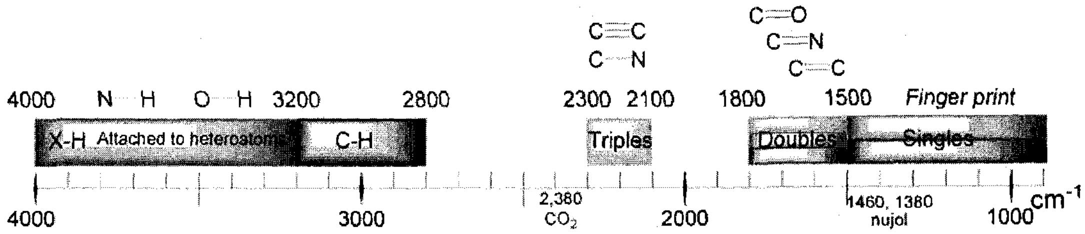


FTIR of coconut shell activated carbon after triple spiking of phenanthrene



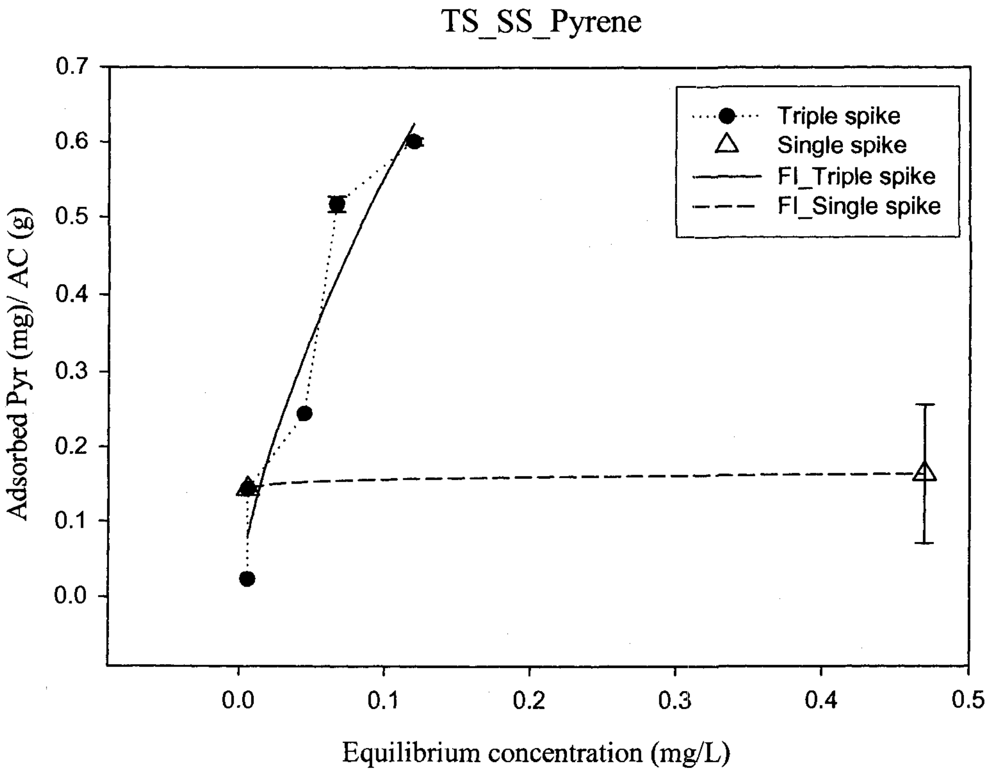
FTIR of coconut shell activated carbon after single spiking of phenanthrene

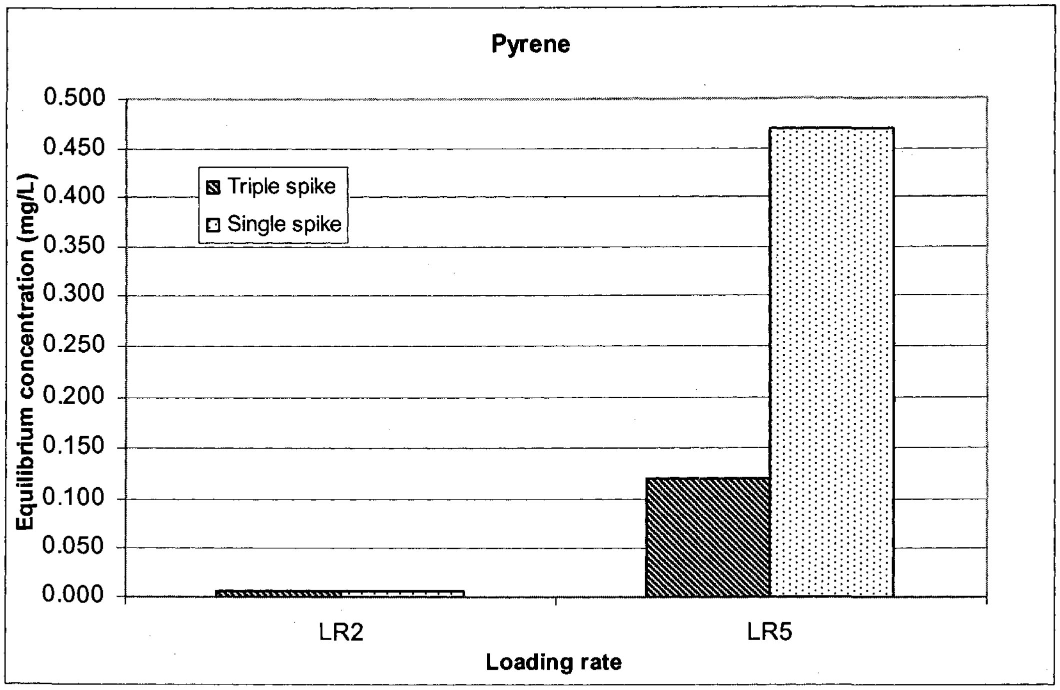
Infrared Spectroscopy Correlation Table

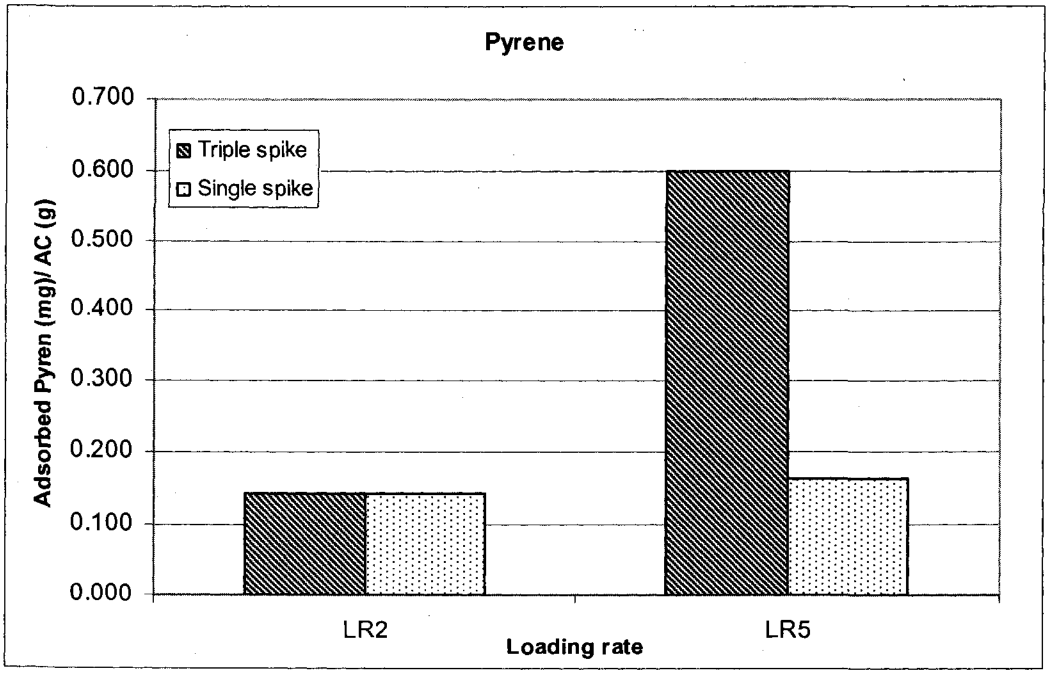


Wavenumbers listed in the table in cm^{-1}.

FTIR of samples were obtained with the help of Dr. Patricia Wilkinson, Parsons Hall, Instrumentation Center, University of New Hampshire.




Pyrene
0.500
0.450
0.400
0.350
0.300
0.250
0.200
0.150
0.100
0.050
0.000
Equilibrium concentration (mg/L)
▧ Triple spike
▨ Single spike
LR2
LR5
Loading rate


Pyrene
0.700
0.600
0.500
0.400
0.300
0.200
0.100
0.000
Adsorbed Pyren (mg)/ AC (g)
▧ Triple spike
▨ Single spike
LR2
LR5
Loading rate

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CHAPTER 5

INTERFERENCES CAUSED BY HUMIC ACID, FULVIC ACID AND NOM PRESENT IN PORE WATER ON PERFORMANCE OF ACTIVATED CARBON AND ORGANOCLAY FOR SEQUESTRATION OF ORGANIC CONTAMINANTS

Abstract

The performances of activated carbon and organoclay were evaluated as reactive cap sorbents that can be used to sequester organic contaminants in the presence of natural organics that are present in sediment porewaters. Experiments were conducted to determine the effect of Aldrich humic acid, Suwannee River humic acid, fulvic acid, natural organic matter and pore water extracted from sediments of the Passaic and Hudson Rivers. Studies were also conducted with a sorbent mixture (containing 35% organoclay, 35% activated carbon and 30% apatite) that was retrieved from reactive core mats deployed in the field for six months to determine the effect of natural organic matter present in the field. The influence of these natural organic materials was determined on the adsorption of 2, 2', 5', 5'-tetrachlorobiphenyl and phenanthrene. Results showed significant effect of Aldrich humic acid on 2, 2', 5', 5'-tetrachlorobiphenyl adsorption on both the sorbents. There was slight enhancement in the adsorption capacity of organoclay for 2, 2', 5', 5'-tetrachlorobiphenyl in the presence of fulvic acid but no effect was observed for activated carbon. There was no effect of

NOM on 2, 2', 5', 5'-tetrachlorobiphenyl adsorption on both the sorbents. In case of phenanthrene adsorption, no effect of any fraction of natural organics was noticed for organoclay. In the case of activated carbon the effects of Aldrich humic acid, Suwannee River humic acid, Suwannee River fulvic acid and Suwannee River NOM were found to have similar reducing effect on phenanthrene adsorption. A significant effect of Hudson River porewater (high humics) was observed on the performance of both the sorbents for both the contaminants, although only small effect was found for the Passaic porewater (which was low in humics).

Introduction

Sediments that provide shelter to a variety of aquatic life are also a major source and sink for hydrophobic organic contaminants (HOCs) such as Polychlorinated Biphenyls (PCBs) and Polycyclic Aromatic Hydrocarbons (PAHs) which are persistent and bioaccumulative in nature. These contaminated sediments can be toxic to benthic organisms that occupy an important position in the food chain and the uptake of HOCs poses a risk to higher tiers of the food chain. The contaminated sediment remediation technologies that are currently in practice are dredging followed by treatment and disposal and monitored natural recovery. For in-situ remediation of riverine or marine sediments, reactive capping technology can be a potential treatment method that may be effective and which is being evaluated in the research reported here. Capping technology includes deployment of reactive caps/ non-reactive sand caps over sediment bed that isolates the contaminated sediments from water body. The reactive caps can be made by direct mixing of reactive material into the sediment (Werner et al., 2005; Zimmerman et al., 2004) or by covering the sediment using geotextile or loose granular reactive material (McDonough et al., 2008). Reactive caps that consist of geotextile mat impregnated with the reactive materials, also known as reactive core mats, are still under research. Using reactive material bound within a geotextile mat is one of the methods for deploying a reactive cap that may reduce the chances of scouring and ensure uniform coverage.

In this research the reactive core mats are being evaluated to understand the effectiveness of combinations of sorbent amendment mixtures and types of geotextiles. These reactive caps are intended to be multi-symptom remedies that will sequester both organic contaminants such as PCBs and PAHs as well as metals. Pilot scale studies have been conducted by deploying 6' x 6' reactive core mats with a sorbent amendment mixture of apatite (a mineral), organoclay and activated carbon in Cottonwood Bay, Texas for six months. Laboratory analysis is being done to determine the effect of biofouling, natural organic matter and clogging of the mats. In this paper results will be discussed for the performance of coconut shell activated carbon and organoclay in the presence of different fractions of ubiquitous natural organic material as well as to determine the effect of natural organic matter (NOM) present in the Cottonwood Bay field site on the performance of sorbent amendment mixture for sequestration of organic contaminants.

Contaminants in sediments can be present either in dissolved phase in pore water or adsorbed to the particulate matrix of sediments, depending on the characteristics of the sediments and the contaminants (Akkanen et al., 2005). In the dissolved phase, HOCs are partitioned between water and dissolved natural organics present in the system. Therefore, it is necessary to understand the complexation behavior of HOCs with NOM including humic acid and fulvic acid that are present in the pore water in addition to understanding the competition of NOM for sorption sites. The pore water can be isolated from the solid phase by means of different techniques depending on whether it is an in-situ or ex-situ extraction method. The most commonly used laboratory scale method for pore water extraction is centrifugation followed by filtration (Akkanen et al., 2005). But filtration can create many problems such as changing the suction pressure leading to change in nature of particulate organic matter or clogging of filters which might not allow colloidal or particulate matter to pass through 0.45 μm filter. By definition, the material that passes through the 0.45 μm is known as dissolved organic material that consist of micro- and macromolecules that are the most important and mobile fraction of natural organic matter. Due to filtration the macromolecules, if associated with each other, are not allowed to pass through the membrane. Brownawell et al.(1985) who studied the biogeochemistry of PCBs in interstitial waters of New Bedford Harbor (NBH) concluded that a high percentage of PCBs in pore water are sorbed to organic colloids and partitioning of HOCs to organic colloids is necessary to evaluate the mobility and bioavailability in sediments. Therefore, only the centrifugation method was used in this study to extract pore water so that all the fractions of NOM, including colloids, could be taken into account to understand their affect on treatment processes of HOCs.

NOM present in the pore water can be fractionated into humic acid, fulvic acid and humin, which may affect the solubility, transport and bioavailability of HOCs in different ways. The fulvic acid, which has lower molecular weight components, is more hydrophilic compared to humic acid that consists of high molecular weight components and is more hydrophobic (Wu et al. 2003). Fulvic acid consist of naphthalene rings substituted with hydroxyl, carboxyl and short aliphatic chains whereas humic acid consists of phenolic groups and quinone structures in addition to carboxylic groups substituted on large aromatic rings (Saparpakorn et al. 2007). NOM is heterogeneous and consists of humic acids, fulvic acids, proteins and peptides having both hydrophilic and hydrophobic properties (Wu et al. 2003). The chemical properties of these NOM fractions, including acid/ base properties, elemental composition and aromaticity, depend on their origin and is different for freshwater, marine or terrestrial environments (Niederer et al., 2007). Therefore, in this study pore water from five different sites was characterized and humic acid, fulvic acid, NOM and pore water from different origins were used to obtain a range of effects that may be encountered under different site conditions. Sorbent amendment mixture obtained from the reactive core mats deployed in a non-contaminated area of the study field site were also evaluated to determine the effect of longer term exposure to NOM concentrations that are present at a study field site. The main objective of this study is to quantify the effects of different fractions of

NOM from different origins on the performance of activated carbon, organoclay and an amendment mixture for sequestration of organic contaminants.

Materials and Methods

Chemicals

Contaminants of concern used in this study were 2, 2', 5, 5'-tetrachlorobiphenyl, and phenanthrene that were obtained from Ultra Scientific (North Kingstown, RI, USA) either in neat form or dissolved in hexane/ methylene chloride respectively. Internal standards 2, 4, 6-trichlorobiphenyl and Acenaphthene d-10 and surrogate standards 2, 4, 5, 6-tetrachloro-m-xylene (TCMX) and 2-fluorobiphenyl were also purchased from Ultra scientific (North Kingstown, RI, USA). Humic acid sodium salt (Ald-HA) was obtained from Sigma-Aldrich (St. Louis, MO, USA), Suwannee River humic acid (2S101H) (SRHA), Suwannee River fulvic acid (2S101F) (SRFA) and Suwannee River Natural Organic Matter (1R101N) (SRNOM) were obtained from International Humic Substance Society (St. Paul, MN, USA). Sodium azide used to avoid biological contamination in the experiments was obtained from EMD Chemicals Inc. (San Diego, CA, USA) and sodium sulfate anhydrous used to remove chemically bound water from extracted samples was obtained from Fisher Scientific (Morris Plains, NJ, USA). All ultra high purity chemicals and GC-grade solvents were used in the study and obtained from Fischer Scientific (Agawam, MA, USA) were used. DAX-8 resin that was used for fractionation of NOM was purchased from Sigma Aldrich (St. Louis, MO, USA).Hydrochloric acid and Sodium hydroxide that were used to maintain pH were obtained from Fisher Scientific (Fair Lawn, NJ, USA).

Sorbents:

Activated carbon: Coconut shell activated carbon, OLC 12 x 40 obtained from Calgon Carbon Corporation (Pittsburg, PA, USA) was used. This material was selected because it is widely used for removal of trace organic compounds and it has high microporosity.

Organoclay: Organoclay was obtained from CETCO (Arlington Heights, IL, USA) as PM 199 which is organically modified bentonite clay. In PM 199, hydrogenated tallow based quaternary amines were used to increase the inter-layer spacing of bentonite clay. Interlayer (d_{001} spacing) of PM 199 was found to be 35.74 A° and organic content to be about 19%.

Amendment mixture: The amendment mixture consisted of 35% activated carbon, 35% organoclay and 30% apatite by weight. Apatite used in this study was obtained from PCS Phosphate Mines (Aurora, NC, USA). Apatite can be used for metal sequestration and is in the mixture for this reason: this paper is focused only on organic contaminants removal. The bare amendment mixture was prepared from the sorbents as obtained from vendors mixed in given proportions to determine the adsorption capacity of the sorbent mixture. The amendment mixture was also obtained from the reactive core mats that were deployed in the study field site for six months to determine the preloading effects of NOM present in the study site. For this purpose 6' x 6' mats that were retrieved from the field were cut into 2' x 2' pieces and each section was dried at room temperature for 3 days. The mixture material was then separated from the geotextiles and was collected in a beaker and stored.

Experiment Protocols

Pore Water Extraction and Characterization:

Pore water was extracted from the sediments of six different sites including Hudson River, Passaic River, New Bedford Harbor (NBH), Cocheco River and Gowanas Canal. Centrifugation method (Beckman Coulter J2-HS centrifuge) was used for laboratory scale isolation of porewater from the solid matrix of sediments. The samples were extracted at 20° C at 7000 rpm for 30 minutes. The supernatant was then separated and collected into glass vials for further analysis including pH, oxidation-reduction potential (ORP), total organic carbon (TOC), dissolved organic carbon (DOC) (Shimadzu TOC-5000A TOC Analyzer) and ultraviolet (UV) absorbance. Humic acid was isolated from the porewater by precipitation after lowering the pH to 1 using HCl. HA fraction was dissolved by using sufficient 0.1 M NaOH. The pH of supernatent fulvic acid fraction was brought to 2.0 with NaOH and passed through DAX-8 resin (Kim et al., 1990; Thurman et al., 1981). The column was then washed with one void volume of distilled water to remove the salt followed by reverse flow of 0.1 M NaOH to elute the column to obtain FA fraction (Thurman et al., 1981). Both HA and FA fraction were analyzed further for DOC (mg C/ L) and TKN (mg N/ L).

Isotherms studies

Isotherm studies were conducted to determine the preloading effect of different fractions of natural organics and extracted sediment pore water on adsorption capacities of activated carbon and organoclay for 2, 2', 5, 5'- tetrachlorobiphenyl (PCB) and phenanthrene (PAH). The studies to determine the preloading effect of Ald-HA, SRHA, SRFA and SRNOM were conducted in 125 ml flasks at five loadings of both selected contaminants (concentration range given in table 5.1). The studies were conducted separately for PCB and PAH adsorption on activated carbon and organoclay to avoid any interference of contaminants in the performance of sorbents at fixed loading of Ald-HA/ SRHA/ SRFA/ SRNOM. Experiments were also conducted to determine the effect of extracted pore water from sediments of Hudson River (HPW) and Passaic River (PPW) on adsorption capacity of activated carbon and organoclay for selected PCB and PAH molecules. Due to the limited availability of extracted pore water these experiments were conducted at three loadings of contaminants in 40 ml vials. This set of experiments was also conducted separately for PCB and PAH. Spiking of PCB and PAH was done to obtain the required concentration of contaminants in extracted pore waters due to absence of any prior PCB/ PAH concentrations in the sediments (Figure 5.1). All the isotherm studies were conducted for an equilibration time of 72 hours.

Effect of different concentrations of Ald-HA/ SRFA/ SRNOM: Studies were also conducted to determine the effect of varied concentration of Ald-HA, SRFA and SRNOM that can be found in different site conditions. For this purpose experiments were conducted in 40 ml vials at fixed loading of selected contaminants (based on the solubility limit in water) including 2, 2', 5, 5'-tPCB and phenanthrene (separately for PCB and PAH) at three different loadings of Ald-HA, SRFA and SRNOM.

Preloading of sorbents: For isotherm studies; 0.1 g of sorbent (activated carbon/ organoclay) was preloaded with 100 mg L^{-1} Ald-HA/ SRHA/ SRFA/ SRNOM solution in separate 125 ml flasks. The stock solution of 100 mg $L^{-1}$was prepared for each Aldrich HA, SRHA, SRFA and SRNOM. The initial pH of SRHA, SRFA and SRNOM were found to in the range of 4 and were adjusted to pH 7 using sodium hydroxide solution (table 5.3). To determine the effect of different loadings of Ald-HA/ SRFA/ SRNOM, 0.2 g of sorbent was preloaded with 20 ml of each HA/ FA/ NOM in separate vials at three loadings (10 mg L^{-1}, 100 mg L^{-1} and 1000 mg L^{-1}) of each. These experiments were conducted without any pH adjustment of stock solutions of Ald-HA/ SRFA/ SRNOM solutions which were in found to be 7.21, 4.02 and 4.12 respectively. The stock solutions for preloading were prepared with the highest concentrations of HA/ FA/ NOM with 10 % sodium azide to avoid any biological contamination followed by required dilutions for lower loadings. Sorbents were also preloaded with 20 ml of extracted pore waters with 10% sodium azide (HPW and PPW). The amount of sorbent was 0.2 g and preloading was done in 40 ml vials. Preloading of all the samples was done for 48 hours and samples were kept on rotary shaker at 150 rpm for continuous mixing.

Contaminants	† Log K_{OW}	†Log K_{DOC}		Organic Contaminant Concentration Range for HA/ FA/ NOM effects (mg/L)	Organic Contaminant Concentration Range for extracted pore water effects (mg/L)	Organic Contaminant Concentration Range for sorbent mixture studies (mg/L)
		HA	FA			
Phenanthrene	4.44	3.85	3.26	0.16 – 2.0	0.1 – 2.0	0.08 – 2.0
2,2',5,5'- tPCB	5.9	4.6	-	0.016 – 0.8	0.050 – 0.250	0.008 – 0.4

† Poerschmann et al. 1999

Table 5.1: Log KOW, Log KDOC values and concentration range of phenanthrene and 2, 2', 5, 5'-tPCB

Sorbent amendment mixture performance

Sorbent amendment mixture analysis: Studies were conducted to determine the effect of natural organic matter present in Cottonwood Bay, Texas (table 5.2) on sorbent mixture present in the reactive core mat. For this purpose, experiments were conducted with virgin Sorbent mixture, the sorbent mixture obtained from reactive core mat that was deployed in Cottonwood Bay for six months and virgin sorbent mixture in Cottonwood Bay sediment pore water. These experiments were conducted at five loadings of a contaminant mixture having 2, 2', 5, 5'-tPCB and phenanthrene. Separate batches were prepared with 0.1 g of sorbent mixture (virgin/ Cottonwood Bay) in 125 ml flasks having DI water spiked with contaminant mixture of 2, 2', 5, 5'-tPCB and phenanthrene depending on the loading rate (table 5.1). After spiking samples were kept on rotary shaker for one week at 150 rpm.

Samples/ sorbents extractions and analysis

Sample extraction: Two sub-samples from each vial/ flask were collected and extracted using a surrogate-spiked solvent. For PCB extraction TCMX in hexane was used as a surrogate standard and for PAH extraction 2-fluorobiphenyl in methylene chloride was used. Solvent vials were shaken vigorously three times at an interval of 30 seconds each. The vials were then stored for at least 24 hours at 4° C. The extracted solvents were passed through sodium sulfate to remove any chemically bound water. The filtered samples were then mixed with internal standards in GC vials followed by GC/MS analysis using internal standard method. For PCB 2, 4, 6,-trichlorobiphenyl was used as an internal standard because there was no overlap in the peaks of 2, 4, 6,-

trichlorobiphenyl and 2, 2', 5, 5'-tPCB and for PAH Acenaphthene d10 was used as an internal standard.

Gas Chromatography/ Mass Spectrometry: All the extracts were analyzed using internal standard method on 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-5ms), 30 m long, 0.25 mm ID and 0.5 µm thick. The ion-trap was operated in selected scan mode (MS/MS) for both PCB and PAH. For PCB the column oven temperature was programmed at 40° C with 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 held time of 2 minutes. For PAH column temperature was programmed at 80° C with hold time of 2 min followed by a temperature ramp up to 315 ° C at the rate of 25° C with final held time of 2 minutes.

Quality Assurance: All the chemicals used in the experiments were of ultra high purity. Experiments were either conducted in Teflon® lined screw cap glass vials or 125 ml glass flasks with the glass stoppers to ensure that there is no volatilization loss. The pyrex glassware was used which was solvent/ soapy water washed and properly rinsed with RO water followed by drying in Muffle furnace at 500° C programmed for 8 hours. Experiments were run in duplicates and from each sample vial/ flask 2 sub-samples were extracted to check if there is any deviation in % surrogate recovery. The surrogate recoveries were in the range of 70-120%. For GC/MS analysis internal standard method was used and in each GC run one read back and one blank was run after every eighth sample. In blanks the concentration of PCB/ PAH was non-detectable.

Results and Discussions

Pore water from aged sediments of six different sites including Hudson River, New Bedford Harbor (NBH), Cocheco River, Passaic River, Gowanus Canal and Cottonwood Bay was extracted and characterized (table 5.2 A-B). The pH of all the six sediments ranged from 7.45 – 7.9. The oxidation-reduction potential of Hudson River sediment pore water was found to be the highest. The TOC values of Hudson River and Passaic River pore water were found to be higher than that of other sediments, therefore, these two sediments pore water were selected for the studies conducted to determine the effect of natural organics present in the extracted pore water on adsorption capacity of sorbents. DOC and TDN analysis was performed to determine the carbon and nitrogen content in humic and fulvic fractions of the extracted pore waters (table 5.2 B).

Table 5.2A: Characteristics of extracted sediment porewater

Sediment samples	pH	ORP(mv)	TOC (mg L-1)	DOC (mg L-1)	UV_{254} (mg L-1)
Hudson River	7.71	175	141.58	24.63	2.919
New Bedford Harbor	7.45	29.3	96.26	93.74	1.387
Cocheco River	7.73	80.5	59.16	57.68	1.257
Passaic River	7.93	70.3	178.86	46.67	0.971
Gowanus Canal	7.94	57.6	85.54	43.3	1.441

Table 5.2B: DOC and TDN in humic and fulvic fraction of extracted sediment porewater

Samples	DOC (mg C/L)	TDN (mg N/L)
Hudson FA	92.7	0.9
Hudson HA	80.2	2.5
NBH FA	52.5	2.1
NBH HA	122.8	1.3
Cocheco FA	94.8	2.3
Cocheco HA	58.7	3.5
Passaic FA	71.8	1.1
Passaic HA	43.6	0.8
Gowanus Canal FA	50.4	1.8
Gowanus Canal HA	50.7	1.2

Results showed high DOC in humic fractions of NBH and Hudson River pore water while the Passaic River pore water showed lowest DOC in humic fraction of porewater. Hudson River porewater with high DOC in the fulvic and humic fractions represents high humic content and Passaic River porewater with high DOC in fulvic fraction and low in HA fraction represents low humic content. Using these two sediment pore waters in the isotherm studies provided a range of effects from high humic content pore water to a mixture of humic and non-humic content of pore water.

Isotherm studies were conducted to evaluate the effect of different fractions of natural organic matter (Ald-HA/ SRHA/ SRFA/ SRNOM) as well as mixture of natural organics present in the extracted pore water on the performance of activated carbon and organoclay for PCB and PAH adsorption. Ald-HA, SRHA, SRFA and SRNOM represented the different fractions that can be present at any given site. The characteristics of these materials are presented in table 5.3. The concentrations of target organic contaminants were achieved by spiking the required doses of PCB and PAH as described in the experimental procedure section (Figure 5.1). Besides evaluating the individual sorbent performance, the adsorption capacity of the sorbent mixture (virgin or aged in Cottonwood bay) for mixture of contaminants was also evaluated.

Sample	pH of solution	C (%)	H (%)	O (%)	N (%)	S (%)	P (%)	Ash (%)
Aldrich HA†	7.21	69.4	5	39.3	0.75	4.25	0.15	31
Suwannee River HA††	7.17	52.34	4.36	42.98	0.67	0.46	0.004	0.58
Suwannee River FA††	7.11	53.04	4.36	43.91	0.75	0.46	< 0.01	0.98
Suwannee River NOM††	7.24	52.47	4.19	42.69	1.1	0.65	0.02	7

† Zhao et al. (1998); †† International Humic Substance Society

Table 5.3: Elemental composition of humic acid, fulvic acid and NOM and pH of the solutions used in this study

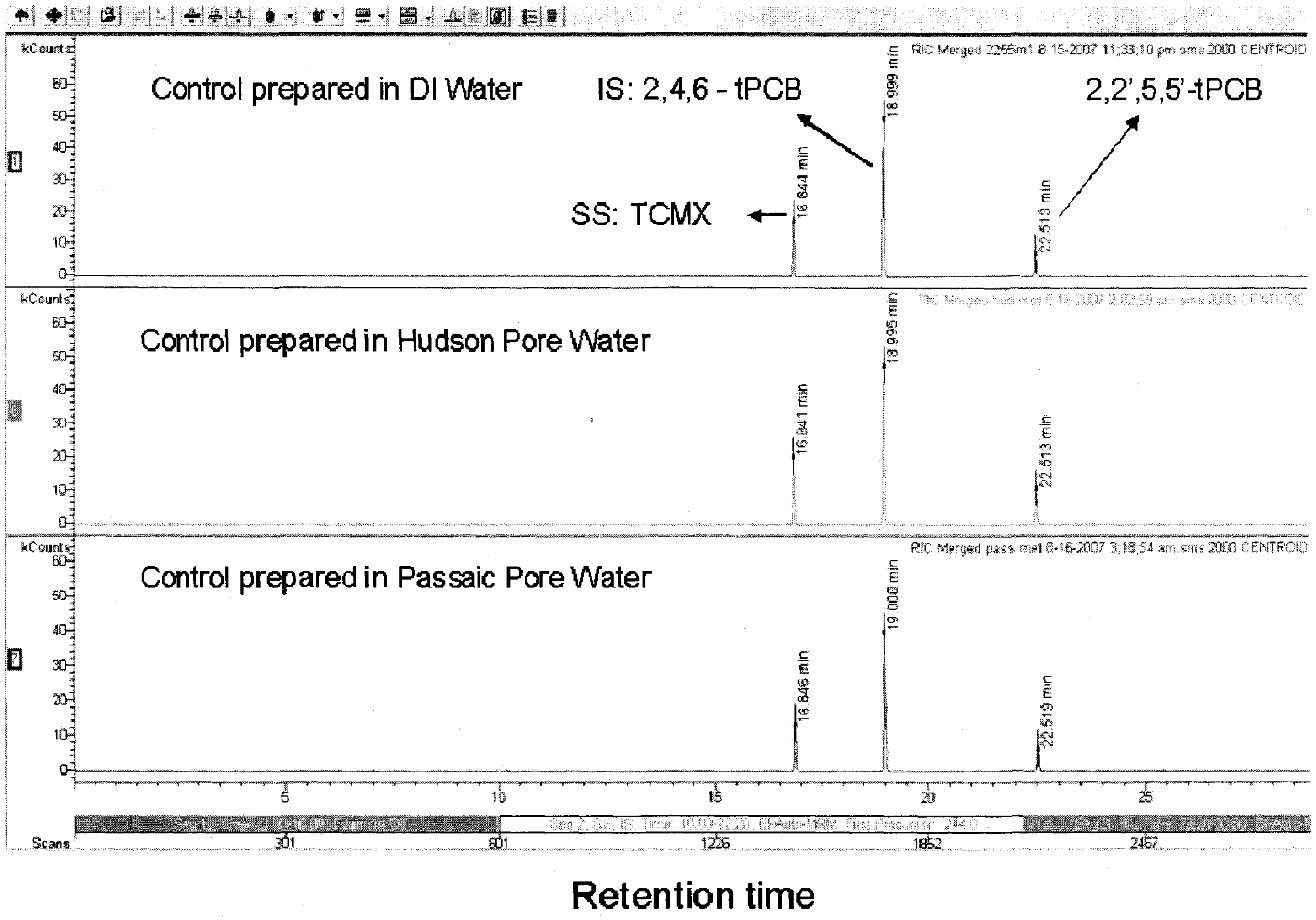


Figure 5.1 A: GC Chromatograms showing peaks of selected contaminants in presence of DI water; Passaic River Pore Water and Hudson River Pore Water: 2, 2', 5, 5'-tPCB

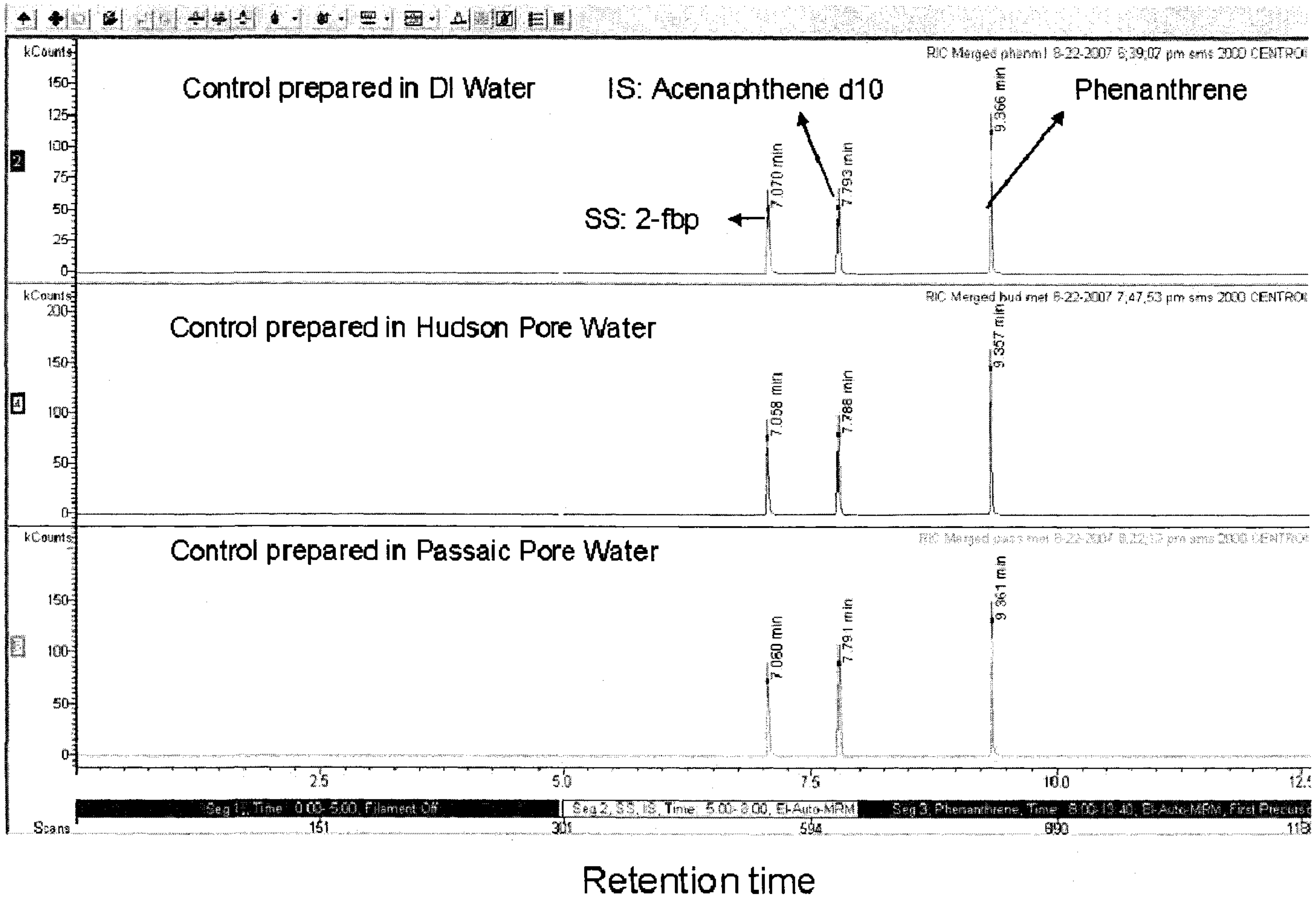


Figure 5.1 B: GC Chromatograms showing peaks of selected contaminants in presence of DI water; Passaic River Pore Water and Hudson River Pore Water: Phenanthrene

The adsorption capacities of the sorbents and sorbent mixture were determined by using a linear partition model (K_d values) developed from the isotherms and the Freundlich isotherm model. The Freundlich isotherm model was used in its non-linear form as:

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

where q_e is the mass of adsorbate adsorbed per mass of sorbent (mg/g), C_e is the equilibrium concentration of solute in the aqueous solution after adsorption (mg L^{-1}), K_f is the Freundlich capacity factor and 1/n is the linearity factor.

Preloading effect of Ald-HA/ SRHA/ SRFA/ SRNOM:

Figure 5.2 shows Freundlich isotherms for adsorption of 2, 2', 5, 5'-tPCB and phenanthrene on organoclay and activated carbon in the presence of Ald-HA, SRHA, SRFA and SRNOM. Figure 5.2 A and B represents adsorption of 2, 2', 5, 5'-tPCB on organoclay and activated carbon respectively. The adsorption capacity of both the sorbents for PCB was found to be reduced in the presence of Ald-HA (table 5.4). In the presence of fulvic acid slight enhancement was noticed in the case of organoclay but there was no effect of fulvic acid on adsorption on activated carbon. The presence of NOM had no effect on the adsorption of 2, 2', 5, 5'-tPCB on both activated carbon and organoclay. In case of organoclay the effect of preloading with AldHA/ SRHA/ SRFA/ SRNOM on adsorption capacity was found to be in the following order: AldHA> SRHA> NOM > FA.

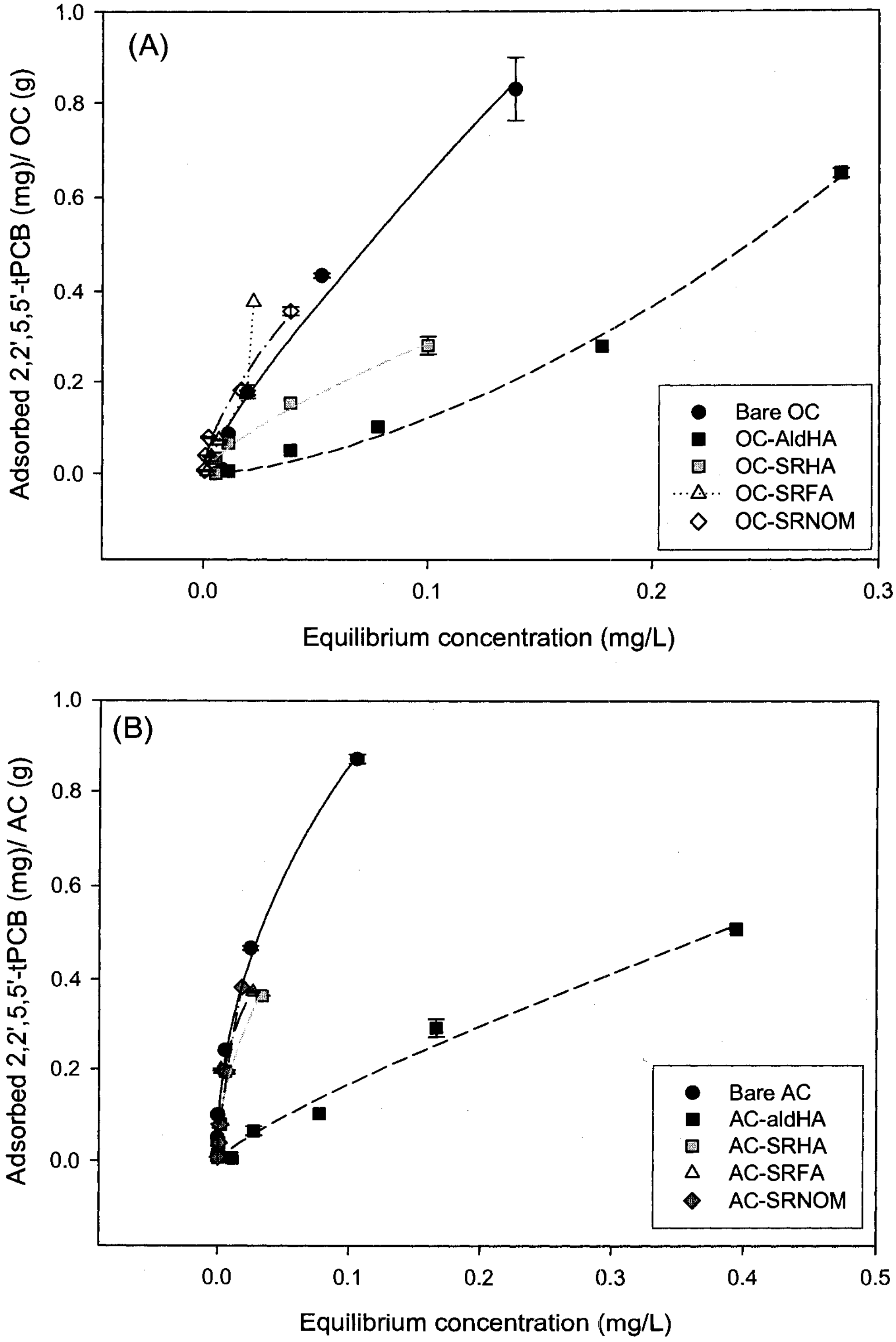
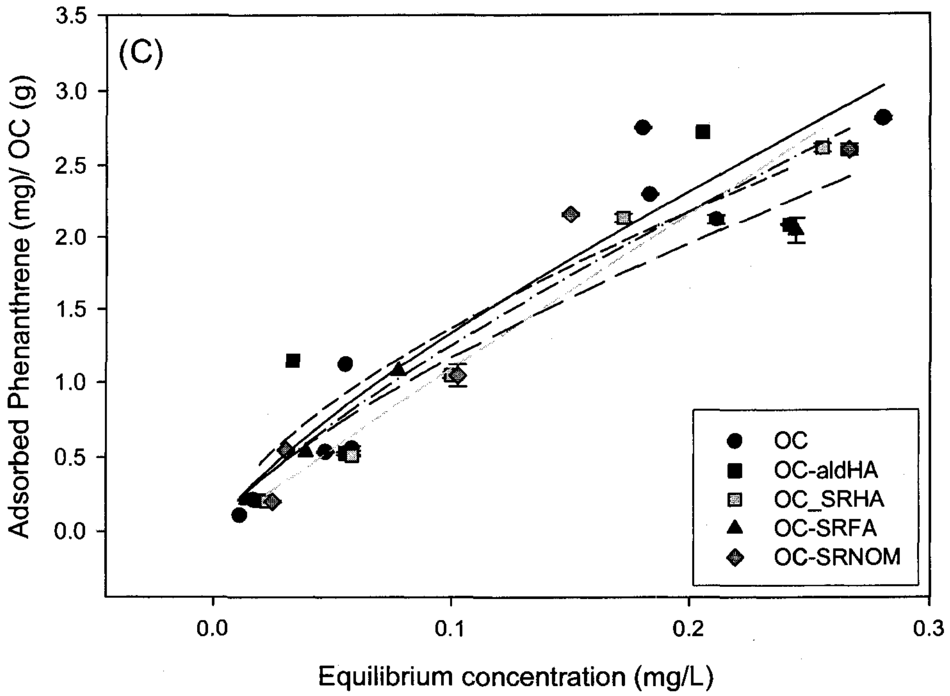


Figure 5.2 A-B: Adsorption of contaminants in presence of different fractions of natural organic matter (A) 2, 2', 5, 5'-tPCB adsorption on OC (B) 2, 2', 5, 5'-tPCB adsorption on AC (OC = Organoclay; AC = Activated Carbon; HA = Humic Acid; FA = Fulvic Acid and NOM = Natural Organic Matter)



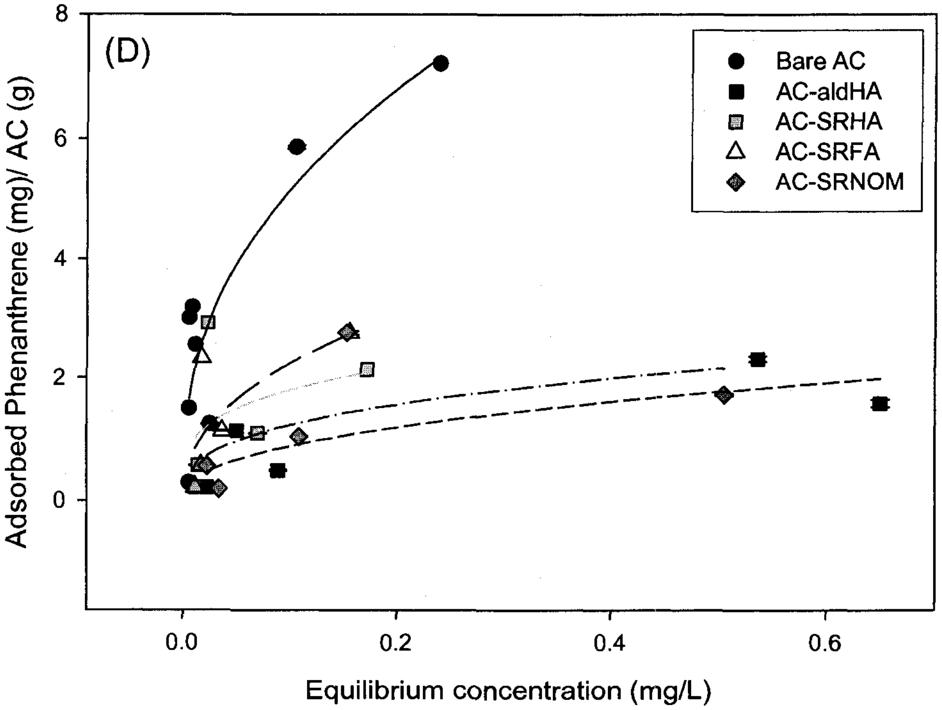


Figure 5.2 C-D: Adsorption of contaminants in presence of different fractions of natural organic matter (C) Phenanthrene adsorption on OC (D) Phenanthrene adsorption on AC (OC = Organoclay; AC = Activated Carbon; HA = Humic Acid; FA = Fulvic Acid and NOM = Natural Organic Matter)

This trend can be supported by the studies conducted by Kohl et al. (1998) who studied the binding of organic contaminants to different fractions of soil organic matter and showed the binding affinity of HA > Humin > FA with 2, 2', 5, 5'-tPCB.

Figure 5.2 C and D represents the adsorption of phenanthrene on organoclay and activated carbon, respectively. The phenanthrene adsorption on organoclay showed no effect of Ald-HA, SRHA, SRFA and SRNOM. In case of activated carbon a significant effect of Ald-HA was noticed (figure 5.2 D). The effect of SRNOM (similar to Ald-HA) was slightly higher than that of SRHA followed by SRFA. This trend can be attributed to the binding affinity of Humin (present in NOM) > HA > FA for phenanthrene as reported by Kohl et al. (1998). Saparpakorn et al. (2007) has also shown that PAHs partition to NOM more strongly as compared to HA and FA due to lower docked energies of NOM (docking is the method to predict orientation of molecule to another to form a stable complex and docked energy is the energy of the overall system with optimized confrontation). The π-π interaction and hydrogen bonding is involved in FA, HA and NOM interactions with PAH in addition to hydrogen bonding with proteinaceous moieties of NOM. Therefore, in the case of phenanthrene, the lowest adsorption was seen in the presence of NOM.

	Adsorption Isotherm Constants		Freundlich Isotherm Constants			
	Kd (L g^{-1})		K_f ($mg^{[1-(1/n)]}$ $L^{(1/n)}$ g^{-1})		1/n	
2,2',5,5'-tPCB	Activated Carbon	Organoclay	Activated Carbon	Organoclay	Activated Carbon	Organoclay
Bare Sorbent	7.69	6.00	2.53	3.51	0.47	0.72
Aldrich HA	1.30	2.30	1.12	4.77	0.82	1.59
SRHA	9.59	2.73	2.23	1.58	0.53	0.74
SRFA	11.73	14.91	1.55	-	0.39	-
SRNOM	20.19	8.49	7.64	2.92	0.75	0.65
Phenanthrene						
Bare Sorbent	24.59	10.67	12.84	8.28	0.39	0.79
Aldrich HA	2.31	8.98	2.38	6.39	0.43	0.67
SRHA	6.35	10.96	3.34	10.46	0.27	0.98
SRFA	12.50	8.34	6.23	6.46	0.45	0.74
SRNOM	2.48	9.91	2.74	7.88	0.35	0.80

Table 5.4: Adsorption coefficients for Isotherm Studies to determine effect of Ald-HA/ SRHA/ SRFA and SRNOM

The isotherm data was analyzed using statistical software JMP® 7 to compare the performance of activated carbon and organoclay for 2, 2', 5, 5'-tPCB and phenanthrene adsorption in presence of Ald-HA/ SRHA/ SRFA and SRNOM (table 5.5 A-B). The full factorial models were developed using type of sorbent, treatment and loading rate as the factors. Due to the non-linear form of the isotherms a quadratic term of loading rate was also used.

Table 5.5 A: Specifications of statistical model 1

Model 1 specification: for 2, 2', 5, 5'-tPCB
Sorbent
Treatment
Sorbent*Treatment
Loading Rate
Sorbent*Loading Rate
Treatment*Loading Rate
Sorbent*Treatment*Loading Rate
Loading Rate*Loading Rate

Table 5.5 B: Specifications of statistical model 2

Model 2 specification: for Phenanthrene
Sorbent
Treatment
Sorbent*Treatment
Loading rate
Sorbent*Loading rate
Treatment*Loading rate
Sorbent*Treatment*Loading rate
Loading rate*Loading rate

The p-value was obtained to be < 0.0001 in analysis of variance (ANOVA) (details in additional information). The F-test was performed on each term used in the model to check the significance. The LS Means student's t- table was obtained for adsorbed concentration and treatment based on the type of sorbents (table 5.6). Results showed slightly higher adsorption capacity of activated carbon for 2, 2', 5, 5'-

tPCB than organoclay. The adsorption was found to be increased in presence of FA but significant reduction was noticed in presence of humic acid for both the sorbents. There was no effect of NOM on adsorption of 2, 2', 5, 5'-tPCB on both the sorbents. Table 5.6 B showed effect of Ald-HA/ SRHA/ SRFA/ SRNOM on performance of sorbents for phenanthrene adsorption. There was no effect of any of the natural organics on the adsorption capacity of organoclay. The performance of activated carbon was found to be different than that of organoclay in the presence of Ald-HA but statistically no difference was noticed in performance of activated carbon in the presence of Ald-HA/ SRHA/ SRFA/ SRNOM.

Table 5.6 A: LS Means Student's t table for performance of activated carbon and organoclay in presence of Ald-HA/ SRHA/ SRFA/ SRNOM for 2, 2', 5, 5'-tPCB t at α=0.050 and t=2.04523

Level					Least Sq Mean
AC,SRNOM	A				0.223
AC,SRFA	A				0.220
OC,SRFA	A	B			0.215
AC,SRHA	A	B			0.215
OC,SRNOM	A	B			0.209
AC,Bare	A	B			0.208
OC,Bare		B			0.199
OC,SRHA			C		0.168
OC,Ald-HA				D	0.133
AC,Ald-HA				D	0.129

Levels not connected by same letter are significantly different

Table 5.6 B: LS Means Student's t table for performance of activated carbon and organoclay in presence of Ald-HA/ SRHA/ SRFA/ SRNOM for phenanthrene adsorption at α=0.050 and t=2.06866

Level			Least Sq Mean
OC,SRFA	A		1.254
OC,SRHA	A		1.241
OC,Ald-HA	A	B	1.196
AC,SRNOM	A	B	1.169
AC,SRHA	A	B	1.161
AC,SRFA	A	B	1.152
OC,SRNOM	A	B	1.107
AC,Ald-HA		B	0.999

Levels not connected by same letter are significantly different

Preloading effect of extracted pore water:

Figure 5.3 represented the adsorption of 2, 2', 5, 5'-tPCB and phenanthrene on activated carbon and organoclay in the presence of extracted pore water from Hudson River and Passaic River sediments. The Hudson River sediment pore water was more colloidal and the Passaic River Pore Water was clear, though both had high TOC values (table 5.2). The significant reduction in the performance of both the sorbents for adsorption of both the contaminants was noticed in the presence of Hudson River pore water (figure 5.3A-D). This reduction in adsorption of both the contaminants in the presence of Hudson River pore water can be attributed to the partitioning of contaminants towards high humics present in the porewater. The Passaic River pore water which was low in humics did not have as much reduction effect on the performance of both the sorbents as that of Hudson River pore water. The TOC value of Passaic River pore water was higher than that of Hudson River pore water but the reduction in adsorption was more in case of Hudson River porewater which can be explained on the basis of high aquatic humics present in the Hudson River pore water. The reducing effect of Passaic pore water was very less in case of 2, 2', 5, 5'-tPCB for both the sorbents but it was slightly higher in the case of phenanthrene adsorption (table 5.9).

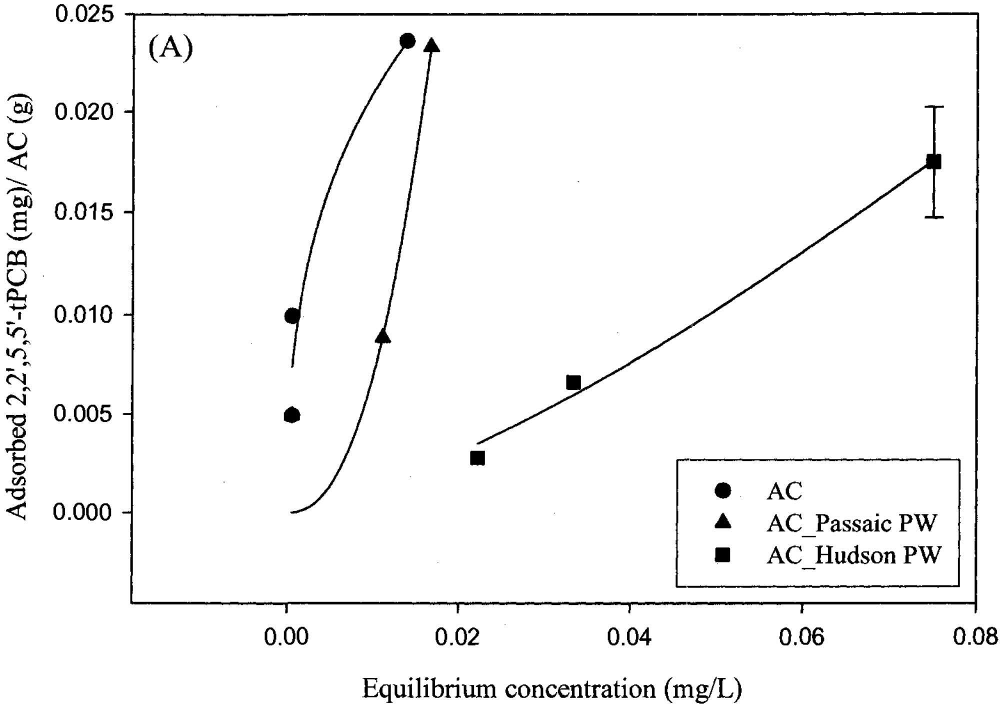


Figure 5.3 A: Adsorption contaminants in presence of extracted pore water: 2, 2', 5, 5'-tPCB adsorption on AC (AC = Activated Carbon and PW = Pore water)

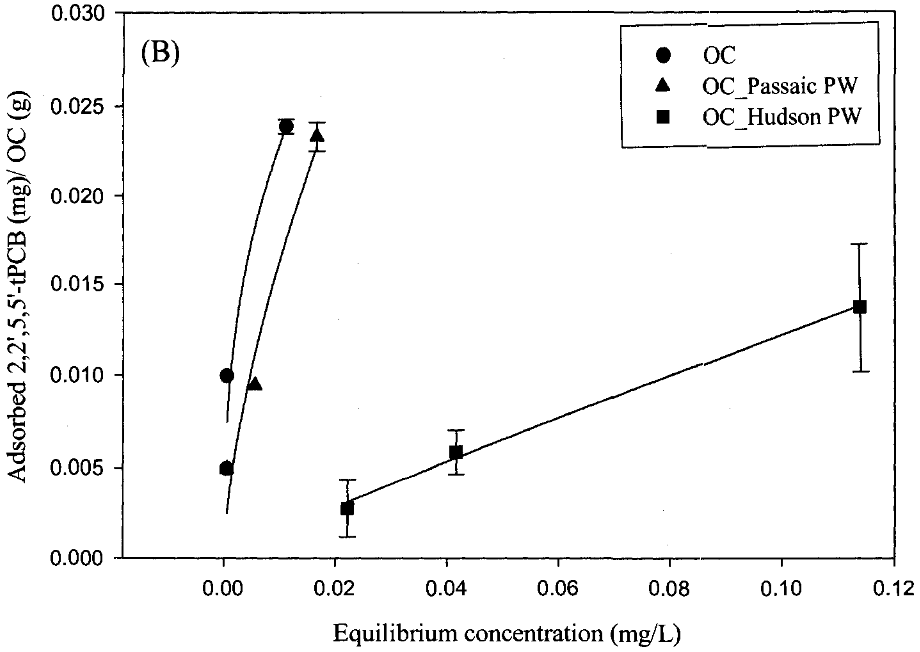


Figure 5.3 B: Adsorption contaminants in presence of extracted pore water: 2, 2', 5, 5'-tPCB adsorption on OC (OC = Organoclay and PW = Pore water)

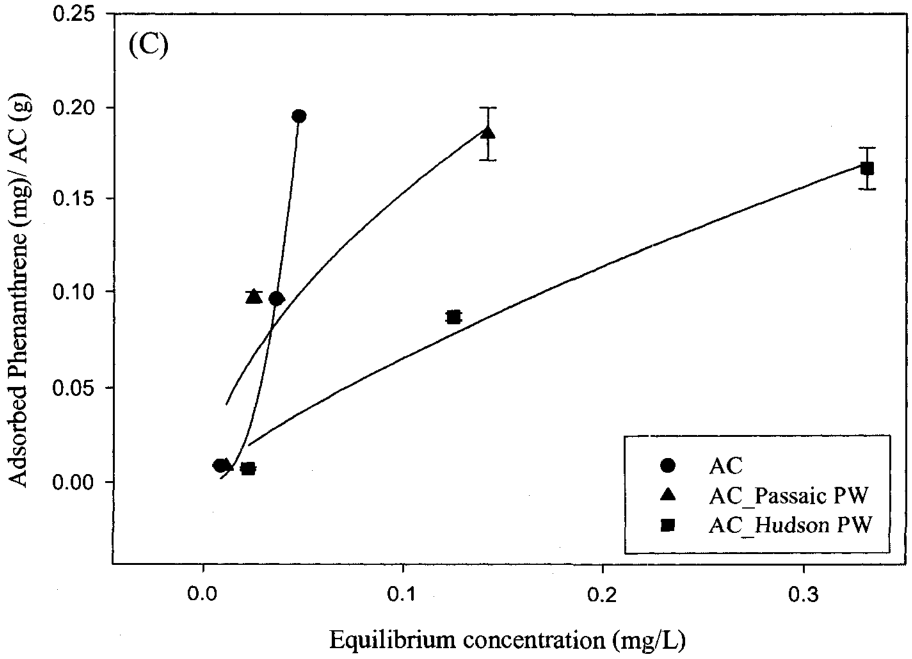


Figure 5.3 C: Adsorption contaminants in presence of extracted pore water: Phenanthrene adsorption on AC (AC = Activated Carbon and PW = Pore water)

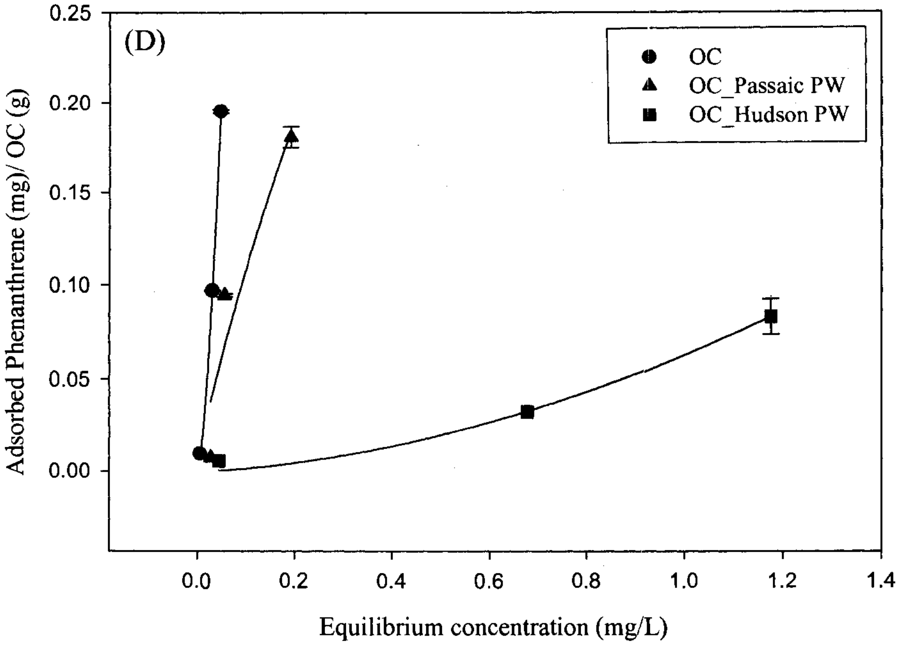


Figure 5.3 D: Adsorption contaminants in presence of extracted pore water (C) Phenanthrene adsorption on AC: Phenanthrene adsorption on OC (OC = Organoclay and PW = Pore water)

The statistical analysis of data was performed to compare the performance of activated carbon and organoclay for 2, 2', 5, 5'-tPCB (model 3) and phenanthrene (model 4) adsorption in presence of extracted pore water (table 5.7).

Table 5.7: Specifications of statistical models 3 and 4

Model 3 and 4 specification:
Sorbent Treatment Sorbent*Treatment Loading Rate Treatment*Loading Rate Loading Rate*Loading Rate

The performance of both the sorbents was found to be reduced in the presence of Hudson River pore water (Figure 5.4 A-B). The reducing effect of Hudson River pore water was more pronounced for both the contaminants for both the sorbents but was very high for phenanthrene adsorption on organoclay (table 5.8 A-B).

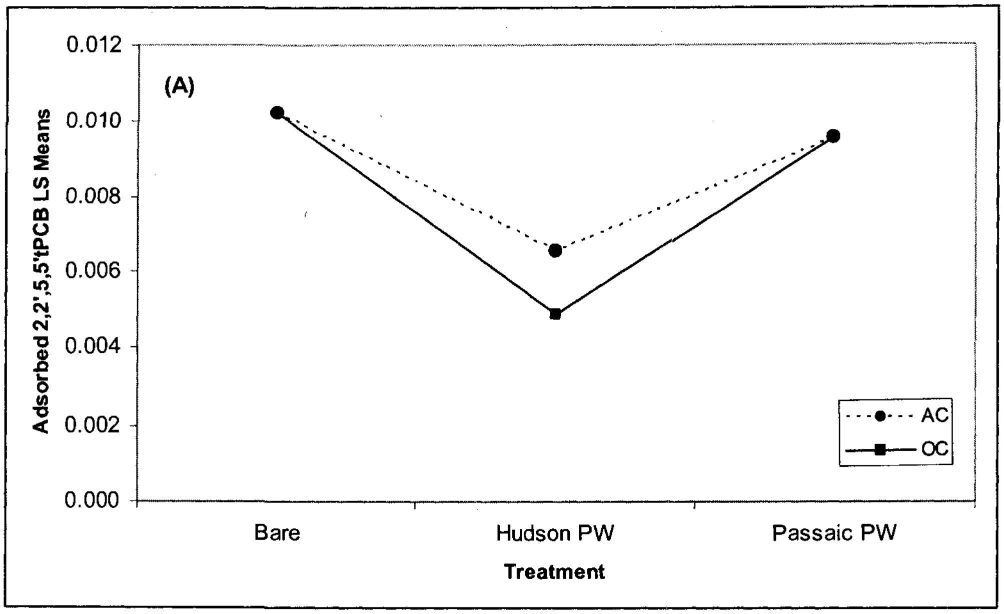


Figure 5.4A: Statistical analysis of performance of sorbents: 2, 2', 5, 5'-tPCB adsorption on AC and OC in presence of extracted pore water (AC = activated carbon; OC = organoclay)

Table 5.8 A: LS Means Student's t table for performance of activated carbon and organoclay in presence of Hudson River and Passaic River porewater for 2, 2', 5, 5'-tPCB adsorption at α=0.050 and t=2.306

Level			Least Sq Mean
AC,Bare	A		0.010
OC,Bare	A		0.010
AC,Passaic PW	A		0.010
OC,Passaic PW	A		0.010
AC,Hudson PW		B	0.007
OC,Hudson PW		B	0.005

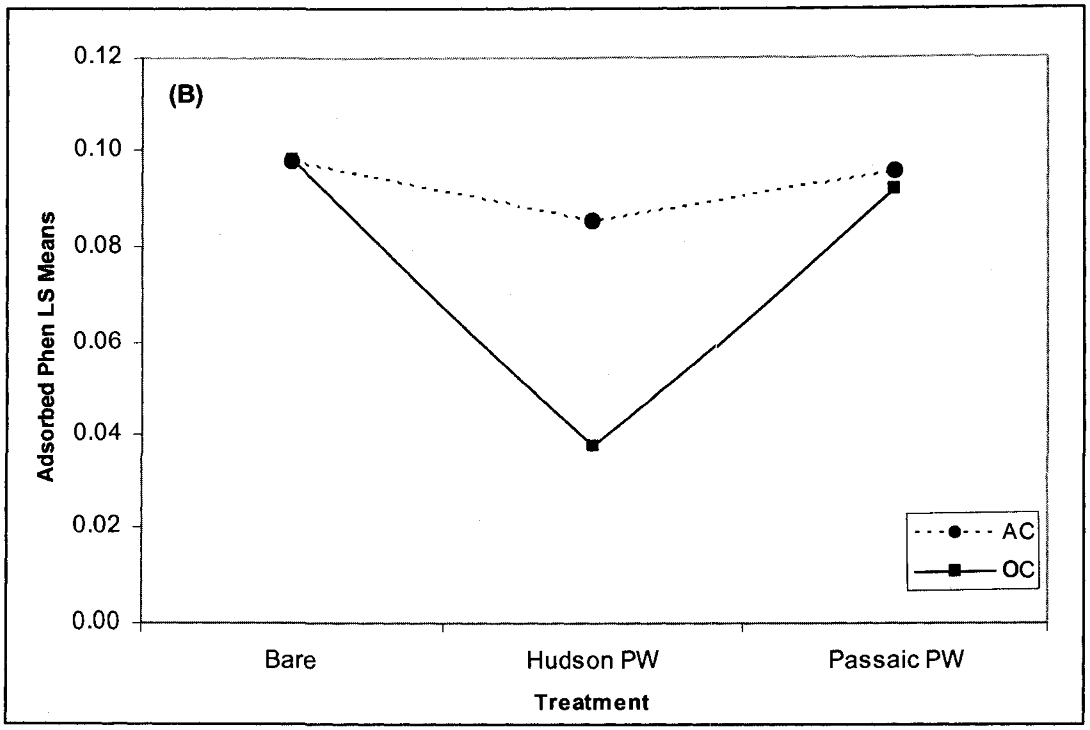


Figure 5.4B: Statistical analysis of performance of sorbents: phenanthrene adsorption on AC and OC in presence of extracted pore water (AC = activated carbon; OC = organoclay)

Table 5.8 B: LS Means Student's t table for performance of activated carbon and organoclay in presence of Hudson River and Passaic River porewater for phenanthrene adsorption at α=0.050 and t=2.570

Level				Least Sq Mean
OC,Bare	A			0.098
AC,Bare	A			0.098
AC,Passaic PW	A			0.095
OC,Passaic PW	A	B		0.092
AC,Hudson PW		B		0.085
OC,Hudson PW			C	0.038

	Adsorption Isotherm Constants		Freundlich Isotherm Constants			
	Kd (L g^{-1})		K_f ($mg^{[1-(1/n)]}$ $L^{(1/n)}$ g^{-1})		1/n	
2,2',5,5'-tPCB	Activated Carbon	Organoclay	Activated Carbon	Organoclay	Activated Carbon	Organoclay
Bare Sorbent	1.13	1.56	0.11	0.14	0.36	0.39
HPW	0.27	0.12	381.12	0.33	2.37	0.65
PPW	1.04	1.16	0.54	0.10	1.32	0.90
Phenanthrene						
Bare Sorbent	4.47	4.38	520.39	24.40	2.58	1.58
HPW	0.50	0.07	0.60	0.71	0.59	0.82
PPW	1.23	0.92	0.41	0.06	0.79	1.67

Table 5.9 Adsorption coefficients for Isotherm Studies to determine effect of extracted porewater

Performance of sorbent amendment mixtures:

In figure 5.5 the performance of virgin sorbent mixture was compared to that of sorbent mixture obtained from Cottonwood Bay and sorbent mixture in presence of Cottonwood Bay porewater for adsorption of 2, 2', 5, 5'-tPCB and phenanthrene.

Table 5.10: Characteristics of Cottonwood Bay porewater

Sediment sample	pH	ORP(mv)	TOC (mg L^{-1})	DOC (mg L^{-1})	UV_{254} (cm^{-1})
Cottonwood Bay	7.59	-32.7	5.715	6.1	0.106

The sorbent mixture that was obtained from the mats represented the realistic scenario having sorbents in the geotextile being deployed over the sediment bed for six months. There was negligible effect of natural organics present in the site on adsorption of 2, 2', 5, 5'-tPCB and the slight reducing effect on phenanthrene adsorption was also found to be statistically negligible. In figure 5.5 the actual trend of isotherms was presented using a dotted line that shows slight S-shaped behavior of the sorbent mixture.

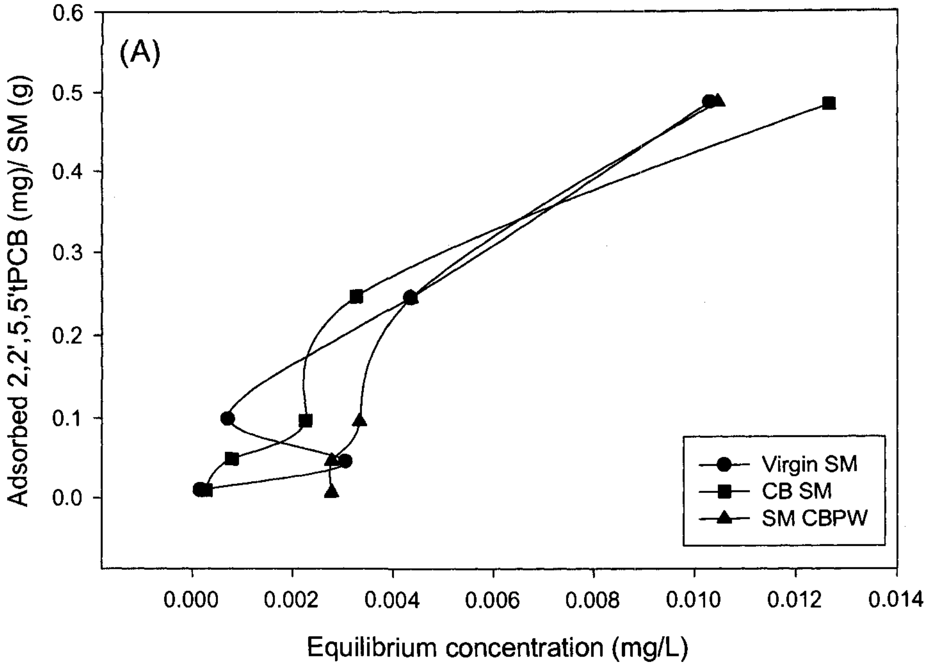


Figure 5.5 A: Comparison of bare sorbent mixture with the sorbent mixture obtained from reactive core mats deployed in Cottonwood Bay for 6 months: 2, 2', 5, 5'-tPCB adsorption(SM = Sorbent mixture; CB = Cottonwood Bay; and PW = Porewater)

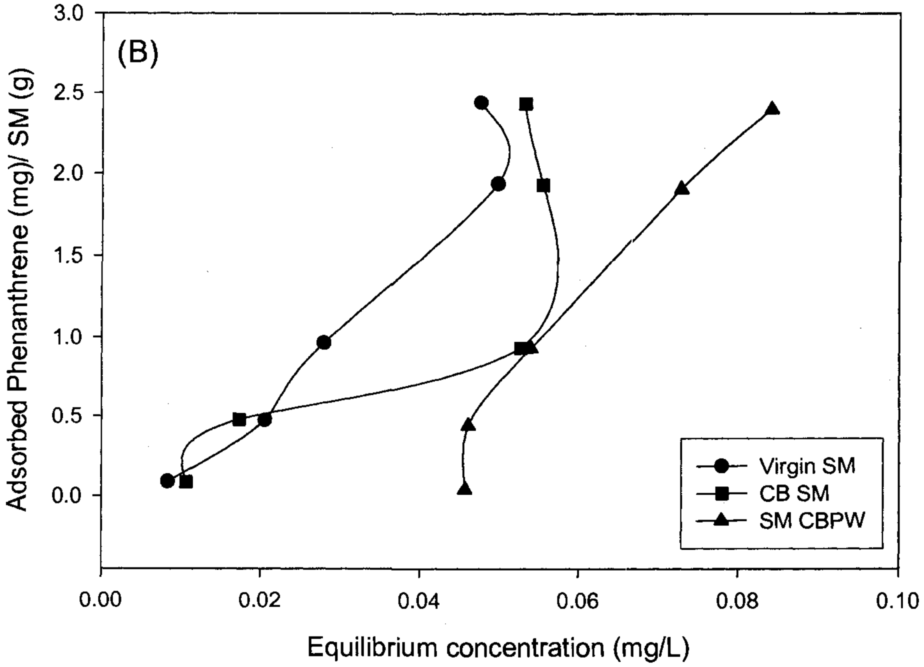


Figure 5.6B: Comparison of bare sorbent mixture with the sorbent mixture obtained from reactive core mats deployed in Cottonwood Bay for 6 months: Phenanthrene adsorption (SM = Sorbent mixture; CB = Cottonwood Bay; and PW = porewater)

The performance of both the sorbent mixtures was also analyzed statistically for adsorption of 2, 2', 5, 5'-tPCB (model 5) and phenanthrene (model 6) (table 5.11). The models were developed on the basis of treatment on sorbent mixture (virgin/ Cottonwood Bay/Porewater) and loading rate (details in additional information).

Table 5.11: Specifications for statistical model 5 and model 6

Model 5 and 6 specification:
Treatment
Loading Rate
Treatment*Loading Rate

LS Mean's plots were obtained to determine the effect of natural organic matter present in Cottonwood Bay (Figure 5.6). The results showed no difference in the performance of virgin sorbent mixture, sorbent mixture obtained from mats and sorbent mixture in Cottonwood Bay porewater (table 5.12 A-B).

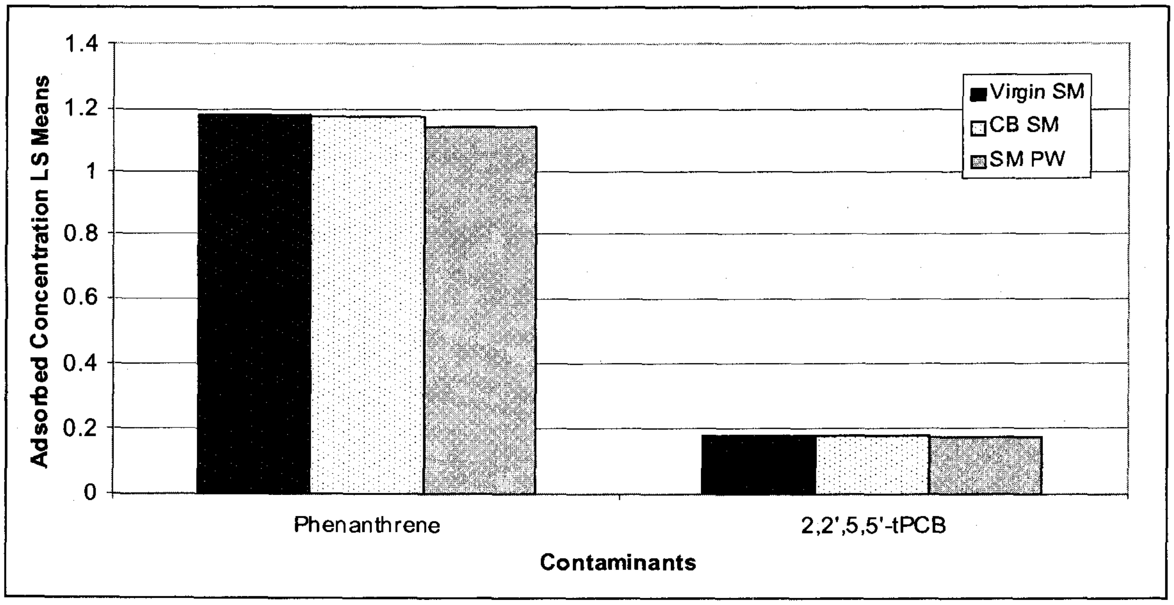


Figure 5.6: Statistical analysis of performance of sorbents: 2, 2', 5, 5'-tPCB and phenanthrene adsorption on SM and CB SM (SM = Sorbent Mixture, CB = Cottonwood Bay and PW = Porewater)

Table 5.12 A-B: LS Means Student's t table for performance of sorbent mixture for 2, 2', 5, 5'-tPCB and phenanthrene adsorption at α=0.050 and t = 2.306

A: 2, 2', 5, 5'-tPCB adsorption

Level		Least Sq Mean
SM	A	0.106
CBSM	A	0.105
SM PW	A	0.104

B: Phenanthrene adsorption

Level		Least Sq Mean
SM	A	1.080
CBSM	A	1.071
SM PW	A	1.042

Levels not connected by same letter are significantly different.

	Adsorption Isotherm Constants			Freundlich Isotherm Constants					
	Kd (L g^{-1})			$K_f (mg^{[1-(1/n)]} L^{(1/n)} g^{-1})$			1/n		
Contaminants	Virgin Sorbent Mixture	Cottonwood Bay Sorbent Mixture	Sorbent mixture in PW	Virgin Sorbent Mixture	Cottonwood Bay Sorbent Mixture	Sorbent mixture in PW	Bare Sorbent Mixture	Cottonwood Bay Sorbent Mixture	Sorbent mixture in PW
2, 2', 5, 5'-tPCB	45.46	36.82	57.53	65.83	11.78	256.43	1.07	0.73	1.37
Phenanthrene	53.90	37.84	56.54	243.21	106.64	2587.33	1.56	1.40	2.80

Table 5.13: Adsorption coefficients for Isotherm Studies for sorbent mixture evaluation

Effect of different loadings of HA/ FA/ NOM:

Studies were also conducted at three loadings of HA/ FA and NOM to determine the effect of different loadings on adsorption of 2, 2', 5, 5'-tPCB and phenanthrene on activated carbon and organoclay (Figure 5.7). Figure 5.7A-C showed results for 2, 2', 5, 5'-tPCB adsorption and figure 5.7 D – F represents results for phenanthrene adsorption.

In figure 5.7A and D it can be noticed that with the increase in concentration of humic acid the performance of sorbents decreases. The effect of FA and NOM did not show much variation in the effect at different loadings on 2, 2', 5, 5'-tPCB but the trend was slightly decreasing for phenanthrene adsorption on activated carbon. The middle loading of HA/ FA and NOM corresponded to the concentration used in preloading the sorbents for isotherm studies.

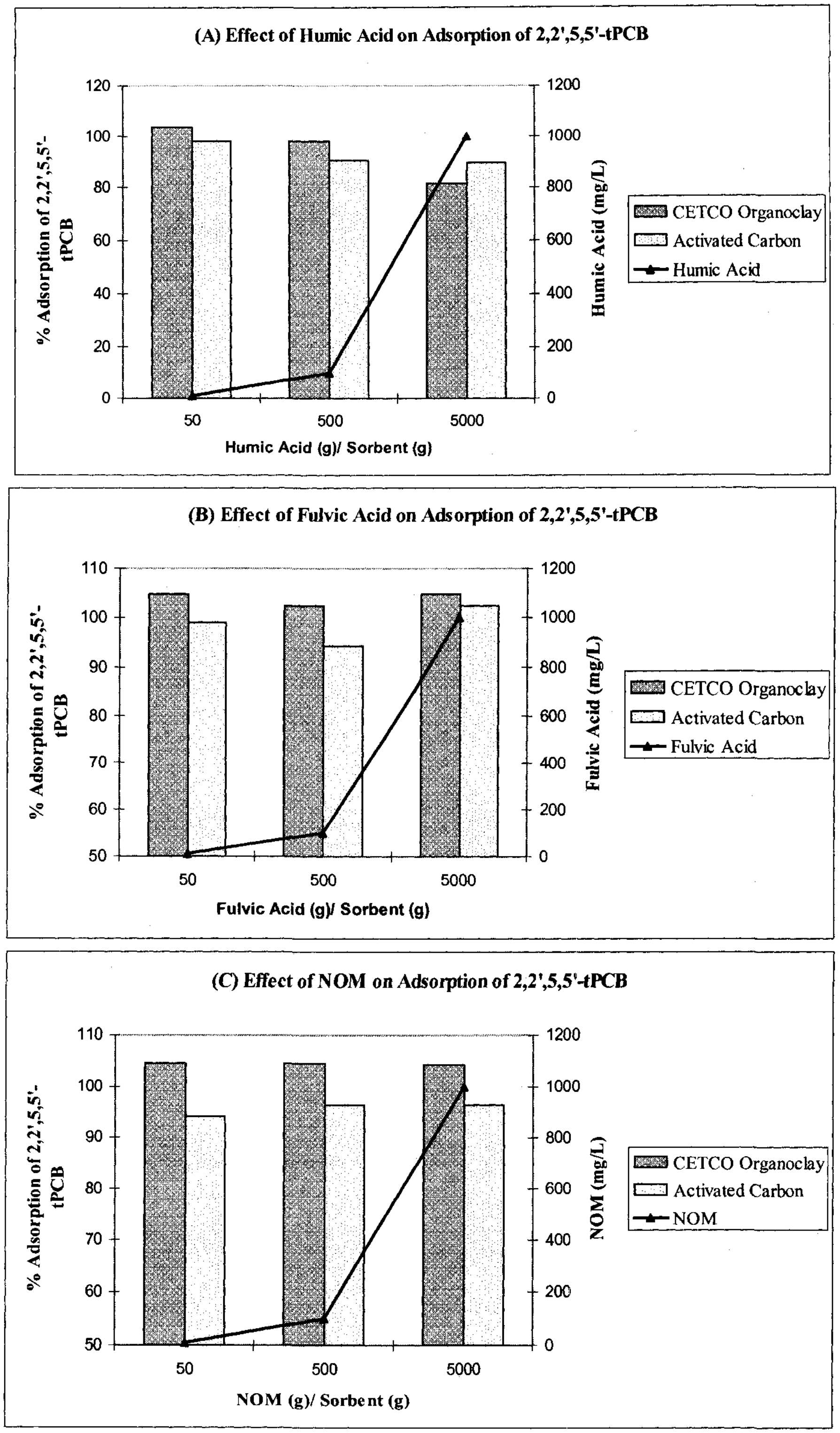


Figure 5.7A-C: Comparison of performance of organoclay and activated carbon for adsorption of 2, 2', 5, 5'-tPCB in the presence of humic acid, fulvic acid and natural organic matter normalized to adsorption on bare materials.

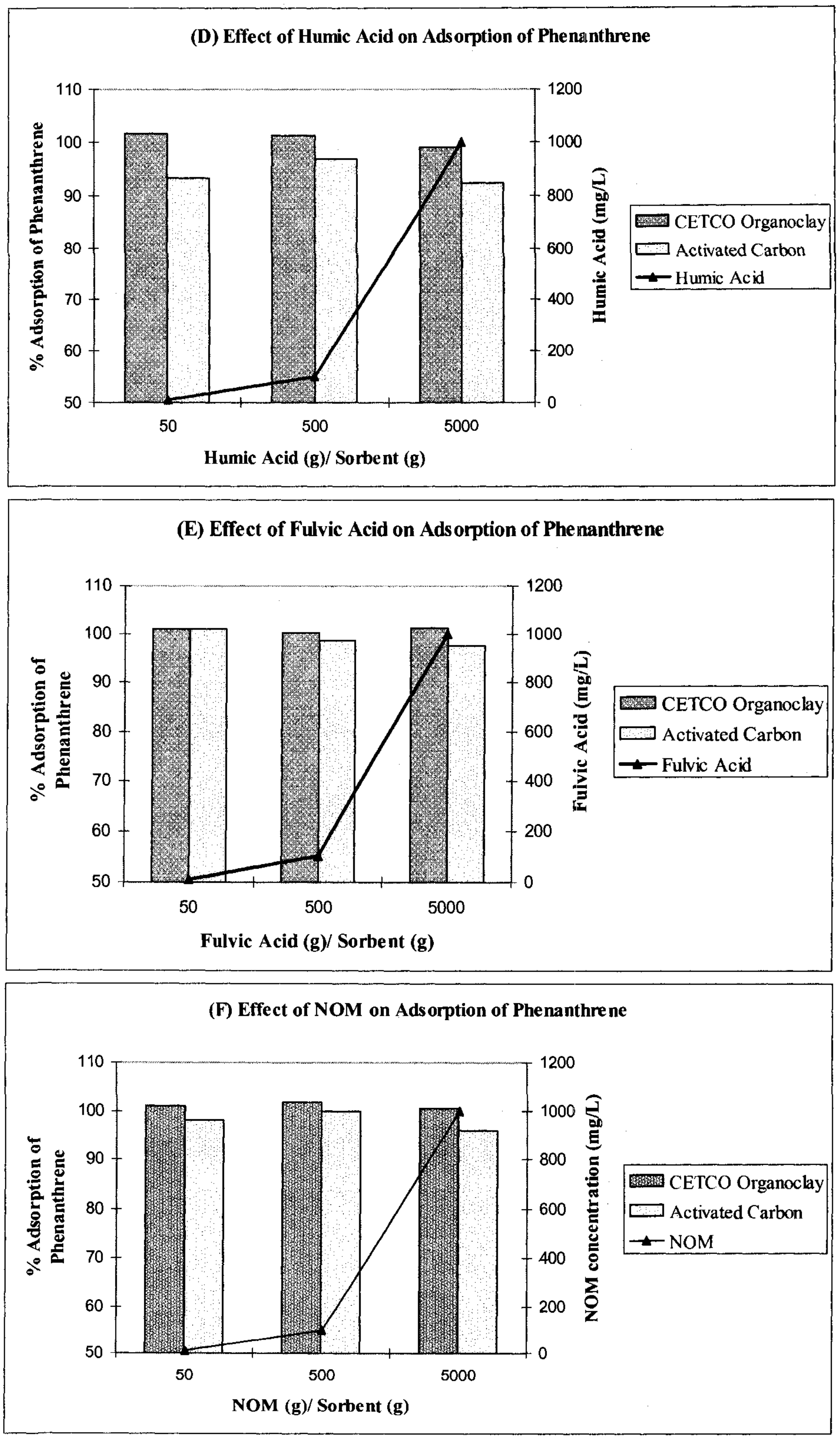
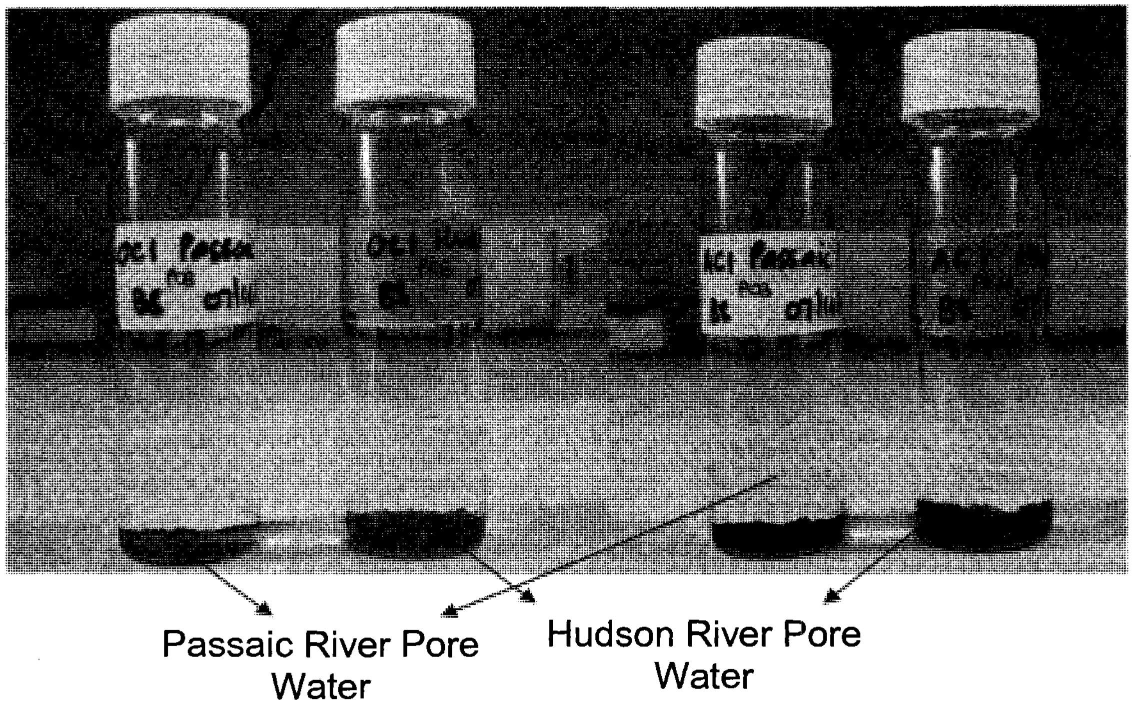


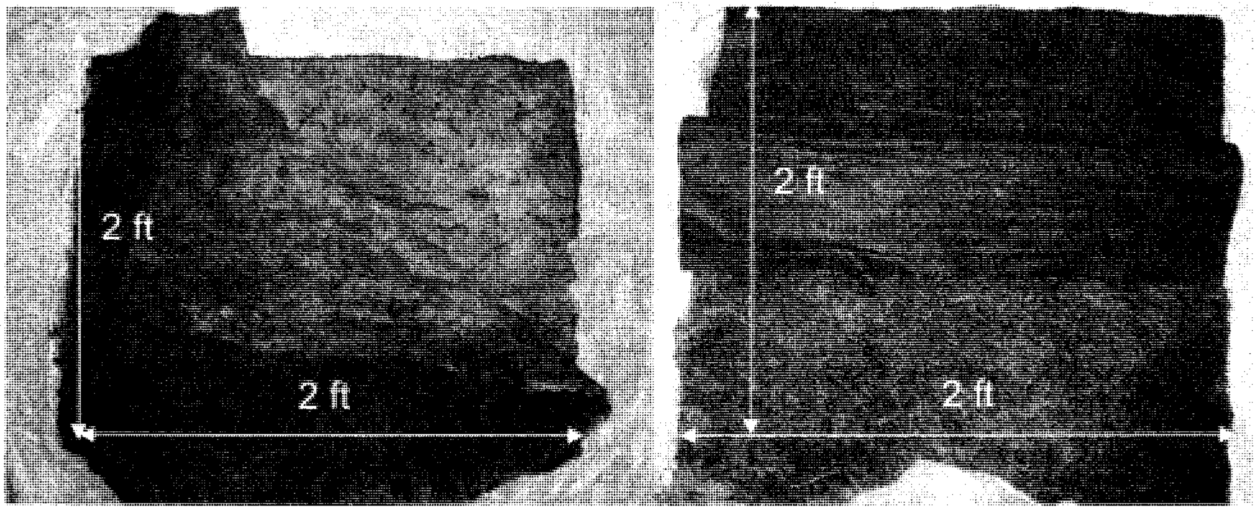
Figure 5.7D-F: Comparison of performance of organoclay and activated carbon for adsorption of phenanthrene in the presence of humic acid, fulvic acid and natural organic matter normalized to adsorption on bare materials.

Summary

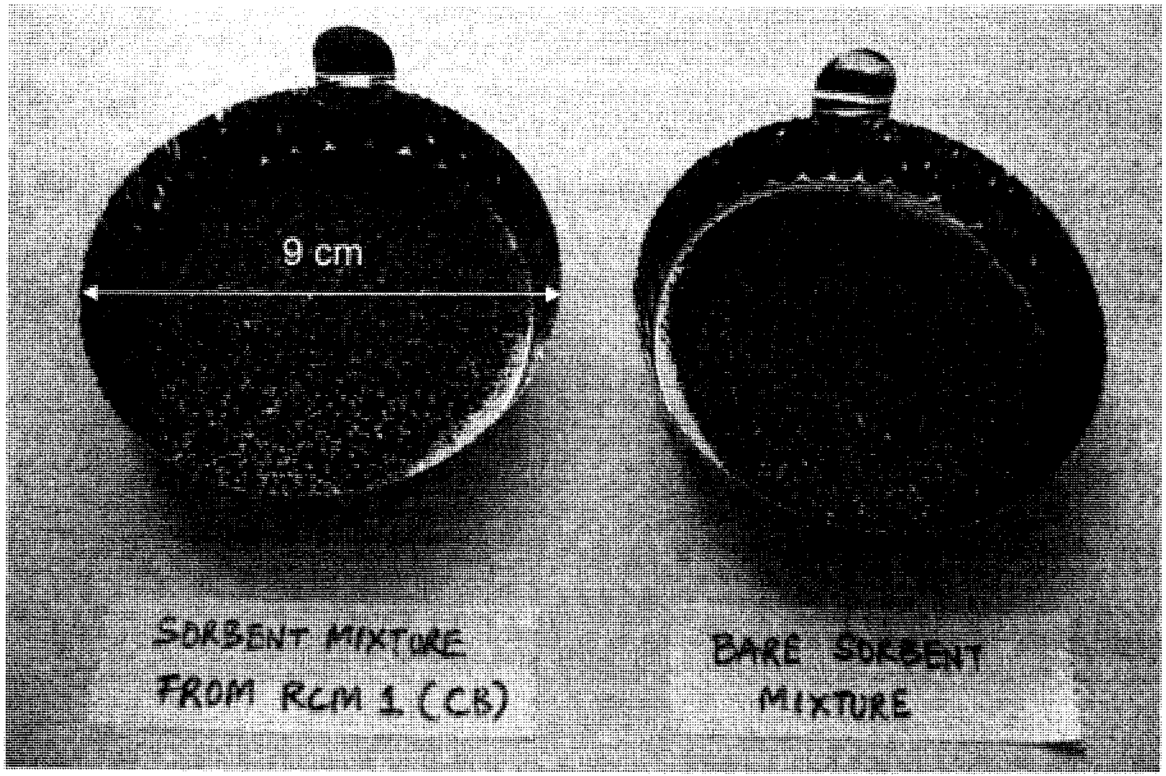
This study has been conducted to evaluate the performance of activated carbon and organoclay for 2, 2', 5, 5'-tPCB and phenanthrene adsorption in the presence of different fractions of natural organic matter and extracted pore water to simulate the actual site conditions. Besides evaluating the different sorbents, the sorbent mixture having a combination of different materials was also analyzed and its performance was compared with the sorbent mixture obtained from the reactive capping mat that was deployed in the study field site (Cottonwood Bay) for six months. The results showed significant effect of AldHA on the adsorption of 2, 2', 5, 5'-tPCB on both the sorbents. The effect of SRHA was more pronounced in case of adsorption of 2, 2', 5, 5'-tPCB on organoclay compared to activated carbon. There was slight enhancement on 2, 2', 5, 5'-tPCB adsorption on organoclay in the presence of SRFA but there was no effect on activated carbon. There was no effect of SRNOM on 2, 2', 5, 5'-tPCB adsorption on both the sorbents. In case of phenanthrene, no effect was noticed in presence of any of the natural organics on organoclay. The reducing effects of AldHA/ SRHA/ SRFA and SRNOM were found to be similar on activated carbon. Besides Ald-HA/ SRHA/ SRFA and SRNOM, extracted pore water was also used to evaluate the performance of sorbents. A significant reducing effect was noticed on the performance of both the sorbents for both the contaminants in case of Hudson River sediment pore water which was high in humics compared to Passaic River sediment porewater that had mixture of humic and non-humic contents. The performance of virgin sorbent mixture was also compared with sorbent mixture obtained from the mat that was deployed in the field for six months and with the effect of Cottonwood Bay pore water on virgin sorbent mixture but negligible effect of natural organic matter that was presented in the field was found. The Ald-HA/ SRFA and SRNOM effects were also determined at different loadings on both the sorbents. The adsorption capacity of both the sorbent was found to be decreased with the increase in Ald-HA concentration. The fulvic acid and natural organic matter did not affect the 2, 2', 5, 5'-tPCB adsorption on both the sorbents but slight reduction was noticed on phenanthrene adsorption on activated carbon.

Additional Information





Reactive core mats drying at room temperature prior to sorbent separation

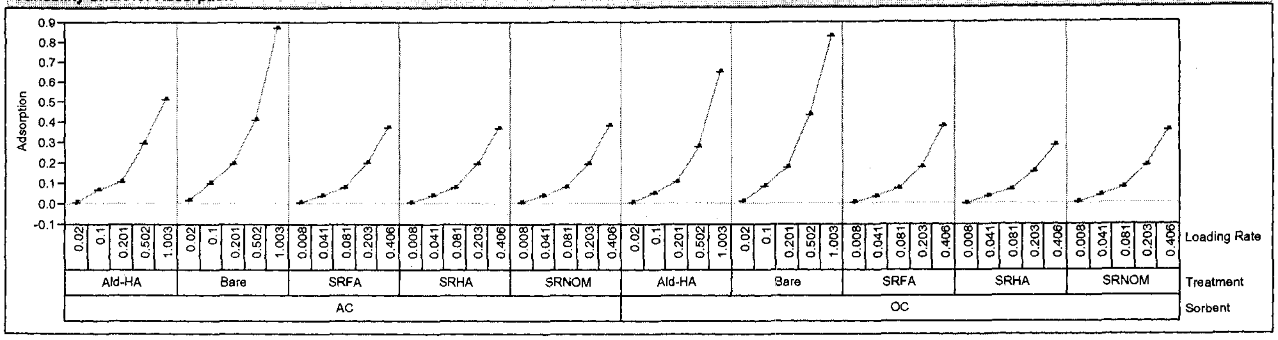


Left: Sorbent mixture obtained from reactive core mat (deployed in the field for 6 months); Right: Virgin sorbent mixture

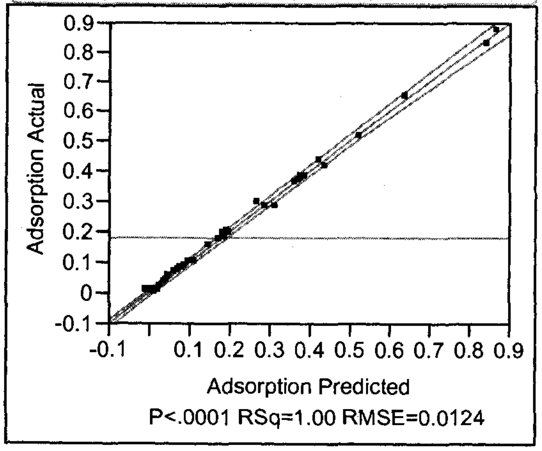
Model 1 detail: for 2, 2', 5, 5'–tPCB adsorption in presence of Ald-HA/ SRHA/ SRFA/ SRNOM

Variability Gauge

Variability Chart for Adsorption



Actual by Predicted Plot



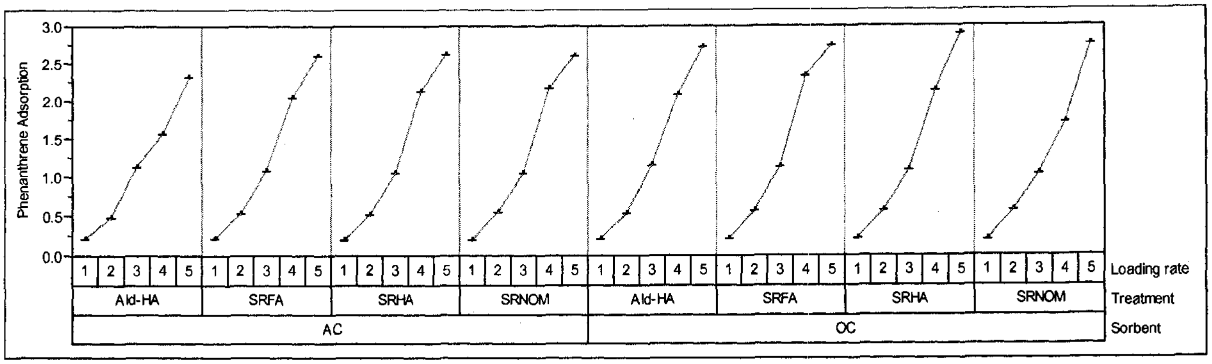
Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	20	2.1011635	0.105058	688.4599
Error	29	0.0044254	0.000153	**Prob > F**
C. Total	49	2.1055889		<.0001*

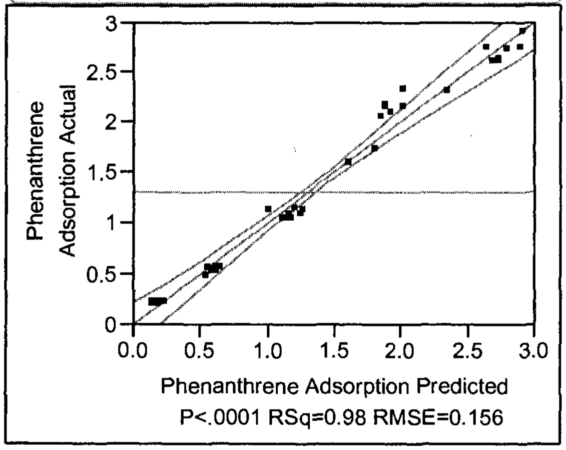
Effect Tests

Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F
Sorbent	1	1	0.00193851	12.7033	0.0013*
Treatment	4	4	0.04126649	67.6062	<.0001*
Sorbent*Treatment	4	4	0.00293094	4.8017	0.0043*
Loading Rate	1	1	0.76939337	5041.935	<.0001*
Sorbent*Loading Rate	1	1	0.00030393	1.9917	0.1688
Treatment*Loading Rate	4	4	0.05156139	84.4721	<.0001*
Sorbent*Treatment*Loading Rate	4	4	0.00821990	13.4665	<.0001*
Loading Rate*Loading Rate	1	1	0.00000233	0.0153	0.9025

Model 2 detail: for phenanthrene adsorption in presence of Ald-HA/ SRHA/ SRFA/ SRNOM



Actual by Predicted Plot



Analysis of Variance

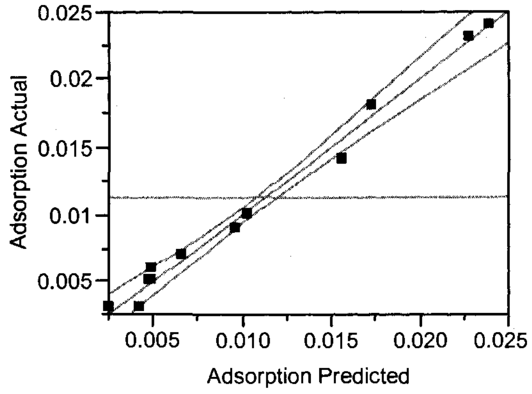
Source	DF	Sum of Squares	Mean Square	F Ratio
Model	16	33.424202	2.08901	85.8206
Error	23	0.559858	0.02434	**Prob > F**
C. Total	39	33.984060		<.0001*

Effect Tests

Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F
Sorbent	1	1	0.062647	2.5737	0.1223
Treatment	3	3	0.079162	1.0840	0.3756
Sorbent*Treatment	3	3	0.086122	1.1794	0.3393
Loading rate	1	1	32.452603	1333.214	<.0001*
Sorbent*Loading rate	1	1	0.058482	2.4026	0.1348
Treatment*Loading rate	3	3	0.064736	0.8865	0.4628
Sorbent*Treatment*Loading rate	3	3	0.052018	0.7123	0.5546
Loading rate*Loading rate	1	1	0.568433	23.3523	<.0001*

Model 3: 2, 2', 5, 5'-tPCB adsorption in presence of extracted porewater

Actual by Predicted Plot



P<.0001 RSq=0.99 RMSE=0.001

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	9	0.00099839	0.000111	122.8786
Error	8	0.00000722	9.028e-7	**Prob > F**
C. Total	17	0.00100561		<.0001*

Effect Tests

Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F
Sorbent	1	1	0.00000139	1.5385	0.2500
Treatment	2	2	0.00007078	39.2000	<.0001*
Sorbent*Treatment	2	2	0.00000278	1.5385	0.2721
Loading Rate	1	1	0.00083333	923.0769	<.0001*
Treatment*Loading Rate	2	2	0.00002067	11.4462	0.0045*
Loading Rate*Loading Rate	1	1	0.00006944	76.9231	<.0001*

Model 4: Phenanthrene adsorption in presence of extracted porewater

Analysis of Variance

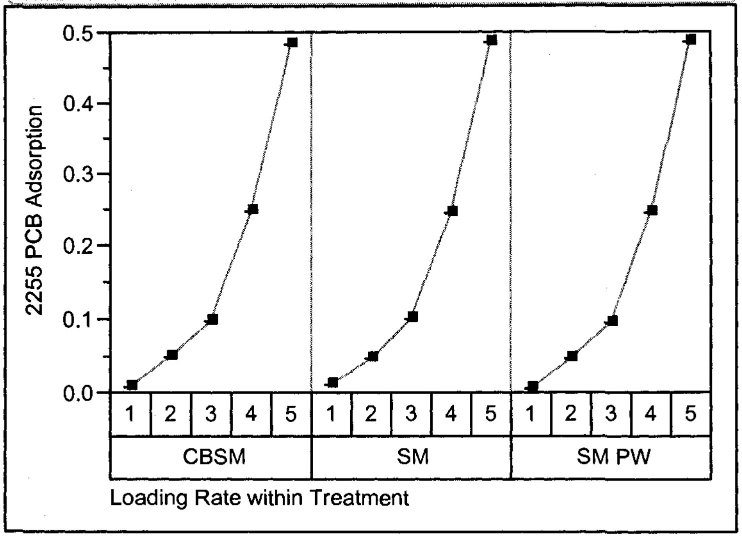
Source	DF	Sum of Squares	Mean Square	F Ratio
Model	12	0.08913506	0.007428	446.2703
Error	5	0.00008322	0.000017	**Prob > F**
C. Total	17	0.08921828		<.0001*

Effect Tests

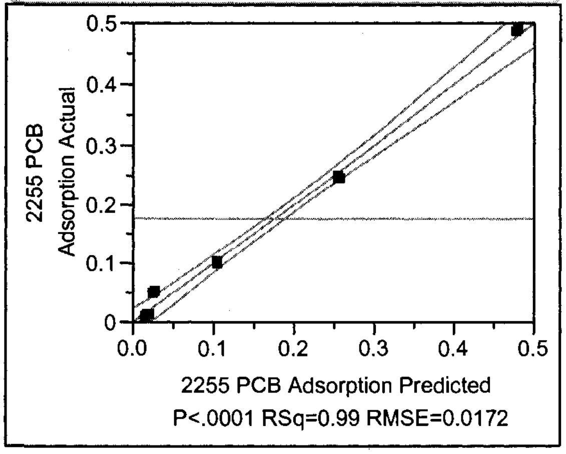
Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F
Sorbent	1	1	0.00130050	78.1342	0.0003*
Treatment	2	2	0.00472578	141.9626	<.0001*
Sorbent*Treatment	2	2	0.00212800	63.9252	0.0003*
Loading Rate	1	1	0.07648033	4594.947	<.0001*
Sorbent*Loading Rate	1	1	0.00061633	37.0294	0.0017*
Treatment*Loading Rate	2	2	0.00272217	81.7740	0.0002*
Sorbent*Treatment*Loading Rate	2	2	0.00110817	33.2894	0.0013*
Loading Rate*Loading Rate	1	1	0.00005378	3.2310	0.1322

Model 5: Performance of sorbent mixture for 2, 2', 5, 5'-tPCB adsorption

Variability Chart for 2255 PCB Adsorption



Actual by Predicted Plot



Analysis of Variance

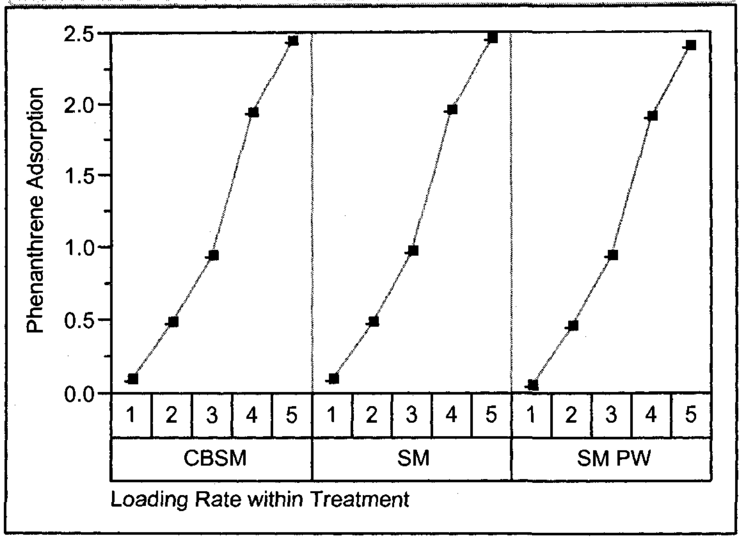
Source	**DF**	**Sum of Squares**	**Mean Square**	**F Ratio**
Model	6	0.45264500	0.075441	254.8702
Error	8	0.00236798	0.000296	**Prob > F**
C. Total	14	0.45501297		<.0001*

Effect Tests

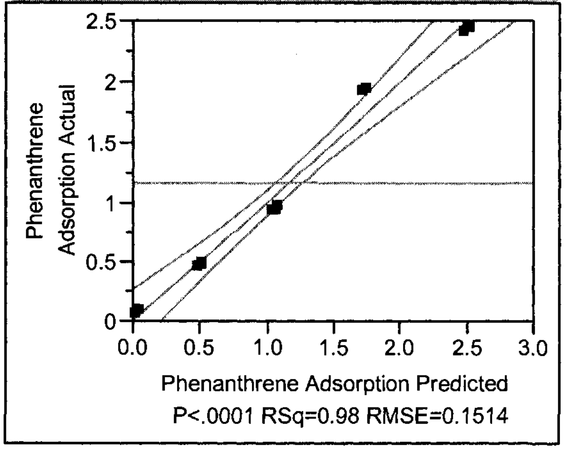
Source	**Nparm**	**DF**	**Sum of Squares**	**F Ratio**	**Prob > F**
Treatment	2	2	0.00000519	0.0088	0.9913
Loading Rate	1	1	0.39852298	1346.375	<.0001*
Treatment*Loading Rate	2	2	0.00000835	0.0141	0.9860
Loading Rate*Loading Rate	1	1	0.05410848	182.8007	<.0001*

Model 6: Performance of sorbent mixture for phenanthrene adsorption

Variability Chart for Phenanthrene Adsorption



Actual by Predicted Plot

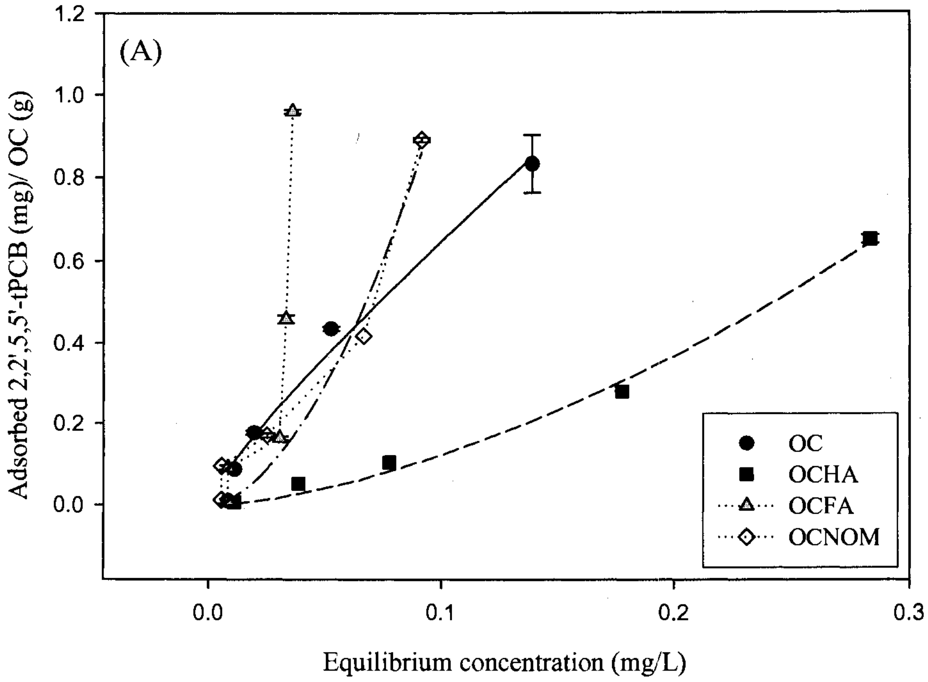


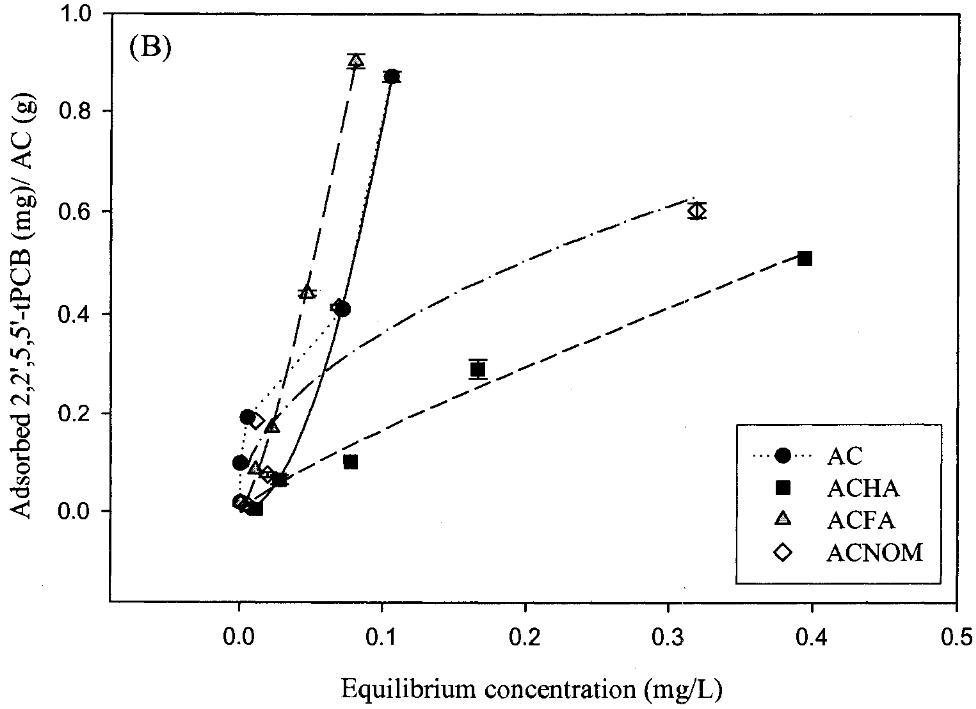
Analysis of Variance

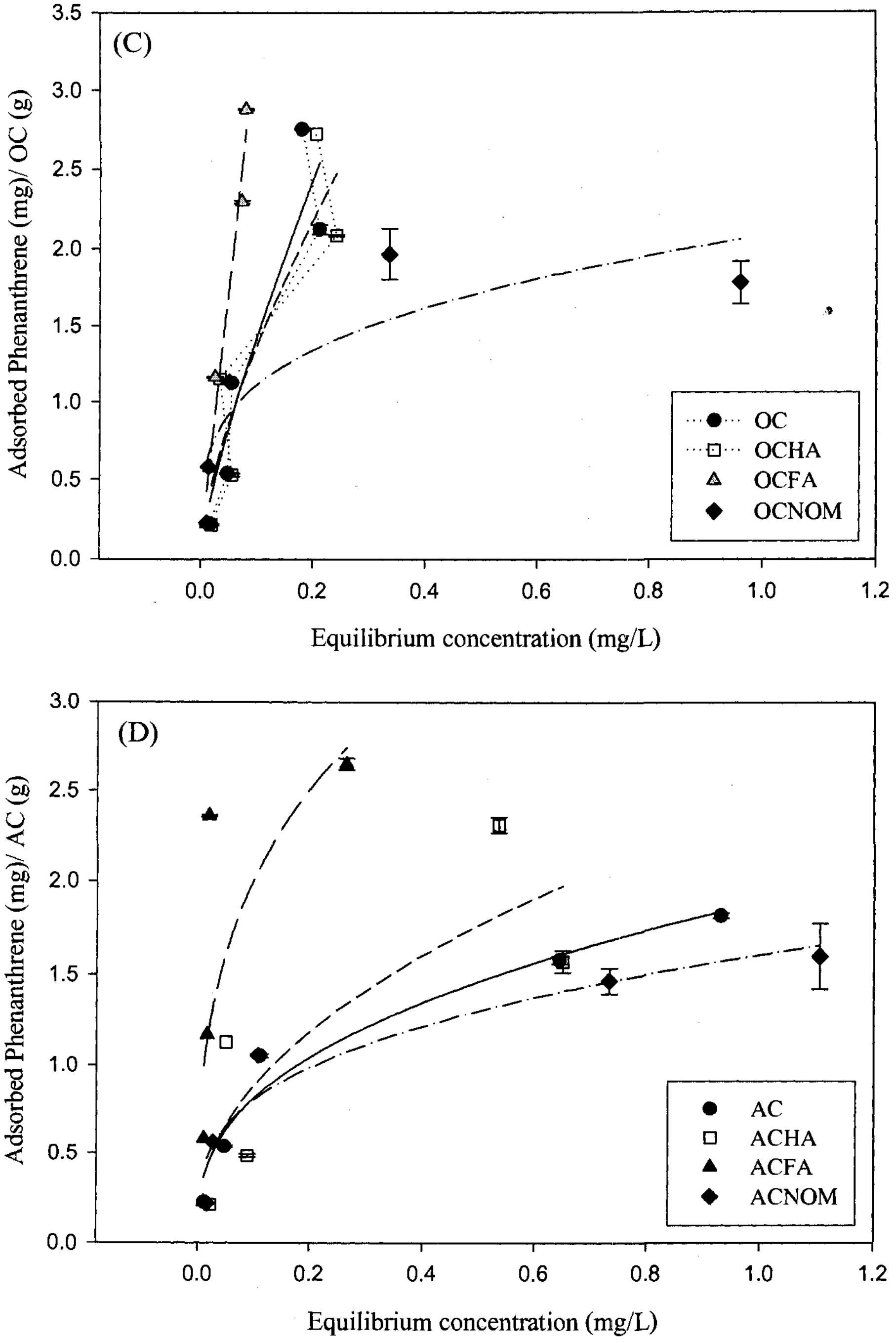
Source	DF	Sum of Squares	Mean Square	F Ratio
Model	6	11.498476	1.91641	83.6549
Error	8	0.183268	0.02291	**Prob > F**
C. Total	14	11.681744		<.0001*

Effect Tests

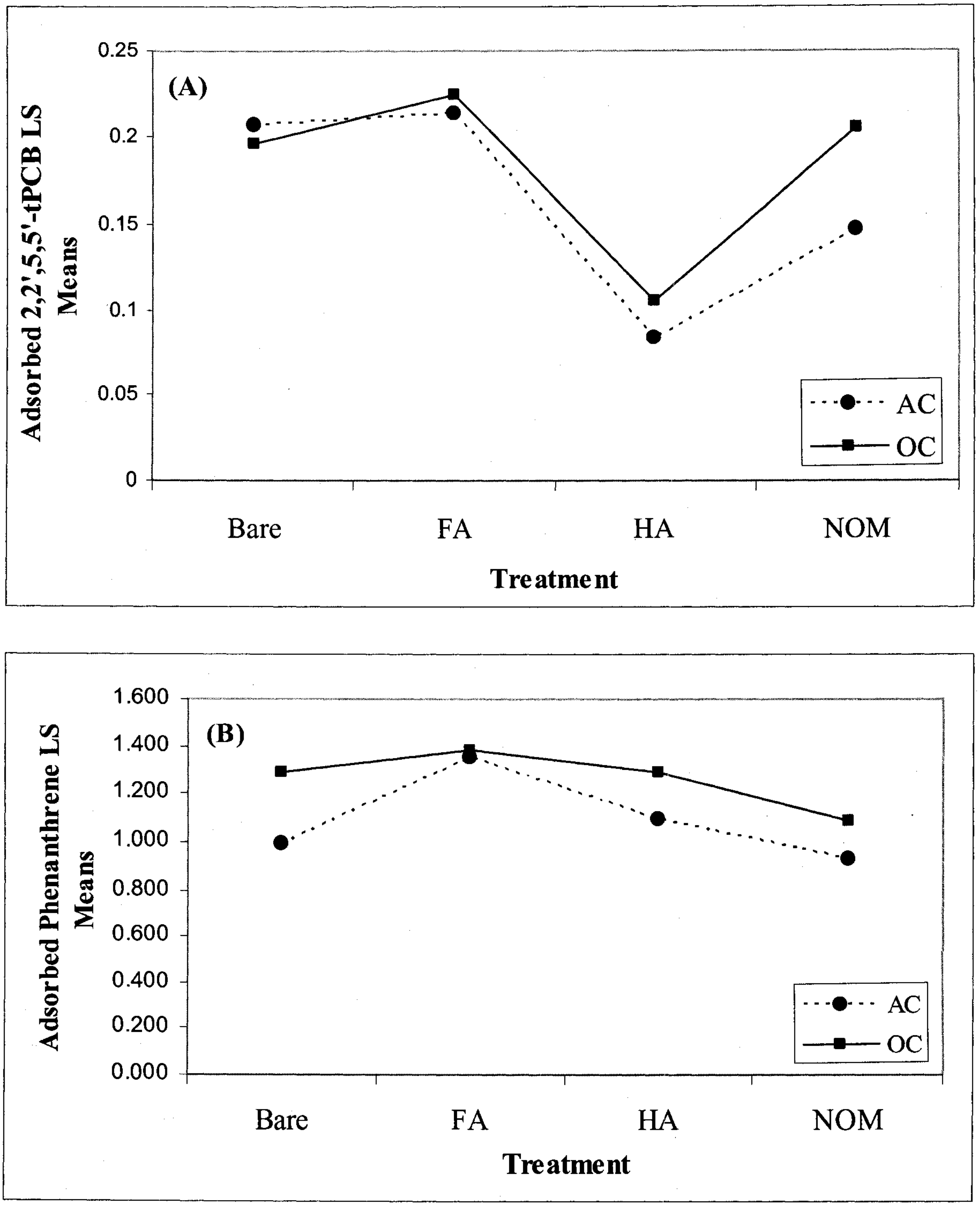
Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F
Treatment	2	2	0.003774	0.0824	0.9217
Loading Rate	1	1	11.385651	497.0045	<.0001*
Treatment*Loading Rate	2	2	0.000033	0.0007	0.9993
Loading Rate*Loading Rate	1	1	0.109018	4.7588	0.0607


(A)
Adsorbed 2,2',5,5'-tPCB (mg)/ OC (g)
Equilibrium concentration (mg/L)
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0.0
0.1
0.2
0.3
OC
OCHA
OCFA
OCNOM

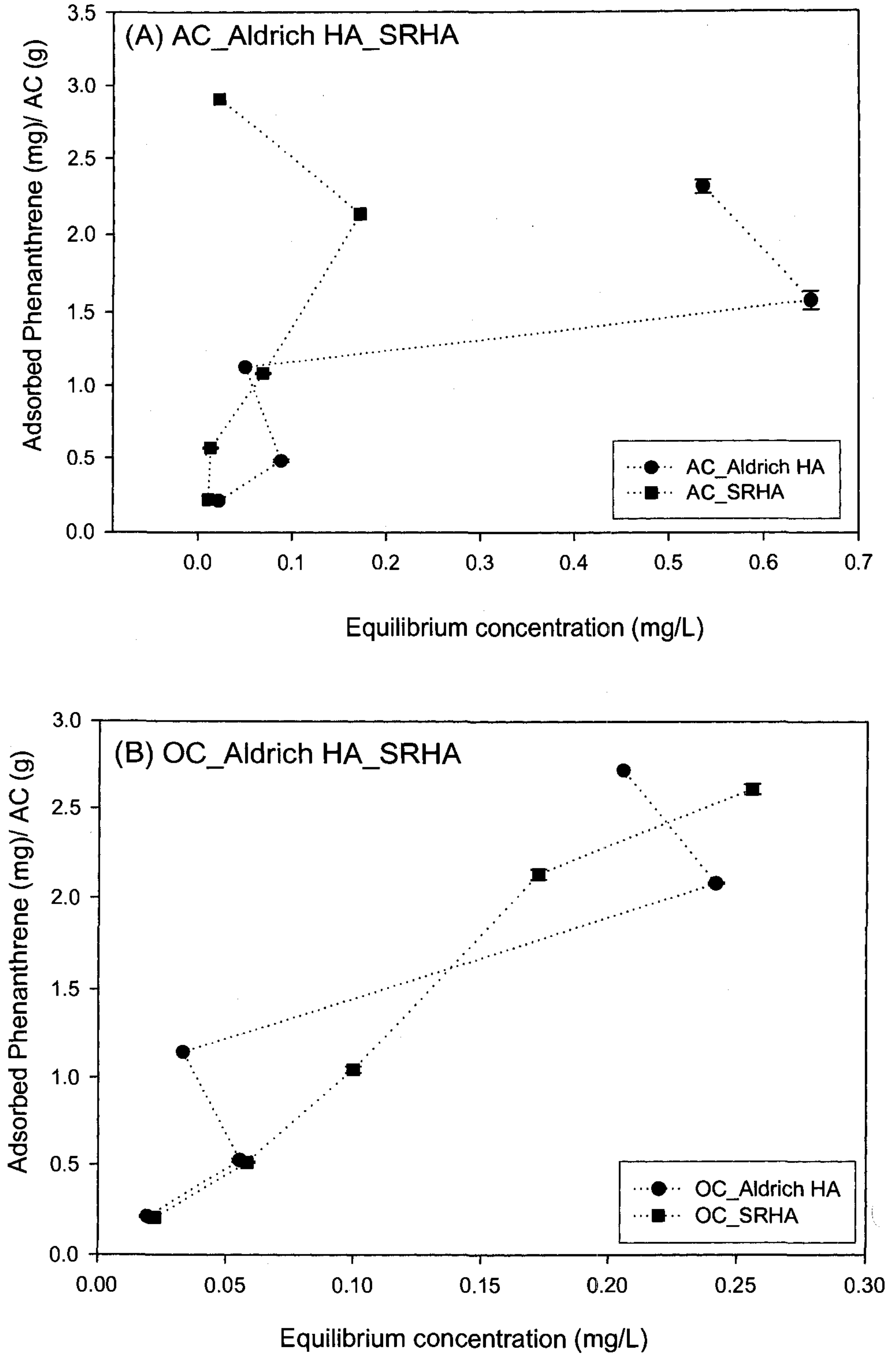

(B)
Adsorbed 2,2',5,5'-tPCB (mg)/ AC (g)
Equilibrium concentration (mg/L)
1.0
0.8
0.6
0.4
0.2
0.0
0.0
0.1
0.2
0.3
0.4
0.5
AC
ACHA
ACFA
ACNOM



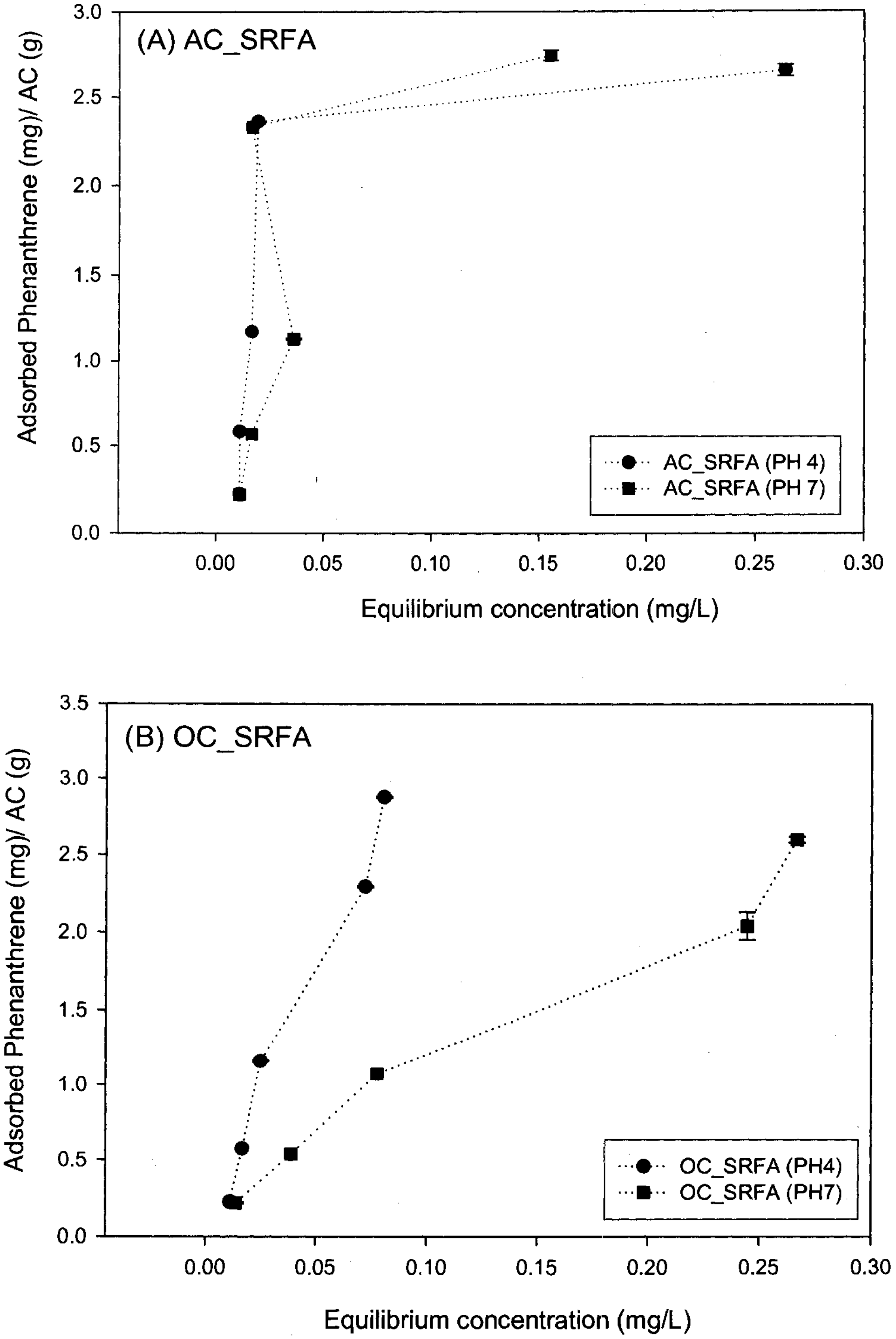
Adsorption of contaminants in presence of different fractions of natural organic matter (A) 2,2',5,5'-tPCB adsorption on OC (B) 2,2',5,5'-tPCB adsorption on AC (C) Phenanthrene adsorption on OC (D) Phenanthrene adsorption on AC (OC = Organoclay; AC = Activated Carbon; HA = Aldrich Humic Acid (pH 7.21); FA = Fulvic Acid (pH 4.02) and NOM = Natural Organic Matter (pH 4.12)



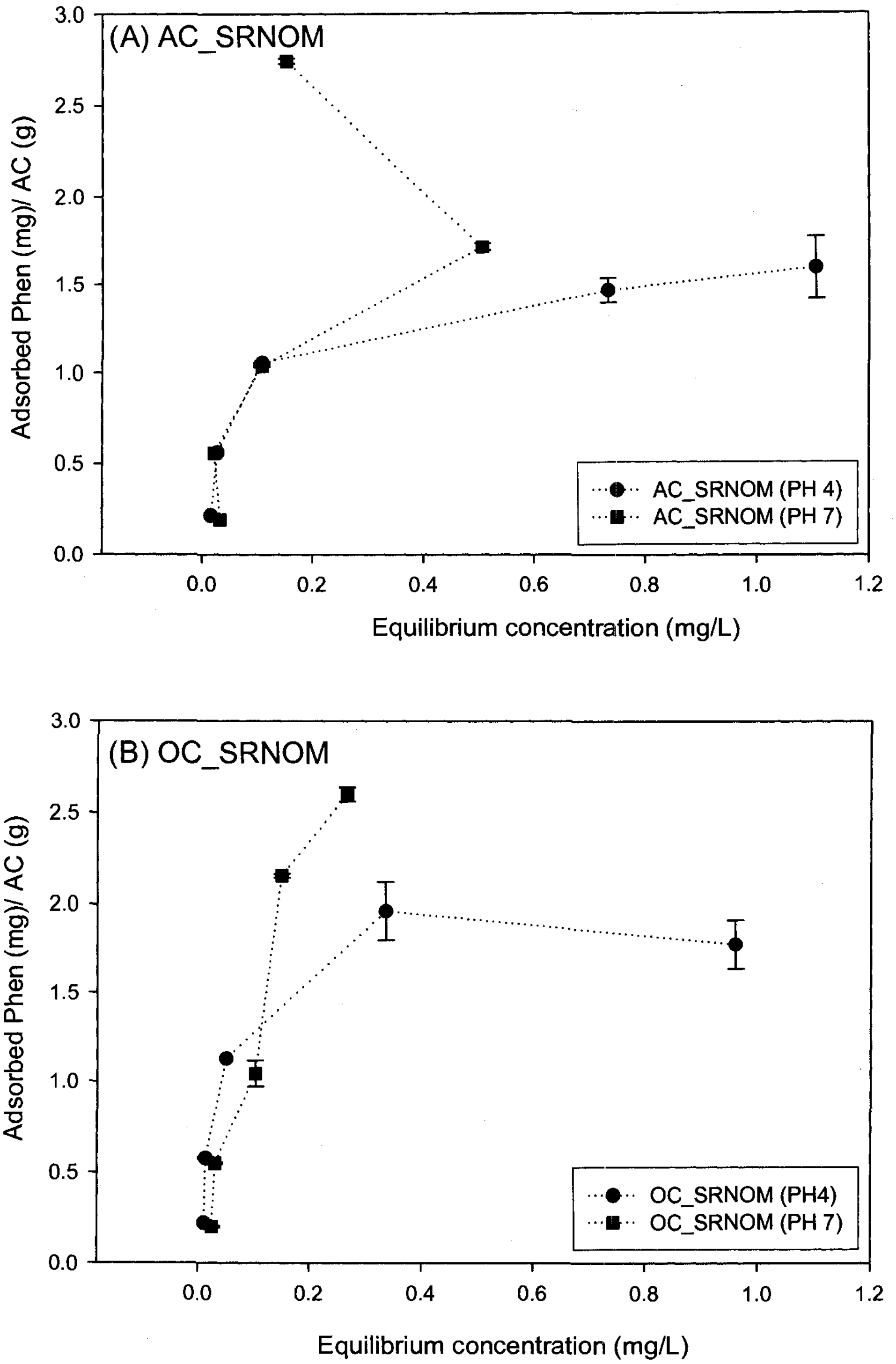
Statistical analysis of performance of sorbents (A) 2, 2', 5, 5'-tPCB adsorption on AC and OC in presence of HA/ FA/ NOM (B) Phenanthrene adsorption on AC and OC in presence of HA/ FA/ NOM (AC = activated carbon; OC = organoclay)



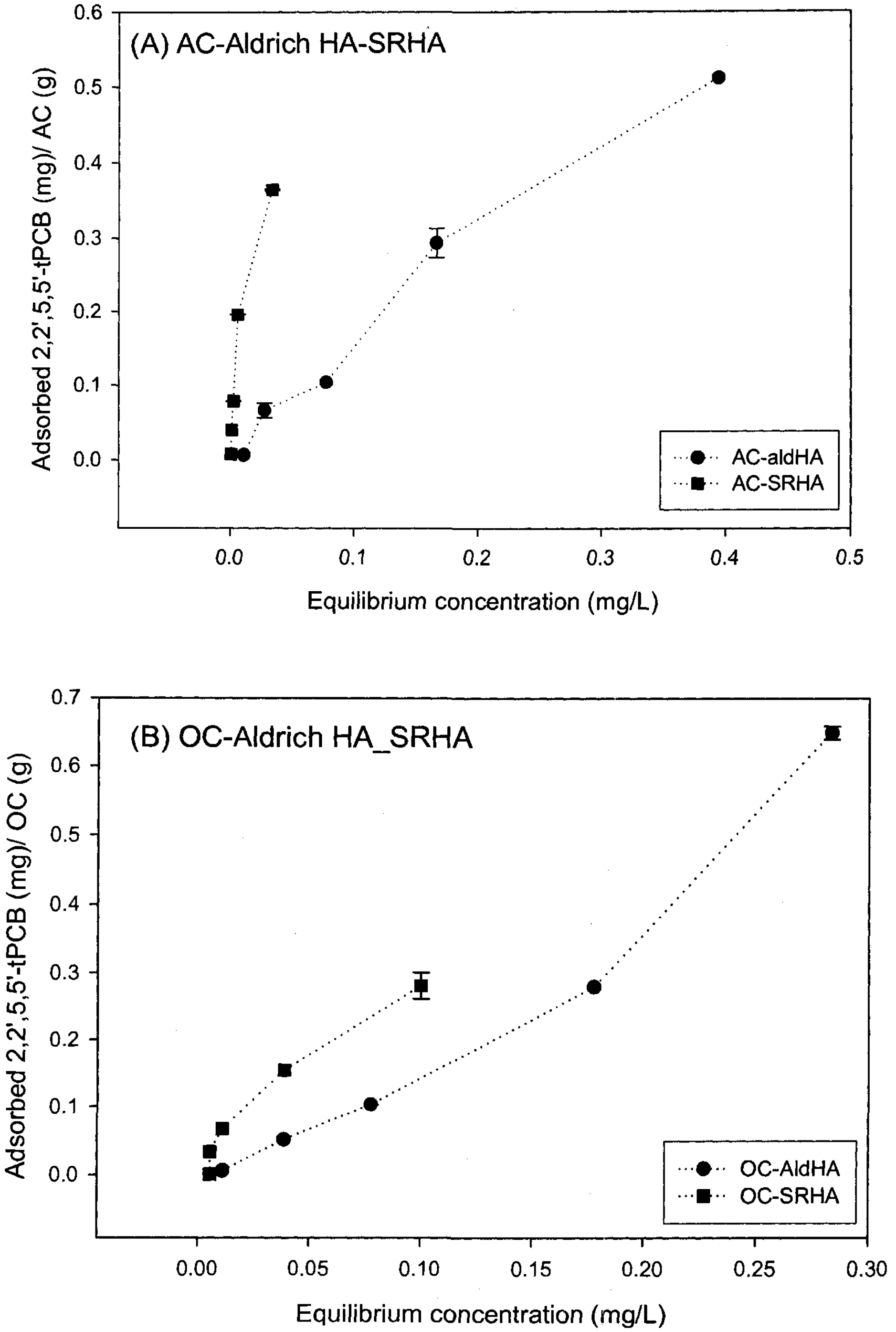
Adsorption of phenanthrene in presence of Aldrich HA and Suwannee River HA (A) Activated carbon (B) Organoclay



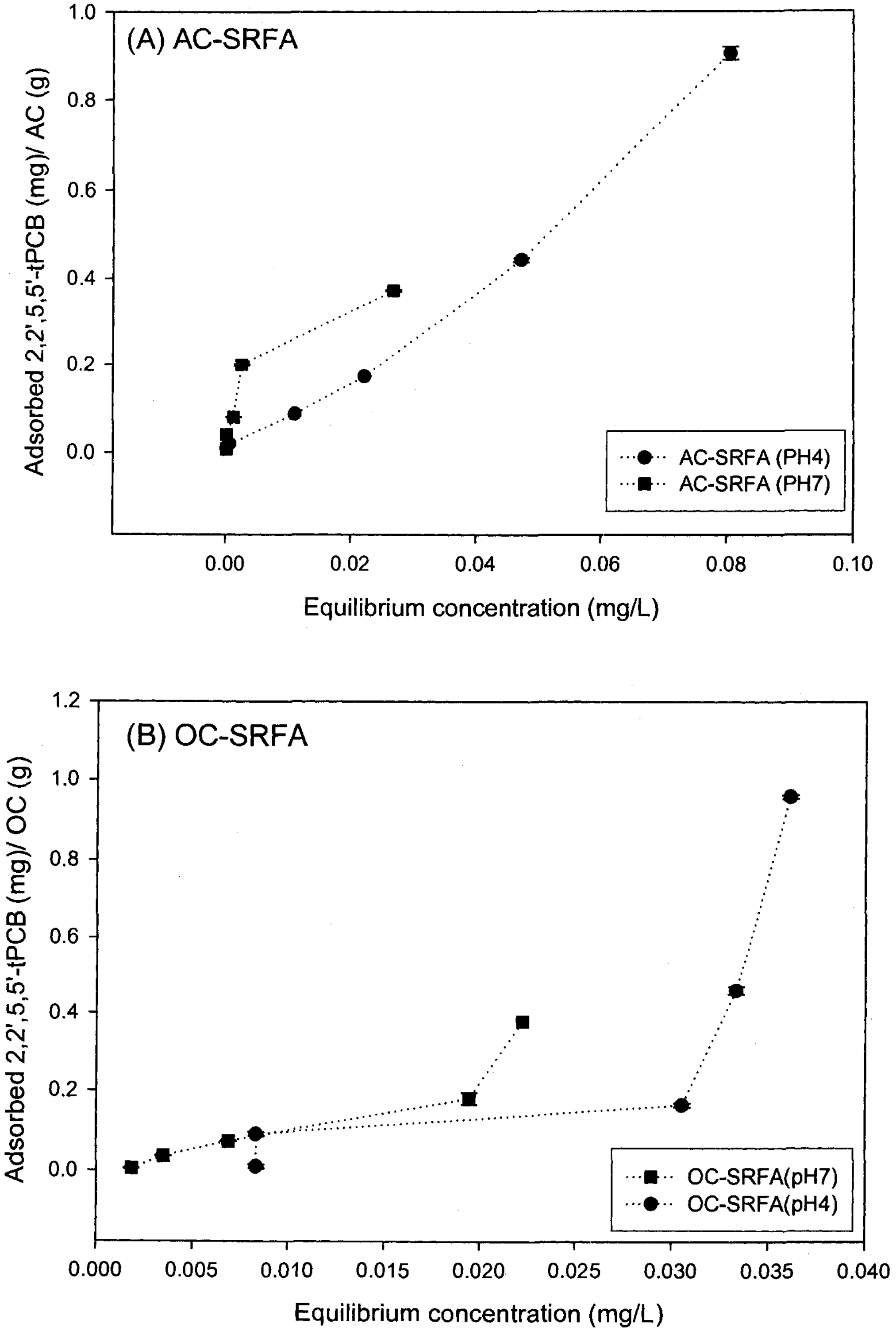
Adsorption of phenanthrene in presence of Suwannee River FA at pH 4 and 7 (A) Activated carbon (B) Organoclay



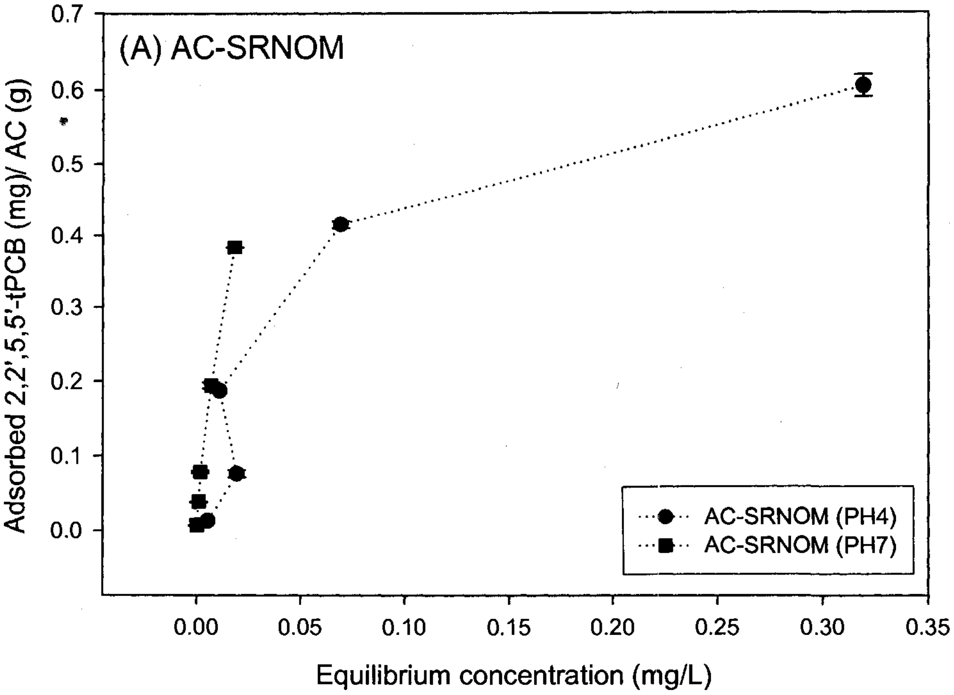
Adsorption of phenanthrene in presence of Suwannee River NOM at pH 4 and 7 (A) Activated carbon (B) Organoclay

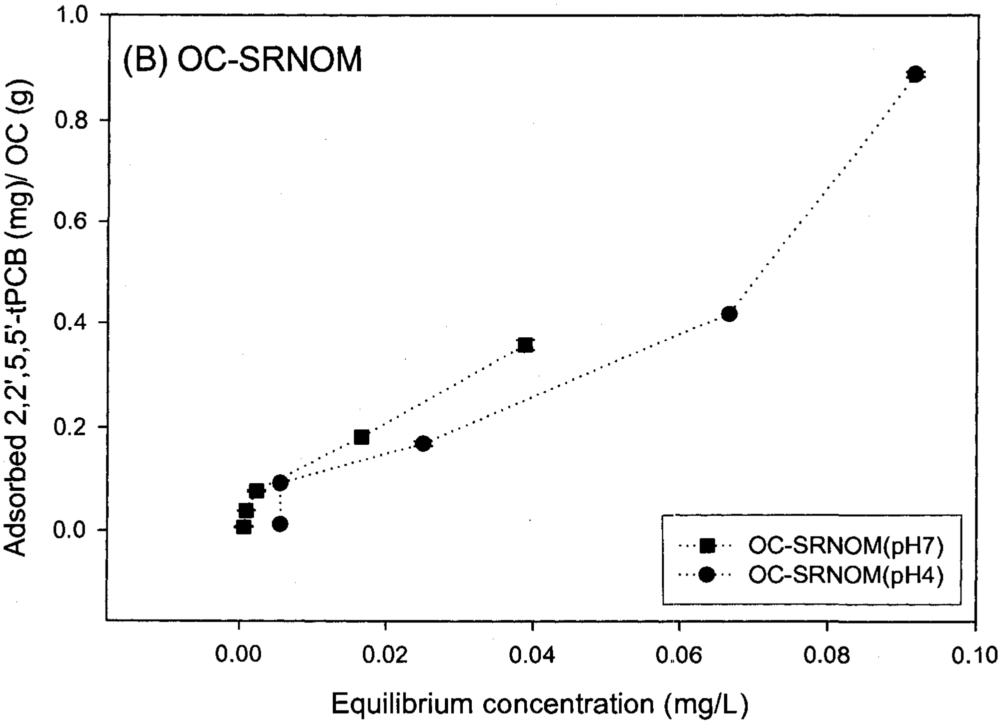


Adsorption of 2, 2', 5, 5'-tPCB in presence of Aldrich HA and Suwannee River HA (A) Activated carbon (B) Organoclay



Adsorption of 2, 2', 5, 5'-tPCB in presence of Suwannee River FA at pH 4 and 7 (A) Activated carbon (B) Organoclay





Adsorption of phenanthrene in presence of Suwannee River NOM at pH 4 and 7 (A) Activated carbon (B) Organoclay

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