

Passive treatment for removal of metal and organic contaminants from runoff and  
effluent at confined disposal facilities

By

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A passive treatment alternative for the removal of metal and organic contaminants from runoff and effluent in CDFs was evaluated in this study. Activated carbon impregnated curtains have been used for different remediation projects; however, very little research has been conducted to understand its sorption behavior, breakthrough time, and exhaustion time of contaminants under high flow rates characteristic of CDF runoff and effluent. The major objectives of this study were to evaluate the efficiency of the curtain in removing contaminants from a synthetic effluent in a flow through regime and estimate the expected life of the curtains. Equilibrium tests, batch sorption tests and column tests were conducted to evaluate the feasibility of this alternative. The copper column tests showed that the curtain is not efficient in the removal of metals; whereas, the Aroclor1016 column tests showed that the curtains could potentially be used as a treatment alternative for organic contaminants.

## DEDICATION

To my mother, my pillar of strength.

To my father, who is watching me from heaven.

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## NOMENCLATURE

$1/n$	- Freundlich isotherm constant
A	- Area
$A_c$	- Area of the curtain
b	- Constant related to the heat of adsorption
C	- Concentration
$C_{background}$	- Background concentration of the receiving waters
$C_{criteria}$	- Most conservative WQC
CDF	- Confined disposal facility
$C_e$	- Contaminant equilibrium concentration
$C_{eff}$	- Curtain layer effluent concentration
$C_{eff}(t)$	- Effluent concentration as a function of time
$C_i$	- Contaminant initial concentration
$C_{inf}$	- Column influent concentration
$C_{inf,layer}$	- Curtain layer influent concentration
$C_{max}$	- Maximum dissolved concentration
COCs	- Contaminants of concern
CTC	- Carbon tetrachloride
DDI	- Distilled de-ionized
$D_H$	- Hydraulic diameter
DOC	- Dissolved organic carbon



$D_{\text{Ratio Max}}$	- Dilution requirement
GAC	- Granular activated carbon
HDPE	- High-density polyethylene
IC	- Inorganic carbon
ICP	- Inductively coupled plasma
ID	- Inner diameter
K	- Freundlich isotherm constant
M	- Weight
$M_{\text{cumulative,layer } i}$	- Cumulative contaminant mass sorbed by curtain layer i
$M_{\text{eff,layer}}$	- Contaminant mass passing curtain layer effluent over a specified time interval
$M_{\text{inf}}$	- Contaminant mass entering column through influent over a specified time interval
$M_{\text{inf,layer } i}$	- Contaminant mass entering curtain layer through influent over a specified time interval ( $M_{\text{inf}}$ for port 1, and $M_{\text{eff } i-1}$ for the remaining ports)
$M_{\text{sorbed,layer } i}$	- Contaminant mass sorbed by curtain layer i (for a specified time interval)
$n_c$	- Total number of curtains per module
OC	- Organic carbon
OD	- Outer diameter
PAC	- Powdered activated carbon
PAHs	- Polycyclic aromatic hydrocarbons
PP	- Polypropylene
Q	- Flow rate
$R^2$	- Coefficient of determination

Re	- Reynolds number
SLRP	- Simplified laboratory runoff procedure
TC	- Total carbon
$t_c$	- Thickness of the curtain
$T_d$	- Detention time
TPH	- Total petroleum hydrocarbons
UTM	- Upland testing manual
V	- Volume
v	- Velocity
WQC	- Water quality criteria
X/M	- Sorption capacity
$X_m$	- Monolayer capacity
$\Delta t$	- Time interval
$\nu$	- Kinematic viscosity
$\phi_c$	- Curtain porosity

# CHAPTER I

## INTRODUCTION

### 1.1 Background information

Dredged material is defined as the sediment removed from the bottom of a waterway through dredging. Sediments could range from fine-grained material to coarse-grained material, and could contain any type of contaminants depending on its nature and origin. Constituents that may be present in sediments include metals, organics, organotins, inorganics, polycyclic aromatic hydrocarbons (PAHs), semi-volatile organic compounds, volatile organic compounds, organic carbon (OC), organophosphorus pesticides, chlorinated pesticides, dioxins, and polychlorinated biphenyls.

Dredged material unsuitable for upland and open water disposal is generally placed in an engineered structure known as a confined disposal facility (CDF), designed to contain a certain volume of dredged material. This practice is one of the most widely used for managing sediments from navigation dredging that are unsuitable for open water disposal or beneficial use. A CDF may be used just for disposal of contaminated dredged material or as a project staging area where the material is stored temporarily and treated for upland beneficial use. In general, CDFs are utilized to isolate and contain contaminants that may be present in the sediment (USEPA 1994, Wunderlich et al. 1999, Richardson et al. 1995).

Section 404 of the Clean Water Act regulates the construction of CDFs in open water or wetlands as well as CDF effluent and runoff that may be discharged into waters

of the United States (USEPA 1994). CDF effluent discharges, rainfall surface runoff, leachate, volatilization to the atmosphere, and direct uptake by plants and animals are the main pathways of concern for migration of contaminants from the CDF site to the environment (receiving waters, atmosphere, and organisms) which could cause potential impacts. Therefore, the dredged material must be evaluated in accordance with section 404 of the Clean Water Act to assess potential impacts resulting from the disposal of the contaminated sediments into a CDF.

Samples must be collected from the dredging site and evaluated through laboratory tests as part of the design considerations for managing the CDF effluent and runoff discharges. The modified elutriate test, which is described in Appendix B of the Upland Testing Manual (UTM) (USACE 2003), is used to evaluate water quality impacts associated with the release of CDF effluent discharges. CDF effluent discharges have the greatest potential for release of large contaminants quantities due to the large volume of water that could be released while the dredged material is being placed hydraulically in a CDF.

Effects of mixing and dispersion should be considered when evaluating effluent discharges. If the water quality criteria (WQC) applicable to the site can be met within the designated boundaries of an approved mixing zone, then the environmental impacts associated with the CDF effluent discharges are considered acceptable. The Simplified Laboratory Runoff Procedure (SLRP) is used to evaluate runoff discharges from a CDF. The volume and total suspended solids concentration is typically lower for runoff discharges as compared to effluent discharges. Runoff can be released at a lower velocity thus minimizing the flow rate and suspended solids concentration, and improving the dilution attainable in the receiving waters. Runoff from wet (unoxidized) and dried

(oxidized) sediments must be considered when conducting the SLRP test. Runoff from wet sediments would be similar in character to CDF effluent; however, contaminant concentrations are expected to be lower because contaminants could be diluted with precipitation. Also, runoff discharges are lower in volume and solids concentrations, and could be released at a lower flow rate as compared to effluent thus resulting in lower contaminant concentrations in the receiving water.

On the other hand, runoff from dried sediments is expected to have higher concentrations of some contaminants, especially metals, which may show higher mobility in the oxidized state (Price and Skogerboe 2000). Runoff discharges must also meet applicable water quality criteria (WQC) within the boundaries of an approved mixing zone. Treatment may be necessary if laboratory testing shows that the predicted effluent and runoff discharges from the CDF will not meet WQC and sufficient dilution is not attainable within an approved mixing zone.

## **1.2 Problem statement**

The basis of this research is a case study related to the replacement of a navigation canal lock with a larger lock in order to accommodate heavier traffic load and modern deep draft vessels. The navigation canal connects several waterways and water bodies. As part of this project, sediment and soil from the area would be dredged to accommodate different project features including the new lock construction site, bypasses, the channel enlargement, and the existing lock demolition.

Samples were collected from different dredged material management units (DMMUs) in the project area, in order to capture samples from the different sediment and soil types as well as suspected areas of contamination. An upland confined disposal

facility (CDF) and two open water disposal areas have been proposed to accommodate the dredged material. The upland CDF would be divided in two different areas, one area would accommodate dredged material determined to be unsuitable for open water disposal and the other would be used to stockpile material that could be used as construction fill around the lock. Effluent and runoff discharges from the CDF are expected to be released into two different waterways, which would be referred as receiving water. The collected samples were evaluated in accordance with section 404 of the Clean Water Act. The modified elutriate test and SLRP test were conducted to evaluate the effluent and runoff discharges respectively. A treatment alternative would be needed if the predicted contaminants concentrations do not meet the WQC and sufficient dilution is not attainable within an approved mixing zone.

Treatment of the contaminated CDF effluent and runoff in a mechanical wastewater treatment plant would preclude its use due to high cost, maintenance issues, and transportation limitations associated with it. The rate of production of effluent would require a high capacity facility which would generally be too costly for a typical navigation project. Further, the intermittent nature of runoff and effluent discharges complicates the issue, as the plant would need to be demobilized during idle periods, and remobilized during active periods. The types of treatments (e.g. biological treatment) that are amenable to these discharges are more limited than for conventional wastewater treatment since maintaining continuous flow through the plant would be difficult.

On the other hand, discharge to municipal wastewater treatment plant may not be a viable treatment option for CDFs. Often there is not a wastewater treatment plant within close proximity of the dredging project. Handling the flow rates associated with effluent and runoff discharges from a large dredging project would be difficult and contaminant

levels in the effluent and runoff may exceed the acceptable levels of the wastewater treatment plant. Costs per gallon associated with the discharge of effluent and runoff to the closest wastewater treatment plant should be considered as well. Treatment of effluent and runoff in a treatment plant may be very costly due to the large volume of water that is generally generated with these types of discharge. To be cost effective for operation in a CDF, a low-cost, low-tech, passive treatment system that can be managed with minimal equipment or technical expertise is needed.

### **1.3 Rationale for the study**

Water samples were collected from the receiving waters as well as sediment and soil samples from a reference area for chemical and physical characterization. As part of the environmental evaluation for this dredging project, sediment samples were collected and evaluated in accordance with section 404 of the Clean Water Act. Laboratory tests were conducted on the collected samples including modified elutriate tests and oxidized and unoxidized SLRP tests. The following general procedure was followed to evaluate the water samples collected for the case study.

- E The dissolved concentrations of organic, inorganic, and metal contaminants of the modified elutriate and SLRP tests samples were determined through chemical analysis.
  - F The mean and maximum dissolved concentrations were estimated for each sample and each contaminant. To be conservative the maximum dissolved effluent concentrations were compared against the most conservative of acute and chronic Federal and State WQC to identify potential exceedances.
- Generally, the chronic criteria were more conservative than the acute criteria.

The maximum dissolved runoff concentrations (oxidized and unoxidized) were compared against the most conservative acute Federal and State WQC. Runoff concentrations are compared against the acute criteria due to the short-term and intermittent nature of discharges.

G The concentrations of the contaminants that exceed the criteria were then used to determine dilution requirements to meet the water quality standards. The following general expression was used to calculate dilution requirements:

$$D_{Ratio\ Max} = \frac{(C_{max} - C_{criteria})}{(C_{criteria} - C_{background})} \quad (1.1)$$

where,

$D_{Ratio\ Max}$  = Dilution requirement

$C_{max}$  = Maximum dissolved concentration

$C_{criteria}$  = Most conservative WQC

$C_{background}$  = Background concentration of the receiving waters

The most conservative applicable WQC was set 10% above background concentration when the background concentration exceeded the WQC.

- The estimated flow rates of the disposal areas and receiving waters were used for the calculation of minimum and maximum attainable dilutions.
- Contaminants that did not meet the WQC and for which sufficient dilution could not be attained were identified. Selected contaminants from this group were the focus of this treatability evaluation.

The effluent flow rates expected in the field were estimated based on typical dredge production and expected operating schedule. A 24-in dredge is estimated to



produce a slurry discharge of approximately 1.34 m<sup>3</sup>/s (47.3 ft<sup>3</sup>/s). The dredge is assumed to operate 24 hr/day, which would produce an effective flow rate for a 24-hour period as indicated above. Therefore, the effluent flow rate results in approximately 1.34 m<sup>3</sup>/s (47.3 ft<sup>3</sup>/s). Expected runoff flow rates were based on local climatological data and release rates adjusted to the mixing requirements and the flow rate of the receiving waters. Runoff from the CDF would be discharged at a rate up to 2.54 cm/day (1 in/day) from the interior area of the CDF. The interior areas of the disposal cells range from about 0.14 to 0.48 km<sup>2</sup> (35 to 120 acres). Therefore, the runoff discharge rate from the CDF ranges from 1.5 to 5 cfs.

Approach velocity to the curtain was estimated based on the effluent discharge rate and assumed minimum curtain dimensions associated with the weir length and freeboard, allowing for progressive reduction in the frontal area of the curtain due to sedimentation. The dimensions assumed for the curtain were approximated to 4.6 m (15 ft) high and 30.5 m (100 ft) long, thus resulting in a field approach velocity of 0.98 cm/s (0.032 ft/s) which is representative of the effluent discharge and conservative for the runoff discharge. The water that would be discharged from the CDF will vary from freshwater to saltwater depending upon which areas are being dredged.

Table 1.1 shows the maximum predicted concentration for the contaminants that exceed the WQC along with the corresponding allowable concentrations which were estimated based on the most conservative WQC, the receiving waters background concentration and the attainable dilution for the case study CDF effluent. The allowable concentrations, rather than the water quality criteria, form the basis for the minimum target treatment objectives since further dilution is available in the mixing zone.

Table 1.1 Maximum effluent concentrations and allowable concentrations for the case study CDF effluent

Contaminant	CDF Maximum Predicted Concentration (ug/L)	Allowable Concentration (ug/L)
<i>Effluent (Modified Elutriate)</i>		
<b>Tributyltin</b>	<b>6.7</b>	<b>0.11825</b>
<b>Total PCBs</b>	<b>2.2</b>	<b>0.19</b>
Aroclor 1016	0.84	0.91
<b>Dieldrin</b>	<b>0.082</b>	<b>0.06174</b>
<b>Copper</b>	<b>281</b>	<b>33.9</b>
<b>Lead</b>	<b>147</b>	<b>36.84</b>
<b>Cyanide</b>	<b>6.6</b>	<b>27.5</b>
*** Contaminants in bold do not meet the most conservative WQC and cannot be sufficiently diluted in a mixing zone to meet the criteria.		

Table 1.2 shows the maximum predicted runoff concentrations for the contaminants that exceed applicable WQC as well as the corresponding allowable concentrations for both unoxidized and oxidized runoff which were estimated based on the most conservative WQC, the receiving waters background concentration and the attainable dilution for the case study CDF runoff. Note that contaminants in bold do not meet the WQC and cannot be sufficiently diluted in the receiving water to meet WQC; the allowable concentration which is estimated based on the receiving waters background concentration, the maximum predicted concentration and the most conservative WQC is lower than the maximum predicted concentration.

Table 1.2 Maximum runoff concentrations and allowable concentrations for the case study CDF oxidized and unoxidized runoff

Contaminant	CDF Maximum Predicted Concentration (ug/L)	Allowable Concentration (ug/L)
<i>Unoxidized Runoff</i>		
<b>Cyanide</b>	<b>34.6</b>	<b>27.5</b>
Copper	23	57.8
Chromium VI	24.2	720
<i>Oxidized Runoff</i>		
Cyanide	25.2	27.5
Copper	25.7	57.8
Chromium VI	22.3	720
*** Contaminants in bold do not meet the most conservative WQC and cannot be sufficiently diluted in a mixing zone to meet the criteria.		

Activated carbon may be effective in reducing the concentration of contaminants that may present CDF effluents and runoff, thus reducing dilution requirements and meeting the most conservative WQC. Activated carbon impregnated geotextile curtains are commercially available and may be effective as a passive flow-through treatment structure. For this study, a material manufactured by Huesker known as FilterMat™ will be examined as basis for a passive, low-cost, low-tech methodology for treatment of contaminated CDF effluent and runoff with the goal of reducing contaminant concentrations sufficiently to meet WQC requirements.

The material that was considered for treatment is a multilayered, engineered geocomposite that consist of two layers of polypropylene (PP) nonwoven geotextile impregnated with two layers of activated carbon. One or more layers of the geocomposite could be hung along the weir as a curtain to treat the contaminated effluent and runoff before being discharged. The layers of geocomposite could be replaced upon exhaustion. The degree of contaminant removal of the geocomposite in a flow through configuration

must be evaluated to determine whether or not the treatment will be effective. Further, the attenuation capacity of the geocomposite combination must be assessed in order to predict the potential life of the curtains and assess the practical feasibility for the flows and water volumes anticipated.

In this study, batch equilibrium tests, batch sorption tests and column tests were conducted to evaluate the performance of the material in treating water with representative contaminant concentrations and to determine the expected life of the curtains. Data from a case study was used as the basis for evaluation of this innovative treatment alternative. All the parameters discussed for the case study including the discharge velocities and the maximum predicted concentrations were considered for the design of the laboratory tests. Note that the laboratory tests were designed based on particular parameters of this case study (flow rate, field approach velocity, weir dimensions, COCs, COCs maximum and allowable concentrations); however, the obtained results could be applicable to CDFs evidencing issues associated with the discharge of effluent and runoff contaminated with metals and organic contaminants.

#### **1.4 Objective**

The purpose of this study was to evaluate a passive, low-cost, low-tech treatment technology for the removal of contaminants from effluent and runoff in confined disposal facilities (CDFs). The major objectives of this research project were to:

- Evaluate the efficiency of the curtain in removing contaminants from a synthetic effluent in a flow through regime
- Estimate the expected life of the curtains

## 1.5 Scope of work

Three different laboratory tests were evaluated in this study including batch equilibrium tests, batch sorption tests, and upflow column tests. Important parameters were obtained from a case study to design the laboratory tests conducted for this study including the following:

- Field approach velocity
- Contaminants of concern and their maximum predicted concentrations
- Allowable concentrations

One of the goals of this study was to evaluate empirically how sorption in a flow-through regime differed from equilibrium sorption as represented by batch testing. Understanding the relative impact of the geocomposite matrix (activated carbon packed in the nonwoven fabric) on the carbon capacity as compared to the activated carbon itself was important in order to determine what adjustments might be required for designing the column studies and predicting the life of the curtains. The feasibility of this treatment alternative was evaluated through the column studies. A short summary of the conducted laboratory tests will be shown in the following sub-sections. Note that all the tests were conducted using freshwater since higher ionic strength of saltwater limits the activity of contaminants to some degree, which may in turn result in reduced dissolved concentrations in the contaminated water testing. Therefore, performing the laboratory tests with freshwater was considered to be more conservative in terms of elutriate contaminant concentrations.

### 1.5.1 Equilibrium studies

Equilibrium studies were conducted using the activated carbon impregnated in the geocomposite to determine the equilibrium time of representative contaminants of

concern presented for the case study. The equilibrium time is the time that would be used to mix the batch sorption studies samples to ensure that the activated carbon and the contaminant reach equilibrium. The constituents evaluated in this part of the study include copper, chromium VI, lead, silver, mercury, DOC, and Aroclor 1016. Note that some of these contaminants are shown on the contaminants of concern tables (Table 1.1 and 1.2). The ones not listed in there but that were also evaluated exceed the WQC and do not meet the attainable dilution associated with a different disposal alternative considered for the case study.

### **1.5.2 Batch sorption studies**

Batch sorption studies were conducted using the carbon-impregnated geocomposite and just the activated carbon contained in the geocomposite to determine the sorption capacity of representative contaminants in both materials and to evaluate the comparative capacity of the two materials to facilitate predictions of curtain life. Contaminant removal efficiencies were also obtained through these studies. This information could be used to determine the potential of sorption of the contaminants of concern to these two different materials. Also, the capacity could be used to predict when the geocomposite and the activated carbon would be exhausted in order to design the upflow column studies. The constituents evaluated using the activated carbon include copper, chromium VI, lead, silver, mercury, DOC, and Aroclor 1016. For the geocomposite batch sorption studies only copper, chromium VI, lead, silver and DOC were evaluated because those were expected to represent the sorption behavior of metal and organic contaminants in general. Sorption between DOC and activated carbon was used to model expected sorption of natural organic compounds in general, which will

compete with target contaminants for sorption sites. Two different adsorption isotherms were evaluated to get a general sorption model for each contaminant.

### **1.5.3 Column studies**

Upflow column studies were conducted for copper to determine exhaustion time and Aroclor 1016 to determine breakthrough time after treating the contaminated water with the geocomposite impregnated with activated carbon. The mass of contaminant sorbed by the geocomposite was estimated using the exhaustion curves for Cu and the breakthrough curves for Aroclor 1016. The concentrations and flow rates used for the column tests were based on case study field conditions; flow rates were adjusted due to practical limits on the volume of water that could be produced and handled in the laboratory, and to ensure sorption of the tested contaminants to the fabric. The feasibility of this treatment method was ultimately evaluated based on the results obtained through the column studies. The results of the column tests could be applicable to organic and metals contaminants in general.

## **1.6 Document organization**

Literature relevant to the present study was reviewed and is summarized in Chapter 2. Chapter 3 presents the materials and methods used to conduct this study. All the procedures followed to conduct the equilibrium, batch sorption and column studies are explained in detail. Chapter 4 summarizes the results obtained from this study as well as a discussion of the results. Important parameters such as equilibrium time, sorption capacity, exhaustion time (Cu), breakthrough time (Aroclor 1016) and mass sorbed by the curtain will be discussed for each contaminant. A summary and conclusions of this study are included in Chapter 5. Also Chapter 5 presents recommendations for future research

work. The references and appendices are presented at the end of the document following Chapter 5.



## CHAPTER II

### LITERATURE REVIEW

A passive treatment alternative is examined in this study for the removal of metal and organic contaminants from runoff and effluent discharges at confined disposal facilities supporting dredge operations. This alternative is based on the use of a geocomposite fabric impregnated with activated carbon. The specific material is commercially known as FilterMat™ 400. This material was selected because of its relative availability and cost.

The alternative treatment approach involves hanging the FilterMat™ as a curtain along the weir in a CDF. The FilterMat™ 400 evaluated for this study has two layers of nonwoven propylene geotextile surrounding two layers of granular activated carbon. According to the manufacturer, this structure creates a two-step containment, one nonwoven layer acts as a puncture protection and pre-filter thus keeping contaminated particles in place whereas the activated carbon sorbs dissolved contaminants passing through the fabric (<http://www.huesker.com/usa>). Typical applications of this material include removal of chemical contaminants in water columns, capping of contaminated sediments in rivers and lakes, containment curtains and geotextile filter tubes.

Reible (n.d.) evaluated the performance of the FilterMat™ 200, which is designed to absorb dissolved hydrophobic contaminants, as an active sediment capping material and determined that it can be an effective component in sediment caps. His tests showed

a high degree of sorption for pyrene, naphthalene and phenanthrene in both the fabric and the activated carbon impregnated within the fabric.

These findings suggest the importance of evaluating the sorption capacity of both the FilterMat™ and the activated carbon impregnated in the fabric. Huesker's FilterMat™ has been used for different remediation projects; however, very little research has been conducted for this engineered geocomposite to understand its sorption behavior, breakthrough time and exhaustion time of metals and organic contaminants under different flow velocities. On the other hand, a lot of research has been conducted to understand the sorption behavior of activated carbon, breakthrough time and exhaustion time of different metals and organic contaminants.

Charcoal, the predecessor of modern activated carbon, was first used for water treatment purposes over 2000 years ago. Subsequently, activated carbon has been used for different purposes including medicine, solvent recovery, air purification, decolorization, removal of bad tastes and odors, water and wastewater treatment, and sediment capping. Powdered activated carbon (PAC) started being use back in 1929 by the Hackensack Water Company in New Jersey to remove odors in water. The development and production of granular activated carbon (GAC) started as a consequence of the First World War, where it was used for gas masks.

Activated carbon is a crude form of graphite, which has a random or amorphous structure, high porosity, and large surface area (Hamerlinck et al. 1994). Activation of the carbon occurs by heating the source material in order to reduce solids within the structure, which results in the creation of pores within the material and increase in the surface area. Basically the activation process (activation conditions and temperature) defines the carbon surface chemistry and pore structure. A broad range of materials with

a carbonaceous base have been use to prepare activated carbon including coconut shells, wood char, lignin, petroleum coke, bone char, peat, sawdust, carbon black, rice hulls, sugar, peach pits, fish, fertilizer waste, and waste rubber tire. Activated carbon adsorption is based on the ability of the material to remove certain chemical species from a liquid solution through adsorption due to factors such as surface area, micro-porous structure, and high degree of surface reactivity (Clark and Lykins 1989, Mohan and Pittman 2006). The surface of activated carbon is non-polar; therefore, it has more affinity for sorption of non-polar contaminants such as organics. Two different types of activated carbon have been classified based on particle size: powdered activated carbon (PAC) consisting of particles with size equal or smaller than standard US Sieve No. 50 and granulated activated carbon (GAC) consisting of particles with size larger than that. The adsorption phenomenon occurs when the adsorbate is held onto the activated carbon surface by Van Der Waal's forces; saturation of the carbon is represented by an equilibrium point (Faust and Aly 1987, CarboChem, Inc).

The equilibrium point between the activated carbon and the sorbate determines the contact time needed to ascertain the sorption capacity of the activated carbon. The contact time required to establish equilibrium is determined by contacting a solution containing the contaminants of interest with a specified amount of carbon, and measuring the final concentration of the solution at different contact times. The equilibrium time is defined by the point at which the final contaminant concentration does not change significantly. The position of equilibrium is characteristic of the entire batch sorption system, the solute, adsorbent, solvent, temperature, and pH (Faust and Aly 1987).

Equilibrium times reported in the literature for a broad range of contaminants including metals and organic ranged from 105 minutes to 4 weeks. However, the

equilibrium times determined for the contaminants that were tested in this study generally ranged from 105 minutes to 48 hrs. Pibazari et al. 1981 reported equilibrium times that ranged from 550 mins to 48 hrs for Aroclor 1016, and 48 hrs for Aroclor 1016 with humic acid. Netzer and Hughes 1984 reported a minimum contact time of 120 mins for lead and copper. Contact times reported for lead by Sekar et al. 2004 ranged from 105 to 120 mins.

A contact time of 2 hrs was used in order to establish equilibrium between copper solution and fine-grained activated carbon functionalized with amine (Yantasee et al. 2004). Huang and Blankenship 1984 used equilibrium times ranging from 60 mins to 24 hrs for the removal of mercury from water solutions through activated carbon adsorption. Rao et al. 2009 used different equilibrium times in his study of mercury removal from aqueous solutions using activated carbon from agricultural by-product and determined that 50% of mercury sorption occurs within the first 10 minutes and sorption equilibrium is achieved between 90 and 110 mins. Zhu et al. 2009 studied mercury ion adsorption by amine-modified activated carbon and determined a minimum contact time of 6 hrs. Huang and Wu 1975 used a contact time of 24 hrs for the removal of chromium VI from aqueous solution with activated carbon, whereas, Khezami and Capart 2005 used a contact time of 12 hrs.

In this study, humic acid was used to prepare the dissolved organic carbon synthetic solutions; therefore, contact times between activated carbon and humic acid were of interest. Contact times ranging from 550 mins to 5.17 days were reported in the literature for naturally occurring humic acids and commercial humic acids (Weber et al. 1982, Youssefi and Faust 1980, Herzing et al. 1977, Lee et al. 1981, and Weber et al. 1980). Note that the reported contact times are outside of the design limits of the

proposed passive treatment alternative being considered here because of the high flow rates and velocities characteristic of effluent and runoff discharges. However, reaching an equilibrium state is important for the determination of the activated carbon sorption capacity for the different contaminants of concern. Given the large variability of equilibrium and contact times reported by different researchers in the literature, equilibrium times ranging from 24 to 72 hrs were tested to determine a conservative contact time between the activated carbon and the tested metal and organic constituents.

Humic and fulvic acids are the principal organic constituents in sediments, which implies that the concentration of these components is part of the DOC concentration in effluent and runoff. Because sediments often have relatively high organic content, evaluating the sorption capacity between DOC and the sorbents evaluated in this study is important to determine whether or not DOC would out compete the target contaminants and affect efficiency and economics of the proposed passive treatment method. Pirbazari and Walter (1984), and Ru et al. 2007 reported that adsorption capacity of activated carbon for dieldrin and associated removal efficiencies appear to be adversely affected by the presence of organic substances such as humic acids. Other contaminants for which the sorption capacity appears to be affected by the presence of humic acids include PAHs and cyanide (Guo et al. 1993 and Cornelissen et al. 2006). Therefore, the literature suggests that the sorption capacity of activated carbon for organic contaminants could be affected by the presence of humic acids.

One parameter that may affect the apparent sorption capacity of activated carbon for metal contaminants is pH (Gomez-Serrano et al. 1998, Viana et al. 2008, and Leyva-Ramos et al. 1995). Some dissolved metals could potentially precipitate at neutral and basic pH values, increasing the apparent sorbed fraction. Hydrogen ion may also

compete for sorption sites, and a greater effect would be expected at low pH where hydrogen ion is most abundant (Pagnanelli et al. 2003). Metals precipitation primarily depends on two factors, the concentration of the metal and the pH of the water (Ayres et al. 1994). Copper, silver, lead and chromium could be affected by the pH of the solution. For chromium VI, the adsorption capacity is reduced at high pH values (greater than 6), greater removals occur at pH values ranging from 2 to 6 (Leyva-Ramos et al. 1995).

For other metals, the adsorption capacity increases at pH near neutral or higher, which suggests that precipitation might be occurring. Precipitation of copper is significant at pH values larger than 6. Similarly, lead could be potentially precipitated at pH values between 5 and 10, 95% of lead removal could be attributed to adsorption at a pH value of 4. At a pH value of 5, 98% of the removal of copper is attributed to adsorption (Netzer and Hughes, 1984). For mercury, greater adsorption occurs at pH of 4. The pH values reported in the literature for the performance of metals batch sorption tests ranged from 3 to 7. The literature suggests that maintaining a pH fairly constant (between 4 and 5) during the performance of the batch sorption tests might be preferred to achieve greater adsorption and prevent precipitation of metals.

The amount of solute adsorbed per unit of adsorbent at equilibrium is defined as adsorption capacity. The presentation of the adsorption capacity as a function of the equilibrium concentration in the solution is called an adsorption isotherm. Qualitative information related to the adsorption behavior, process, and the extent of surface coverage by the adsorbate can be obtained from the isotherms. Brunauer et al. (1940) classified adsorption isotherms in six different types (see Figure 2.1). Isotherms should fit at least one, but possibly a combination of two or more of the different types of isotherm (Fletcher 2008). Fletcher 2008, and Faust and Aly 1987 provided a description of the

different types of isotherms, which are mainly related to the adsorption behavior and thermodynamics of the different classifications. These descriptions are based on Brunauer's classification for gases. However, the different isotherm types and their description are also applicable to aqueous phase contaminants, where the relative pressure behavior is similar to the adsorbate equilibrium concentration behavior.

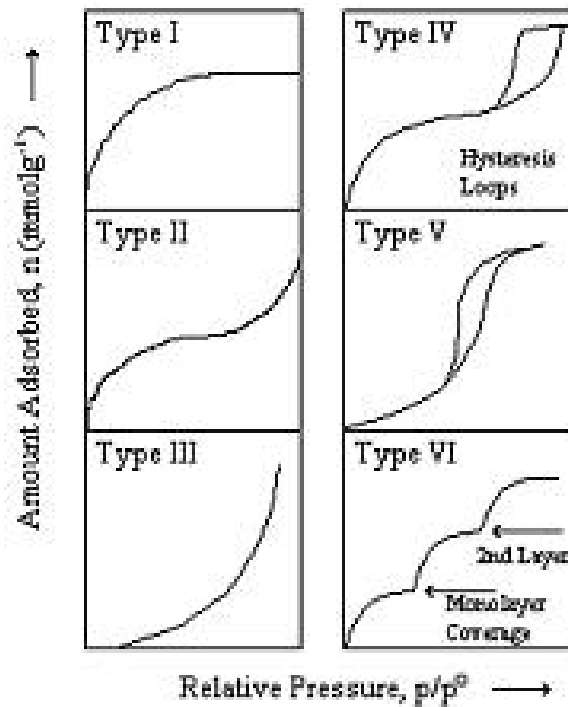


Figure 2.1 Adsorption isotherms classification (Brunauer et al. 1940)

- Type I isotherms – Associated with systems where adsorption occurs in the monomolecular layer. Typical of adsorbents with a predominantly microporous structure, micropore filling occurs at relative pressures ( $p/p_0$ ) below 0.1.

- Type II isotherm – Characteristic of physical adsorption of gases by non-porous solids. Monolayer adsorption is followed by multilayer adsorption. Involves multilayer adsorption at high relative pressures.
- Type III isotherm – Associated with systems where multilayer adsorption is encountered. Characteristic of weak adsorbate and adsorbent interactions. It is associated with both non-porous and microporous adsorbents. Basically, there are weak interactions between the adsorbate and the adsorbent at low relative pressures, which leads to low sorption capacities. The interactions become stronger when a molecule is adsorbed at a primary sorption site, thus resulting in accelerated uptakes at high relative pressures.
- Type IV isotherm – Associated with a hysteresis loop that commonly occurs with the presence of mesoporosity. This isotherm shows limited uptake at high relative pressures. Also, associated with multilayer adsorption.
- Type V isotherm – This isotherm is convex to the relative pressure, characteristic of weak interactions between the adsorbate and adsorbent, and indicative of microporous or mesoporous solids. Involves multilayer adsorption.
- Type VI isotherm – Also known as the hypothetical isotherm, this isotherm involves complete formation of monomolecular layers before progression to a subsequent layer. Therefore, it also involves multilayer adsorption.

Typically, the adsorption behavior of activated carbon in aqueous solutions is described by adsorption isotherm type I when adsorption does not proceed beyond the monomolecular layer (monolayer adsorption) (Faust and Aly 1987). This type of isotherm shows a steep increase in the amount sorbed at low relative pressures resulting



from the initial drop of the adsorption heat. This indicates that the first molecules that arrive at the surface of the adsorbant are preferably sorbed on the most attractive sites, or positions where the potential energy is minimum (Young and Crowell 1962). Then, the less active sites become occupied, which means that adsorption occurs on sites of progressively decreasing activity. The Freundlich and Langmuir adsorption isotherms are commonly used for the description of this type of adsorption behavior, which are classified as isotherm type I adsorption. The Freundlich model encompasses the heterogeneity of the activated carbon surface and the exponential distribution of the adsorption sites and their energies (Young and Crowell 1962, Sips 1948). Several assumptions are made for Langmuir model including:

- The molecules are adsorbed on definite sites on the adsorbent surface
- Only one molecule can be accommodated at each site
- The area of each site is a fixed quantity determined by the geometry of the adsorbent surface
- The adsorption energy is the same at all sites
- The adsorbed molecules cannot move across the adsorbant surface or interact with other molecules

Langmuir's equation was derived on the basis of statistical mechanics, thermodynamics, the law of mass action, theory of absolute reaction rates and the Maxwell-Boltzmann distribution law (Young and Crowell 1962). Langmuir and Freundlich equations are written in linear and logarithmic form respectively for linearization of the data. The isotherm constants, which are characteristic of a sorption system, are then obtained from the regression equations of the sorption capacity as a function of equilibrium concentration plots. Different parameters characteristic of batch

sorption tests that have been conducted in the past with activated carbon and the contaminants of concern were searched in the literature including sorption capacity, partitioning coefficients, removal percentages, solubility, concentration range, carbon amount and solution volume. Table 2.1 shows a summary of the parameters that were found in the literature for the contaminants that were tested in the laboratory including copper, chromium VI, lead, silver, mercury, and PCBs. This table illustrates that a broad range of conditions has been used for conducting batch sorption tests for the contaminants of concern. These values were useful for the design of this study; however, the experiments were not based solely on those. Note that estimated parameters such as distribution coefficients, sorption capacity and removal percentage are characteristic of the tested batch sorption system.

Table 2.1 Batch sorption studies parameters found in the literature

Reference	Capacity (X/M)	log kd	% removal	Solubility	Concentration range	Amount of carbon range	Volume
<b>Metals</b>							
Netzer and Hughes 1984					~10 mg/L	0.002-1 g	100 mL
<b>Copper</b>							
Faur-Brasquet et al. 2002	11.05 mg/g (AC cloths)						
Jssabayeva et al. 2010	20-32 mg/g				0-350 mg/L		
Yantasee et al. 2004							
	21.41 mg/g	2.86					
Copper ions	0.23-0.26 mmol/g						
<b>Chromium</b>							
Aggarwal et al. 1999	38-68 mg/g				20-1000 mg/L	0.2 g	
Kesraoui and Neufeld 1989					250-300 mg/L		
Huang and Wu 1977							
Khezami and Capart 2005	124.6-180.3 mg/g		>50%		<1000 mg/L (stock sln) Ce=0-70 mg/L	40 mg	
Mohana and Pittman 2006	147.1 mg/g (GAC), 75.6 mg/g (AC), 36.1-116.9 mg/g (AC fabric cloth)						
Leyva-Ramos et al. 1995	8-12 mg/g				0-25 mg/L	2 g for 2-10 mg/L sln	
Viana et al. 2008		2.7 L/kg(pH=4), 2.1 L/kg (pH=7), 0.88 L/kg (pH=9)		0.021-20500 mg/L, P50=20 mg/L			
Selvi et al. 2001	3.46 mg/g		84.06-98.84		5-20 mg/l	50-750 mg/50 ml	50

Table 2.1 (continued)

Reference	Capacity (X/M)	log kd	% removal	Solubility	Concentration range	Amount of carbon range	Volume
<b>Lead</b>							
Goel et al. 2005	21.88-29.44 mg/g				5-70 mg/L		
Issabayeva et al. 2010					0-350 mg/L		
Lead ions	0.09-0.11 mmol/g						
Gomez-Serrano et al. 1998	0.2 mmol/g				3.8 x 10 <sup>-2</sup> - 7.3 mol litre <sup>-1</sup>		
Viana et al. 2008		2.6 L/kg (pH=4), 3.4 L/kg (pH=7), 3.8 L/kg (pH=9)					
Sekar et al. 2004	26.50 mg/g		76.9-99		10-50 mg/l	50 mg, 10-100 mg	50 ml
<b>Mercury</b>							
Gomez-Serrano et al. 1998	1.2 mmol/g				3.8 x 10 <sup>-2</sup> - 7.3 mol/L		
Huang and Blankenship 1984			>90		2x10 <sup>-4</sup> M		
Madhava-Rao et al. 2009	22.88-25.88 mg/g				40 mg/L, 10-140 mg/L	25-300 mg	50 mL
Skodras et al. 2008	130-1003 ng/mg		>90		0.1 and 0.35 ng/cm <sup>3</sup>	20 mg	
	Pine wood= 421 ng/mg, Oak wood=379 ng/mg, Waste tires= 188-342 ng/mg, Olive seed Waste=795-869 ng/mg				0.35 ng/cm <sup>3</sup>	20 mg	
Viana et al. 2008		4.9 L/kg (pH = 7.0)		0.002-101000 mg/L, P50=15 mg/L			
Zhua et al. 2009	74.56 mg/g				1000 mg/L (std), 40 mg/L	0.1 g	300 mL
<b>Silver</b>							
Viana et al. 2008		3.6 L/kg (pH=7)		0.17-390 mg/L, P50=8 mg/L			

Table 2.1 (continued)

Reference	Capacity (X/M)	log kd	% removal	Solubility	Concentration range	Amount of carbon range	Volume
PCBs							
Blum et al. 1994							
PCB-221		3.09					
PCB-1232		3.85					
Hale et al. 2010		log Kac = 7.39-9.59 cm <sup>3</sup> /g			0.00043-0.61 ng/L 0.1-1000 ng/L, 0.2 - 200mg/L	5 mg	
McDonough et al. 2008							
	Virgin (ng/kg)/DOM loaded (ng/kg)						
PCB-18 (2,20,5-trichlorobiphenyl)	10000000000/3162277660						
PCB-52 (2,20,5,50-tetrachlorobiphenyl)	10000000000/3162277661						
PCB-77 (3,30,4,40-tetrachlorobiphenyl)	10000000000/3162277662						
PCB-126 (3,30,4,40,5-pentachlorobiphenyl)	10000000000/3162277663						
Sun and Ghosh 2008			69-97				
Werner et al. 2005		log Kac (cm <sup>3</sup> /g)	95				
22'5'-PCB		8.2					
244'-PCB		8.4					
22'55'-PCB		8.4					
22'455'-PCB		9.2					
23'44'5'-PCB		9.5					

Table 2.1 (continued)

Reference	Capacity (X/M)	log kd	% removal	Solubility	Concentration range	Amount of carbon range	Volume
ATSDR, 1995; Callahan et al. 1979; Erickson, 2001; Monsanto, 1974; and WHO, 1993; Lee and Chia 1979							
Atroclor 1016				0.42-0.906 mg/L			
Atroclor 1242				0.24-0.703 mg/L			
Atroclor 1254				0.012-0.07 mg/L			
Atroclor 1260				0.0027 mg/L			
Atroclor 1254				0.07 mg/L			

The design of the column tests was based on the maximum capacity estimated from batch sorption tests conducted for copper (activated carbon and FilterMat™) and Aroclor 1016 (activated carbon), preliminary tests, Cu and Aroclor 1016 concentrations obtained from the case study, and an approach flow velocity range characteristic of the case study CDF effluent. One important factor that must be considered is the detention time of the contaminated flow while passing through the fabric. Varying the flow rate and the total number of curtains used for treatment could control detention time. The effect of detention time on the performance is to alter the time of breakthrough defined in the literature as the point where the contaminant concentration in the effluent exceeds the treatment objective. Shorter relative detention times result in earlier breakthrough, whereas, longer relative contact times delay breakthrough (Clark and Lykins 1989). The activated carbon utilization also improves as the detention time increases.

Several researchers have conducted breakthrough and exhaustion studies using relatively low flow velocities as compared to CDF effluent velocities, which are characteristic of groundwater flow, water column advection and diffusion. A column with a small diameter was designed for the column tests due to the large velocity that was required to simulate the CDF effluent velocity; a column with a large diameter would have required a significantly larger volume of water. A smooth transition was needed to prevent jet flow at the column inlet. A diffuser, defined as an expansion or area increase to reduce velocity in order to recover pressure head of the flow (White 1999), was designed to create a smooth transition between the used fittings and the column inlet diameter. According to White (1999) and Sparrow et al. (2009), the development of vortices, swirls, superimposed pulsations, downstream obstruction, turbulent flow, stall

flow (transitory stall or bistable steady stall), and jet flow may be caused if the diffuser is not designed properly.

Sparrow et al. (2009), implemented a numerical simulation using the universal flow-regime model which is capable of automatically predicting the appropriate flow regime and providing the proper solution for the self-selected flow regime, flow separation would not occur for a diffuser with a divergence angle of  $5^\circ$  and Reynolds number larger than 2000 at the diffuser inlet. The diffuser should have a slope in the walls smaller than 0.1 (x:y  $\leftrightarrow$  10:1) to prevent abrupt changes in slope that may cause flow separation (Personal communication Dr. Richard L. Stockstill September 29, 2010). The diffuser located at the column inlet was designed according to the aforementioned design considerations.



## CHAPTER III

### MATERIALS AND METHODS

#### 3.1 Activated Carbon and FilterMat™

Aquasorb®, the granular activated carbon contained in Huesker's FilterMat™ 400 (see Figure 3.1), was used to conduct the batch equilibrium and sorption tests. This type of carbon is coconut shell based with a particle size of 40 – 60 US mesh. Table 3.1 shows some typical properties of this type of activated carbon along with the standard methods that were used by the manufacturer to determine those. Before conducting the laboratory tests, the activated carbon was cleaned with distilled de-ionized (DDI) water to remove dust and fines that may be present in the carbon. The carbon was placed inside a 2.54-cm (1-in.) diameter Plexiglas® column with a height of 61 cm (24 in.), DDI water was pumped into the column until the effluent was fairly clear with no dust and fines suspended in it, then dried in the oven at 105°C for 2 hours and cooled in the desiccator.



Figure 3.1 Aquasorb® activated carbon

Table 3.1 Typical properties of the Aquasorb® activated carbon

Parameter	Unit	Value	Test Method
Carbon tetrachloride (CTC) activity	% w/w	70	ASTM D3467
Density	g/mL	0.45	ASTM D2854
Geometric mean particle diameter	Mm	0.297	US standard sieve
Volume	mm <sup>3</sup> /particle	0.004	---
Surface area	mm <sup>2</sup> /particle	0.277	---
Particle number	per gram	508943	---
Surface area	m <sup>2</sup> /particle	0.141	BET N <sub>2</sub>

Huesker's FilterMat™ 400 was used to conduct batch sorption tests and column studies. FilterMat™ 800 was used to conduct one column study for comparison between the 400 and 800. FilterMat™ 400 and 800 are multilayered – engineered geocomposites that consist of two layers of polypropylene nonwoven geotextile impregnated with two layers of the Aquasorb® activated carbon (see Figure 3.2). Both types of FilterMat™ contain the same type of granular activated carbon, but the carbon in the 800 has a larger particle size (20 – 40 US mesh) thus having less surface area.

The basic functions of the nonwoven geotextile are to provide puncture protection and filtration of contaminated particles, whereas, the basic function of the activated carbon is to sorb dissolved contaminants that may be present in contaminated water that passes through the nonwoven material. The FilterMat™ is inert to biological degradation, natural occurring contaminants, alkalis and acids (<http://www.huesker.com/usa>). Typical properties of FilterMat™ 400 and 800 determined by the manufacturer are shown on Table 3.2.

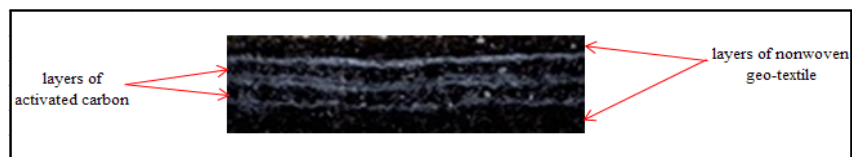


Figure 3.2 FilterMat™ with two layers of nonwoven geotextile and activated carbon

Table 3.2 Typical properties of the FilterMat™ 400 and 800

Parameter	Unit	Value		Test Method
		<i>FilterMat™</i> 400	<i>FilterMat™</i> 800	
Mass Per Unit Area (Carbon)	g/m <sup>2</sup>	400	800	ASTM D-5261
Permittivity	sec <sup>-1</sup>	0.66	0.47	ASTM D-4491
Flow Rate	L/(s*m <sup>2</sup> ) (gpm/ft <sup>2</sup> )	33 (49)	24 (35)	ASTM D-4491
Grab Tensile Strength (Machine Direction)	g (lbs)	170 (375)	181 (400)	ASTM D-4632
Grab Elongation (Machine Direction)	%	>50	>50	ASTM D-4632
Trapezoid Tear Strength (Machine Direction)	g (lbs)	59 (130)	64 (140)	ASTM D-4533
Puncture Strength, (5/16)	g (lbs)	91 (200)	104 (230)	ASTM D-4833
Mullen Burst Strength	MPa (psi)	5.5 (800)	6.2 (900)	ASTM D-3786
Apparent Opening Size	US Standard Sieve	200	200	ASTM D-4751
Roll Size – Length	m (ft)	91 (300)	91 (300)	---
Roll Size – Width	m (ft)	≤5.2 (≤ 17)	≤5.2 (≤ 17)	---

### 3.2 Synthetic Solutions

Synthetic solutions of selected organic and metal contaminants were prepared to conduct the batch equilibrium tests, the batch sorption tests and the column studies. Inductively Coupled Plasma (ICP) standards diluted in nitric acid were obtained from Ricca Chemical Company, LLC to prepare the synthetic solutions for the metal contaminants (CrVI, Cu, Ag, Pb, Hg) that were tested in this study. A standard diluted in methanol was obtained from Absolute Standards, Inc. to prepare the synthetic solutions for Aroclor 1016 that were used to conduct the different tests that were part of this study.

The dissolved organic carbon (DOC) synthetic solutions were prepared using humic acid sodium salt (technical grade), which has a carbon content of approximately 28%. The carbon content was determined by calculating an estimated humic acid concentration in the solutions and then measuring the corresponding DOC concentrations in the solution. The synthetic solutions prepared for all the tests conducted for this study were diluted in DDI water. The following equation was used to estimate the amount of liquid standard and DDI water needed to obtain the final concentration of the synthetic solutions:

$$V_1 = \frac{C_2 V_2}{C_1} \quad (3.1)$$

where,

$C_1$  = Standard original concentration

$V_1$  = Volume of standard to be added to the synthetic solution

$C_2$  = Desired concentration of the synthetic solution

$V_2$  = Total volume of the synthetic solution

The following expression was used to determine the amount of humic acid sodium salt needed for the DOC solutions:

$$M = \frac{CV}{\left(\frac{\% \text{ Carbon}}{100}\right)} \quad (3.2)$$

where,

$M$  = Weight of humic acid sodium salt

$C$  = Desired concentration of the DOC synthetic solution

$V$  = Total synthetic solution volume

% Carbon = Approximate percent carbon in the humic acid

The synthetic solutions for the metals batch equilibrium and sorption tests were prepared in a glass volumetric flask, and for the column studies in an 83-L (22-gal) high-density polyethylene (HDPE) rectangular tank. The amount of standard required to achieve the desired concentration was added into the container using a Fisherbrand electronic pipette, then the needed volume of water was added into the container and finally the solution was mixed for approximately 2 minutes to ensure that it was completely homogenous. For the column studies, the needed volume of water added to the HDPE rectangular tank was determined by weight in a tared bucket.

For the DOC batch equilibrium and sorption tests, the amount of humic acid sodium salt required to achieve the desired concentration was weighed in a weighing dish. Then the required amount was added to a volumetric flask by flushing the dish with distilled de-ionized (DDI) water until all the humic acid was added to the flask. The needed amount of DDI water was then added (considering the amount of DDI water used to flush the dish) into the flask. The volumetric flask was covered with aluminum foil and the solution was stirred for approximately 12 hours to make sure that the humic acid sodium salt was completely dissolved into the water.

The Aroclor 1016 synthetic solutions used for the batch equilibrium and sorption tests were prepared in a 15-L glass jug and for the column studies in 322-L (85-gal) stainless steel drums. The required amount of the Aroclor 1016 standard solution was added into the needed amount of DDI water using a gastight® syringe, then the solution was mixed to ensure complete mixing.

### 3.3 Equipment Decontamination

All equipment used in this study was appropriately decontaminated according to the requirements of the intended analyte to prevent cross-contamination of both metals and organics. The procedures are described in the following sub-sections.

#### 3.3.1 Metals

The following procedure was followed to decontaminate equipment used to conduct tests associated with metal contaminants:

- A clean brush and Liqui-Nox® phosphate-free liquid detergent were used to clean inner and outer surface of the equipment
- Equipment was rinsed thoroughly with tap water
- All surfaces were washed down with a solution of 20% nitric acid (trace metal grade) or equipment was placed in a 20% nitric acid (trace metal grade) bath contained in a Nalgene® rectangular container
- Surfaces were rinsed three times with DDI water
- The equipment was allowed to air dry or placed in the oven at 105°C for 30 minutes, removed from the oven and allowed to reach room temperature

#### 3.3.2 Organics

The following procedure was followed to decontaminate equipment used to conduct tests associated with organic contaminants:

- A clean brush and Liqui-Nox® phosphate-free liquid detergent were used to clean inner and outer surfaces of the equipment
- Equipment was rinsed thoroughly with tap water

- All surfaces were washed down with a solution of acetone (pesticide grade)
- Surfaces were rinsed three times with DDI water
- The equipment was allowed to air dry or placed in the oven at 105°C for 30 minutes, removed from the oven and allowed to reach room temperature

### **3.4 Analytical Procedures and QA/QC**

The analytical procedures described in the following sub-sections were used to analyze samples for metal constituents including: copper, silver, lead, chromium VI, and mercury, and for organic constituents including: dissolved organic carbon (DOC) and Aroclor 1016. A single analytical procedural replicate was analyzed for the metal and organic contaminants samples collected for the batch equilibrium tests and the column studies. Three analytical procedural replicates were analyzed for the metals and DOC samples collected for the batch sorption tests. A single analytical replicate was analyzed for the Aroclor 1016 samples collected for the batch sorption tests.

#### **3.4.1 Metals**

The copper, chromium VI, lead and silver water samples collected for chemical analysis were preserved by adding 2 – 3 drops of 70% nitric acid (trace metal grade), which prevents precipitation of the metals dissolved in the water. The samples were analyzed for metals using a Perkin Elmer Optima 4300 DV Inductively Coupled Plasma - Optical Emission Spectrometer (ICP-OES). Metal concentrations were determined from a liquid phase sample injection with a flow rate of 1 mL/min. An injection volume approximated to 3 mL is used for the metals analysis. The instrument was calibrated

using Perkin Elmer Pure Quality Control Standards manufactured under the ISO 9001 Quality Assurance System. Quality Control samples were analyzed immediately after the initial calibration, then after every 20 samples during the sample run, and at the end of the analysis. The lower detection limit of the instrument is 25 µg/L.

The mercury water samples were analyzed using a modified EPA SW-846 Method 7470A (cold-vapor analysis). For each sample, 10 mL were placed in a plastic 50-mL centrifuge tube with 10 mL of de-ionized (DI) water, 1 mL of concentrated HCl and 400 µL of a 2.38% KBr/0.54% KBrO<sub>3</sub> solution. The solution was mixed and digested at room temperature overnight. The following day, 100 µL of 5% Hydroxylamine HCl were added to neutralize the solution prior to analysis. The samples were diluted with 1% HNO<sub>3</sub> if necessary prior analysis. A PSA Millenium Merlin atomic fluorescence spectrometer was used to analyze the samples. The standard detection limit (MDL) for this method is 0.000005 mg/L and the standard reporting limit (MRL) is 0.00001 mg/L.

### **3.4.2 Organics**

The samples collected for DOC analysis were preserved by adding 2 – 3 drops of hydrochloric acid to maintain the pH near 2. DOC samples were analyzed through a catalytic combustion method using the Shimadzu Corp. TOC-VCSH. The injection volume for the DOC analysis was approximated to 500 µL, the instrument injects 3 or 4 times depending on the reproducibility of each result. A total sample volume of 8 mL was used for the injection and for the two washes that are conducted by the instrument. The instrument, which has a detection limit of 4 ppb, was calibrated through linear regression using 3 standards prior the analysis of each sample set. The instrument measures the total carbon (TC) and inorganic carbon (IC). The total organic carbon



(TOC), which is equal to the DOC in this study since the humic acid was completely dissolved in the sample, was obtained by subtracting the IC from the TC.

The water samples collected for Aroclor 1016 analysis were preserved in a cooler at 4°C. EPA SW-846 Method 3510C, known as the separatory funnel liquid-liquid extraction method, was used for isolating Aroclor 1016 from the water sample. The samples were analyzed through EPA SW-846 Method 8082A (PCBs by gas chromatography) using a GC/ECD, dual column Rtx CLPest & Rtx CLPestII 30m x 0.25 ID x 0.25um. Quality control samples, including a blank, laboratory control sample and laboratory control duplicate, were analyzed with each submitted sample set. The reporting detection limits used for the equilibrium and batch sorption tests were 0.03 µg/L and for the column studies were 0.002 µg/L.

### **3.5 Equilibrium Studies**

Batch equilibrium tests were conducted separately for each metal and organic contaminant to determine the time required for the contaminant and the activated carbon to reach an equilibrium state. The contact time required for the batch testing of the individual contaminant solutions was based on the results of the equilibrium study.

#### **3.5.1 Metals**

The initial concentration used for the solution prepared for copper, chromium VI, lead, silver, and mercury was approximated to 30, 5, 30, 5, and 25 mg/L respectively. At these concentrations the metals are completely soluble in water. Two separate equilibrium tests were conducted individually for copper, chromium VI, lead and silver using 0.05 and 0.25 g of activated carbon. Initially, a carbon dosage of 0.05 g was used; this amount was adjusted to 0.25 g in order to establish a measurable change between the

initial and the final concentration since concentration reduction was not significant for the carbon amount that was used initially. A single equilibrium test was conducted for mercury using 0.25 g of activated carbon. The following procedure was followed to conduct the batch equilibrium tests:

- All the glassware and equipment used for this test was decontaminated as specified in the metals equipment decontamination section (3.3.1).
- The synthetic solutions were prepared individually for each metal contaminant as described in the synthetic solutions section (3.2).
- A total solution volume of 100 mL was added to a glass Erlenmeyer flask. The total weight of the solution was recorded.
- The required amount of activated carbon (0.05 g for one test and 0.25 g for the other) was weighed out in an aluminum dish, and then added to the solution. The weight of the activated carbon was recorded.
- The samples were placed in an orbital shaker and shaken at a velocity of 250 rpm for the specified period of time.
- For the equilibrium test where 0.05 g of activated carbon were added, samples were collected at 24, 36, and 48 hours; three individual samples were prepared and collected individually for Cu, Cr VI, Ag and Pb.
- For the equilibrium test where 0.25 g of activated carbon were added samples were collected at 24, 36, 48, 60, and 72 hours; five individual samples were prepared and collected individually for Cu, Cr VI, Ag, Pb, and Hg.
- The samples were filtered through a 0.45  $\mu\text{m}$  Millipore™ membrane filter, mixed cellulose esters, hydrophilic filter using a filtration apparatus that

consists of a filtering flask, base, funnel and clamp assembled together and connected to a vacuum source.

- The filtered sample was then collected in a 125-mL Nalgene® HDPE sample bottle, preserved with nitric acid and submitted for chemical analysis.

### 3.5.2 Organics

The target initial concentration for the Aroclor 1016 solution was 0.42 µg/L and for DOC 9.5 mg/L. Two separate equilibrium tests were conducted individually for the DOC using 0.05 and 0.25 g of carbon. A single equilibrium test was conducted for Aroclor 1016 using 0.05 g of activated carbon. The following procedure was used to conduct the batch equilibrium tests:

- All the glassware and equipment used for this test was decontaminated as specified in the organics equipment decontamination section (3.3.1)
- The synthetic solutions were prepared individually for each organic contaminant as described in the synthetic solutions section (3.2)
- Approximately 100 mL of the DOC solution were added to a 250mL stainless steel bottle (250mL amber glass bottles were not available) and the total weight of the solution was recorded. For the Aroclor 1016 study, approximately 1000 mL of the synthetic solution were added to a 2L glass jar.
- The required amount of activated carbon (0.05 g for one of the tests and 0.25 g for the other) was weighed out in an aluminum dish; then added to the solution. The weight of the activated carbon was recorded.

- The DOC samples were placed in an orbital shaker and shaken at a velocity of 250 rpm. The Aroclor 1016 samples were placed in a tumbler and shaken at a velocity of 40 rpm since the containers were too large for the orbital shaker.
- For the equilibrium test where 0.05 g of activated carbon were added, samples were collected at 24, 36, and 48 hours; three individual samples were prepared and collected individually for both DOC and Aroclor 1016.
- For the DOC equilibrium test where 0.25 g of activated carbon were added, samples were collected at 24, 36, 48, 60, and 72 hours; five individual samples were prepared and collected individually.
- The samples were filtered through a 0.70  $\mu\text{m}$  glass fiber filter with a filtration apparatus that consists of a filtering flask, base, funnel and clamp assembled together and connected to a vacuum source.
- The DOC filtered samples were collected in a 125-mL amber glass bottle, preserved with hydrochloric acid and submitted for DOC analysis. The Aroclor 1016 filtered samples were collected in a 1000-mL amber glass bottle, preserved at 4°C and submitted for PCB analysis.

### 3.6 Batch Sorption Studies

Batch sorption studies were conducted using the activated carbon (the same carbon contained in the FilterMat™), in addition to the carbon impregnated FilterMat™, in order to assess the relative impact of the FilterMat™ matrix (i.e. the carbon packed in the nonwoven fabric) on the carbon capacity for each metal and organic contaminant.

The isotherms constants were obtained from sorption isotherms developed using the

batch testing data; carbon capacity and percent removal was also calculated for each contaminant.

Preliminary tests were conducted with copper to test the planned approach for conducting the batch sorption tests for each contaminant. A concentration range and carbon dosage was selected for each contaminant of concern through these preliminary tests and relevant information obtained from the literature review. The pH of the copper solution was monitored during the performance of these preliminary tests to determine whether buffering would be necessary for the metals batch tests.

### 3.6.1 Buffering

The metals solutions used for the batch sorption tests were buffered to maintain a constant pH through the test (i.e. ideal conditions) and to prevent precipitation of the metals that are not soluble at high pH values. Acetic acid ( $\text{CH}_3\text{COOH}$ ) and sodium acetate ( $\text{CH}_3\text{COONa}$ ) were used to buffer the metals solutions in order to maintain a pH near 4.75, the pKa of acetic acid. This acid buffer was selected since its pKa was nearest to the desired pH, which is optimum for the prevention of precipitation of the tested metals. Three different tests were conducted in order to determine the lowest effective acetic acid buffer concentration. The pH measurements were monitored using a Thermo Orion combination pH probe, which was connected to a Thermo Orion meter model 720A (see Figure 3.3). The samples were stirred with stir bar and magnetic plate until READY was indicated in the meter. The tests that were conducted to select the acetic acid buffer concentration are summarized below:

- A copper solution with a concentration of approximately 30 mg/L was titrated with acetic acid for a period of 48 hrs. The initial pH of the

solution was measured before and after adding 3.0 g of activated carbon to 100 mL of solution. An approximate volume of 5  $\mu\text{L}$  of acetic acid was added to the solution with carbon and the pH was measured. This process was repeated until the pH reached a level approximated to the acetic acid pKa (4.75) and was fairly constant. The pH was measured at 24 hours and the solution was titrated as mentioned previously until the pH was approximated to 4.75, the same process was repeated at 48 hrs. The concentration of acetic acid needed to maintain a pH near 4.75 at 48 hrs was estimated for the copper solution. This test was conducted in triplicate.

- DDI water was also titrated with acetic acid for a period of 48 hrs. The initial pH of the DDI water was measured before and after adding 3.0 g of activated carbon to 100 mL of DDI water. An approximate volume of 5  $\mu\text{L}$  of acetic acid was added to the solution with carbon and the pH was measured. This process was repeated until the pH was approximated to 4.75 and fairly constant. The pH was measured at 24 hours and the solution was titrated as mentioned previously until the pH was approximated to 4.75; the same process was repeated at 48 hrs. The concentration of acetic acid needed to maintain a pH approximated to 4.75 at 48 hrs was estimated for DDI water. This test was also conducted in triplicates.
- Three different acid buffer strengths (0.002 M, 0.02 M, and 0.2 M) were used to conduct a sorption test on a Cu solution with a concentration of approximately 30 mg/L and 3.0 g of activated carbon, resulting in 3

samples one for each acid buffer strength. The initial pH of the buffered solution was measured. The samples were then shaken for 48 hrs using an orbital shaker and filtered with a 0.45  $\mu\text{m}$  Millipore™ membrane filter. A portion of the sample was collected in a 125 mL Nalgene® HDPE sample bottle for chemical analysis and the other portion was collected in a glass beaker to measure the pH. Two different parameters were evaluated through this test: the change in pH, Cu removal and sorption capacity as a function of the buffer strength. The same process was repeated with the Cu titrated solution to compare the evaluated parameters.

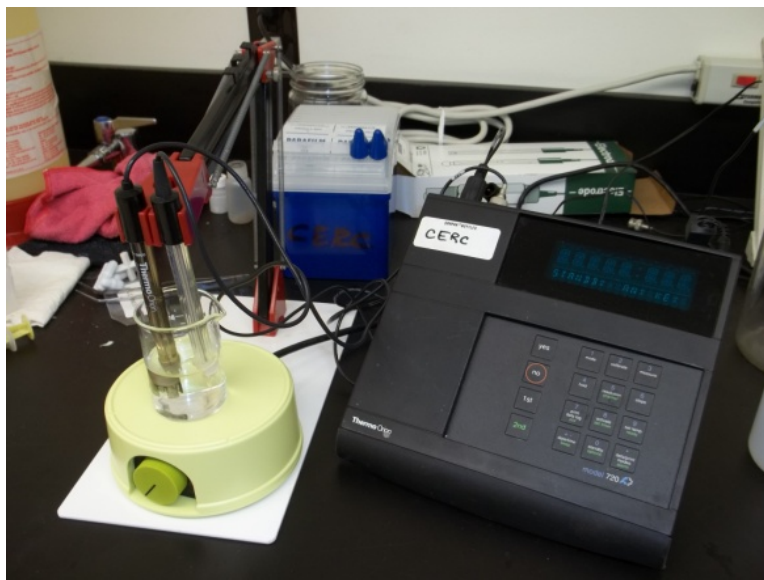
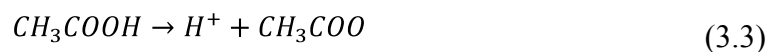


Figure 3.3 Thermo Orion meter used to take the pH measurements

The following parameters and expressions were used to estimate the needed amounts of acetic acid and sodium acetate in order to get the desired buffer strength.



$$pH = pKa + \log \frac{[base]}{[acid]} \quad (3.4)$$

For this case,

$$pH = pKa + \log \frac{[CH_3COO]}{[CH_3COOH]}$$

$$4.75 - 4.75 = \log \frac{[CH_3COO]}{[CH_3COOH]}$$

$$10^0 = \frac{[CH_3COO]}{[CH_3COOH]}$$

$$1 = \frac{[CH_3COO]}{[CH_3COOH]}$$

$$\text{Acetic acid volume} = \frac{[CH_3COOH] * (CH_3COOH MW)}{(CH_3COOH density)} \quad (3.5)$$

$$\text{Sodium acetate mass} = [CH_3COONa] * (CH_3COONa MW) * V \quad (3.6)$$

where,

$$pH = 4.75$$

$$pKa = CH_3COOH \quad pKa = 4.75$$

$$CH_3COOH \text{ density} = 1.049 \text{ g/mol}$$

$$[CH_3COOH] = CH_3COOH \text{ desired molarity}$$

$$[CH_3COO] = CH_3COO \text{ (acetate) desired molarity}$$

$$[CH_3COONa] = CH_3COONa \text{ desired molarity}$$

$$CH_3COOH \text{ molecular weight (MW)} = 60.05 \text{ g/mol}$$

$$CH_3COO \text{ MW} = 59.05 \text{ g/mol}$$

$$CH_3COONa \text{ MW} = 82.03 \text{ g/mol}$$

$$V = \text{total volume of solution}$$



### 3.6.2 Activated Carbon

Batch sorption tests were conducted for the metals and the organic contaminants using the same activated carbon used in the FilterMat™ geotextile. A summary of the procedures followed for conducting the batch sorption tests for the metals and organics is summarized below.

#### 3.6.2.1 Metals

For the metals samples, the batch sorption tests were conducted in triplicate for copper, chromium VI, lead and silver, and in duplicate for mercury. With the exception of copper and lead, each of the metals samples was buffered with acetic acid and sodium acetate using a buffer strength of 0.2M since pH variability is small at this strength, with the exception of copper and lead for which a buffer strength of 0.002 M was used. A weaker buffer strength (0.002 M) was used for copper and lead since the preliminary buffer tests showed that this strength was adequate for the Cu and Pb solutions. A linear trend was observed in the isotherm data obtained with this buffer and the removal that could potentially be attributed to precipitation at elevated pH (>6.0) was relatively small. A stronger buffer (0.2 M) was used for the other contaminants to prevent the large pH variations observed in preliminary tests. A subsequent test conducted for silver using a buffer strength of 0.002 M showed large pH variations and an indefinable data trend for the isotherm data; therefore, a 0.2 M buffer was used for chromium VI, mercury, and silver. This will be explained in more details in Chapter IV. The following procedure was used to conduct the activated carbon batch sorption tests:

- All the glassware and equipment used for this test was decontaminated as specified in the metals equipment decontamination section (3.3.1).

- The synthetic solutions were prepared individually for each metal contaminant as described in the synthetic solutions section (3.2) and buffered with acetic acid and sodium acetate using the buffer strengths mentioned above. The buffer was added to the solution as part of the total solution volume. The initial pH of the buffered solution was measured.
- A total solution volume of 100 mL was added to a glass Erlenmeyer flask. The total weight of the solution was recorded.
- The required amount of activated carbon was weighed out in an aluminum dish, and then added to the solution. The weight of the activated carbon was recorded.
- The samples were placed in an orbital shaker and shaken at a velocity of 250 rpm for 48 hrs.
- The samples were filtered through a 0.45 µm Millipore™ membrane filter, mixed cellulose esters, hydrophilic filter using a filtration apparatus that consists of a filtering flask, base, funnel and clamp assembled together and connected to a vacuum source.
- Approximately 15 mL of the filtered sample were collected for taking a pH measurement. The rest of the sample was collected in a 125-mL Nalgene® HDPE sample bottle, preserved with nitric acid and submitted for chemical analysis.

Each metal sample was analyzed in triplicate to capture analytical variability of the instrument analysis process. Table 3.3 illustrates a matrix of the batch sorption tests conducted for the metals, which shows the target initial concentrations used for each constituent along with the approximated amounts of activated carbon and solution that

were used for the test. A blank process test was prepared using DDI water and following the procedure described above to determine if there was any metals contamination during the batch sorption test process that may be caused by the activated carbon and the glassware.

Table 3.3 Matrix of the activated carbon batch sorption tests for metal constituents

Constituent	Constituent Target Initial Concentration (mg/L)	Approximate Solution Volume (mL)	Approximate amount of carbon (g)				
			0.1	0.5	1.0	2.0	3.0
Chromium VI	5	0.1	0.1	0.5	1.0	2.0	3.0
Copper	30	0.1	0.1	0.5	1.0	2.0	3.0
Lead	30	0.1	0.1	0.5	1.0	2.0	3.0
Mercury	25	0.1	0.1	0.5	1.0	2.0	3.0
Silver	5	0.1	0.1	0.5	1.0	2.0	3.0

### 3.6.2.2 Organics

Batch sorption tests were conducted for Aroclor 1016 and DOC for which the tests were conducted in duplicate and triplicate respectively. The organics samples were not buffered since organics do not absorb through an ionic mechanism, and the buffers can complex with the organics or cause other analytical interferences. The acetate will act as a surfactant, thus causing solubility issues and creating a hydrophobic coating around the surface of the surfactant molecule (Personal communication with Dr. Anthony J. Bednar October 21, 2011). Also, the solubility of organic compounds is not pH dependent; therefore, sorption is not expected to be significantly affected by pH changes and there is no need for buffering the organic solutions. The following procedure was used to conduct the activated carbon batch sorption tests:

- All the glassware and equipment used for this test was decontaminated as specified in the organics equipment decontamination section (3.3.2).
- The synthetic solutions were prepared individually for each organic contaminant as described in the synthetic solutions section (3.2). The initial pH of the solution was measured.
- Approximately 100 mL of the DOC solution were added to a 250mL stainless steel bottle (250mL amber glass jars were not available) and the total weight of the solution was recorded. For the Aroclor 1016 study, approximately 1000 mL of the synthetic solution were added to a 2L glass jar.
- The required amount of activated carbon was weighed out in an aluminum dish; then added to the solution. The weight of the activated carbon was recorded.
- The DOC samples were placed in an orbital shaker and shaken at a speed of 250 rpm for 48 hrs. The Aroclor 1016 samples were placed in a tumbler and shaken at 40 rpm for 48 hrs since the containers were too large the orbital shaker.
- The samples were filtered through a 0.70  $\mu\text{m}$  glass fiber filter with a filtration apparatus that consists of a filtering flask, base, funnel and clamp assembled together and connected to a vacuum source.
- The DOC filtered samples were collected in a 125-mL amber glass bottle, preserved with hydrochloric acid and submitted for DOC analysis. The Aroclor 1016 filtered samples were collected in a 1000-mL amber glass bottle, preserved at 4°C and submitted for PCB analysis.

Each DOC sample was analyzed in triplicate to capture analytical variability of the instrument analysis process. Table 3.4 illustrates a matrix of the batch sorption tests conducted for the organic constituents which shows the target initial concentrations used for each constituent along with the approximate amounts of activated carbon and solution that were used for the test. A blank process test was prepared for the DOC using DDI water and following the procedure described above to determine if DOC contamination was caused during the batch sorption test process due to the activated carbon and the glassware. Figure 3.4 illustrates the process that was followed to prepare an activated carbon batch sorption test for DOC. Note that the same general process is applicable to the metals and organics samples batch tests (batch equilibrium tests, activated carbon batch sorption tests, and FilterMat™ batch sorption tests).

Table 3.4 Matrix of the activated carbon batch sorption tests for organic constituents

Constituent	Constituents Target Initial Concentration (mg/L)	Approximate Solution Volume (mL)	Approximate amount of carbon (g)				
			0.1	0.5	1.0	2.0	3.0
Aroclor 1016	0.42	1000	0.1	0.5	1.0	2.0	3.0
DOC	9.5	0.1	0.1	0.5	1.0	2.0	3.0

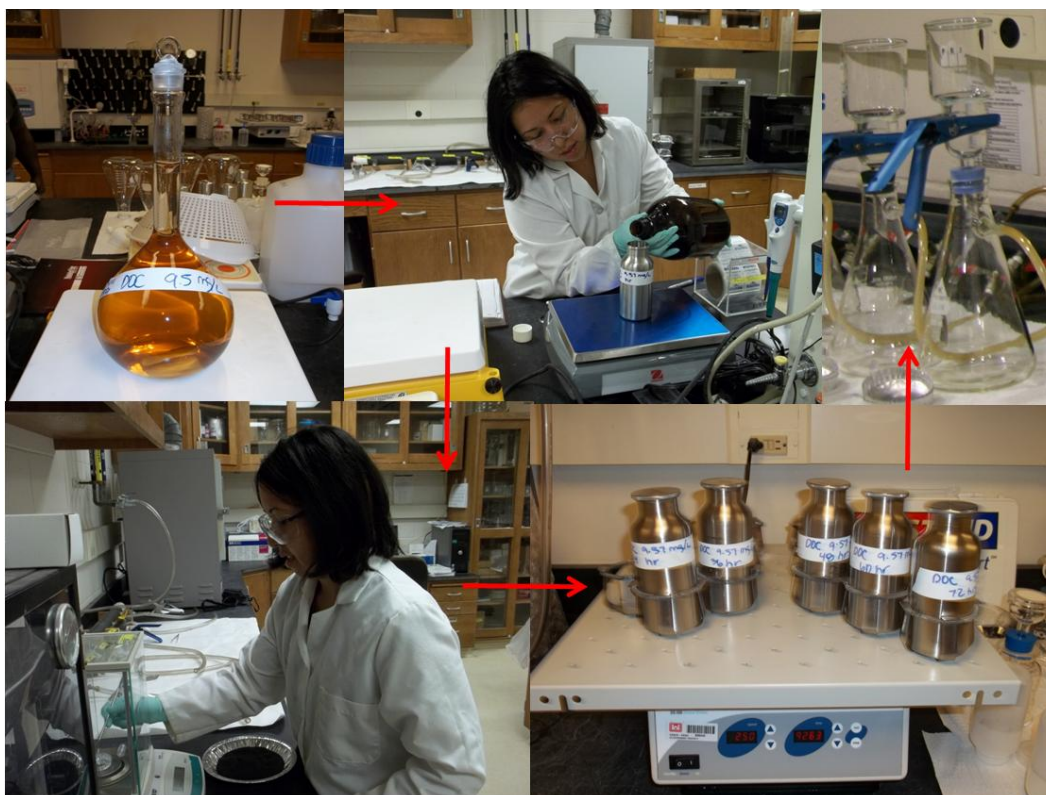


Figure 3.4 Activated carbon batch sorption test process for DOC

### 3.6.3 FilterMat™

Batch sorption tests were conducted for selected metals and organic contaminants using the FilterMat™ geotextile impregnated with activated carbon, in order to assess the relative performance of the material as compared to the carbon alone. A summary of the procedures followed for conducting the batch sorption tests for the metals and organics is shown below.

#### 3.6.3.1 Metals

A single replicate was conducted for the metals batch sorption tests conducted using the FilterMat™ 400. This test was conducted for copper, chromium VI, lead and silver. Each of the metals samples was buffered with acetic acid and sodium acetate using

a buffer strength of 0.2 M to minimize pH variation during the test. The following procedure was used to conduct the FilterMat™ batch sorption tests for the metals:

- All the glassware and equipment used for this test was decontaminated as specified in the metals equipment decontamination section (3.3.1).
- The synthetic solutions were prepared individually for each metal contaminant as described in the synthetic solutions section (3.2) and buffered with acetic acid and sodium acetate using a buffer of 0.2M. The buffer was added to the solution as part of the total solution volume. The initial pH of the solution was measured.
- A total solution volume of 100 mL was added to a glass Erlenmeyer flask. The total weight of the solution was recorded.
- Pieces of FilterMat™ 400 (also referred as curtains throughout the report) were cut with a diameter of 1.27 cm (0.5 in.)
- The required pieces of FilterMat™ were counted and weighted in an aluminum dish, then added to the solution. The weight and the total number of FilterMat™ pieces were recorded.
- The samples were placed in an orbital shaker and shaken at a velocity of 250 rpm for 48 hrs.
- The samples were filtered through a 0.45 µm Millipore™ membrane filter, mixed cellulose esters, hydrophilic filter using a filtration apparatus that consists of a filtering flask, base, funnel and clamp assembled together and connected to a vacuum source.
- Approximately 15 mL of the filtered sample were collected for taking a pH measurement. The rest of the sample was collected in a 125-mL

Nalgene® HDPE sample bottle, preserved with nitric acid and submitted for chemical analysis.

Each metal sample was analyzed in triplicate to capture analytical variability of the instrument analysis process. Table 3.5 illustrates a matrix of the batch sorption tests conducted with the pieces of geotextile. This table shows the target initial concentrations, total number of FilterMat™ pieces, approximate amounts of activated carbon contained in the geotextile, total area of the pieces of fabric, and solution volume used for the metal constituents. Note that the pieces of fabric contain less carbon than the amounts used for the activated carbon batch sorption tests since we anticipate that the geotextile will tend to absorb the metal constituents as well. If the same activated carbon amount used for the activated carbon batch sorption test would have been used for this test then the metals concentration might have been unmeasurable. A blank process test was prepared using DDI water and following the procedure described above to determine if there was any metals contamination during the batch sorption test process that may be caused by the activated carbon and the glassware.

### **3.6.3.2 Organics**

The FilterMat™ 400 batch sorption test was only conducted for DOC because this constituent was expected to represent the sorption behavior of organic contaminants in general. A single replicate was conducted for this part of the study. As for the batch testing conducted with activated carbon, the DOC solutions were not buffered. The following procedure was used to conduct the FilterMat™ batch sorption tests with DOC:

- All the glassware and equipment used for this test was decontaminated as specified in the organics equipment decontamination section (3.3.2).



- A synthetic solution was prepared for the DOC as described in the synthetic solutions section (3.2). The initial pH of the solution was measured.
- Approximately 100 mL of the DOC solution were added to a 250mL stainless steel bottle (250mL amber glass bottles were not available) and the total weight of the solution was recorded.
- Pieces of FilterMat™ 400 were cut with a diameter of 1.27 cm (0.5 in.)
- The required pieces of FilterMat™ were counted and weighted in an aluminum dish, then added to the solution. The weight and the total number FilterMat™ pieces were recorded.
- The samples were placed in an orbital shaker and shaken at a velocity of 250 rpm for 48 hrs.
- The samples were filtered through a 0.70 µm glass fiber filter with a filtration apparatus that consists of a filtering flask, base, funnel and clamp assembled together and connected to a vacuum source.
- The DOC filtered samples were collected in a 125-mL amber glass bottle, preserved with hydrochloric acid and submitted for DOC analysis.

To capture the analytical variability of the instrument analysis process each DOC sample was analyzed in triplicate. The matrix of the batch sorption tests conducted with the pieces of geotextile is given in Table 3.6, including target initial concentration, total number of FilterMat™ pieces, approximate amount of activated carbon contained in the geotextile, total area of the fabric, and solution volume. The pieces of fabric contain less carbon than the amounts used for the activated carbon batch sorption test since we anticipate that the geotextile will tend to absorb the DOC. If the same amount of activated

carbon used for the activated carbon batch sorption test would have been used for this test then the DOC concentration might have been unmeasurable. A blank process test was prepared using DDI water and following the procedure described above to determine if DOC contamination was caused during the batch sorption test process due the glassware and the geotextile pieces.

### **3.7 Column Design**

An upflow column was designed to accommodate a velocity of 0.94 cm/sec (0.031 ft/sec), which is the estimated velocity for the case study CDF effluent based on the dredge production assumptions. The column was built out of anodized aluminum in order to minimize sorption of the contaminants to the column walls; in other testing conducted at ERDC, anodized aluminum has been shown to perform equally well as compared to stainless steel in this regard. A column with a small diameter was appropriate for this case due to the large velocity that was required to simulate the CDF effluent velocity. Also, a column with a large diameter would have required a volume of water infeasible for laboratory testing. Therefore, a column with a 3.18-cm (1.25-in.) inside diameter was designed for this study. The main objectives of the upflow column design were to accommodate the design flow rate, variable layers of the FilterMat™, and multiple sampling ports. A smooth transition was needed to transition from the 0.64-cm (1/4-in.) Tygon® tubing from the pump to the 3.18-cm (1.25-in.) diameter column while maintaining laminar flow. A diffuser was designed to provide a gradual increase in area and reduce the velocity of the flow prior to entering the body of the column.

Table 3.5 Matrix of the FilterMat™ batch sorption tests for metal constituents

Constituents	Constituents Target Initial Concentration (mg/L)	Approximate Solution Volume (mL)	Approximate amount of carbon <sup>a</sup> (g)				Approximate fabric area <sup>a</sup> (in <sup>2</sup> )					
			1	2	4	6	8	1	2	4	6	8
Chromium VI	5	0.1	0.05	0.1	0.2	0.3	0.4	0.20	0.39	0.78	1.18	1.57
Copper	30	0.1	0.05	0.1	0.2	0.3	0.4	0.20	0.39	0.78	1.18	1.57
Lead	30	0.1	0.05	0.1	0.2	0.3	0.4	0.20	0.39	0.78	1.18	1.57
Mercury	25	0.1	0.05	0.1	0.2	0.3	0.4	0.20	0.39	0.78	1.18	1.57
Silver	5	0.1	0.05	0.1	0.2	0.3	0.4	0.20	0.39	0.78	1.18	1.57

<sup>a</sup> As a function of the total number of fabric pieces

Table 3.6 Matrix of the FilterMat™ batch sorption tests for DOC

Constituent	Constituent Target Initial Concentration (mg/L)	Approximate Solution Volume (mL)	Approximate amount of carbon <sup>a</sup> (g)				Approximate fabric area <sup>a</sup> (in <sup>2</sup> )					
			1	2	4	6	8	1	2	4	6	8
DOC	9.5	0.1	0.05	0.1	0.2	0.3	0.4	0.20	0.39	0.78	1.18	1.57

<sup>a</sup> As a function of the total number of fabric pieces

The design of the diffuser was based on rules of thumb and parameters found in the literature. The divergence angle of the expansion piece is critical to preventing the development of vortices, swirls, superimposed pulsations, downstream obstruction, turbulent flow, stall flow (transitory stall or bistable steady stall), and jet flow (Sparrow et al. 2009, White 1999) that would interfere with utilization of the entire area of the column and geotextile fabric. According to Sparrow et al. 2009, flow separation will not occur for a diffuser with a divergence angle of  $5^\circ$  and Reynolds number larger than 2000 at the diffuser inlet. Alternatively, the diffuser should have a slope in the walls smaller than 0.1 (x:y  $\leftrightarrow$  10:1) to prevent abrupt changes in slope that may cause flow separation (Personal communication Dr. Richard L. Stockstill September 29, 2010).

To design the diffuser, the velocity that was estimated based on the estimated CDF effluent flow rate was set as the diffuser outlet velocity. The CDF approach flow rate was approximated to  $1.34 \text{ m}^3/\text{s}$  ( $47.3 \text{ ft}^3/\text{s}$ ) and the dimensions assumed for the curtain that could be hung along the weir were 4.6 m (15 ft) high and 30.5 m (100 ft) long, thus resulting in a field approach velocity of 0.98 cm/s (0.032 ft/s). The inlet velocity, 46.9 cm/s (1.54 ft/s), was estimated based on the continuity equation for incompressible flow (i.e. conservation of mass) using an outlet velocity and diameter of 0.98 cm/s (0.032 ft/s) and 3.18 cm (1.25 in.) respectively, and an inlet inner diameter of 0.46 cm (0.18 in.), 0.64 cm (0.25 in.) nominal diameter:

$$Q_1 = Q_2 \quad (3.7)$$

$$v_1 = \frac{v_2 A_2}{A_1} \quad (3.8)$$

where,

$Q_1$  = inlet flow rate

$v_1$  = inlet velocity

$A_1$  = inlet area

$Q_2$  = outlet flow rate

$v_2$  = outlet velocity

$A_2$  = outlet area

The following expression was used to verify if the Reynolds number at the inlet was within the flow regime described by Sparrow et al. 2009.

$$Re = \frac{vD_H}{\nu} \quad (3.9)$$

where,

Re = Reynolds number

$v$  = inlet velocity

$D_H$  = hydraulic diameter (inlet ID)

$\nu$  = kinematic viscosity at 21°C (70°F)

The Reynolds number at the inlet resulted in 2200 assuming a kinematic viscosity of  $0.984 \times 10^{-6} \text{ m}^2/\text{s}$  ( $1.05 \times 10^{-5} \text{ ft}^2/\text{s}$ ) at 21°C (70°F), a velocity of 46.9 cm/s (1.54 ft/s) and a hydraulic diameter of 0.46 cm (0.18 in.). Based on the geometry of the diffuser, its total length must be equal or greater than 31.06 cm (12.23 in.) if a divergence angle ( $\theta$ ) of 5° is assumed.

A diffuser length of (31.12 cm) 12.25 in. was used for the column design, thus resulting in a wall slope of 0.082, which is smaller than 0.1. Figure 3.5 shows a sketch of the diffuser including the dimensions and Figure 3.6 shows a picture of the column's diffuser. Separate interchangeable modules were constructed that could be connected in series to allow us to create a column with multiple layers of FilterMat™ and sample

ports. The FilterMat™ was basically squeezed in between each module. The modules are then connected with a circular piece of aluminum that is secured with two semi-circular pieces of metal and a Velcro® strap. Figure 3.7 illustrates a picture of the interchangeable modules separated and interconnected.

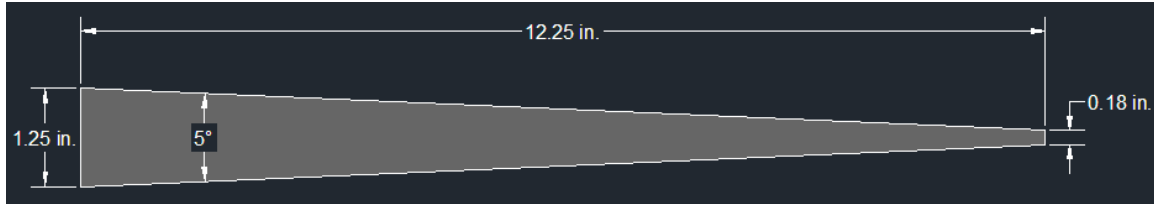


Figure 3.5 Diffuser sketch



Figure 3.6 Diffuser designed for the upflow column

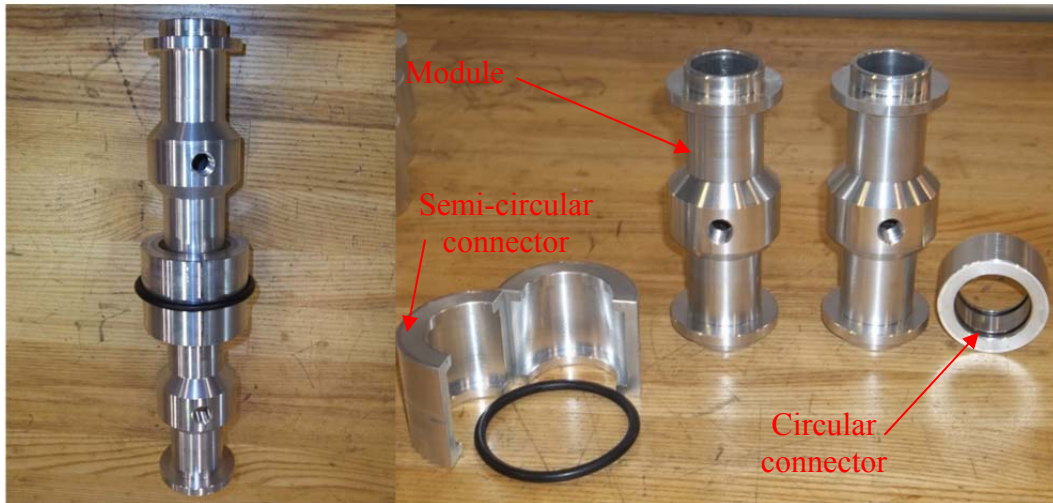


Figure 3.7 Upflow column modules and connections

The diffuser was permanently connected to a module with a length of approximately 25.4 cm (10.00 in.) and 3.18-cm (1.25-in.) inner diameter to ensure uniform flow development along the rest of the column. Then, separate interchangeable modules with a length of 15.2 cm (6.00 in.) and an inner diameter of 3.18 cm (1.25 in.) were constructed. Single or multiple layers of FilterMat™ could be placed between the column modules. The following general configurations could be used for the column setup: no material in between, 2 pieces of FilterMat™ in between, and one piece of FilterMat™ held in place with a Teflon® O-ring on top and bottom to prevent flow around the edges of the single piece of fabric.

Another diffuser was constructed for the column outlet with a length of 15.2 cm (6.00 in.), which was within a 15.2-cm (6.00-in.) long module. A sample port was located on the 25.4-cm (10.00-in.) column segment (bottom) to permit collections of samples from the untreated influent. Also, a sample port was installed in each 15.2-cm (6.00-in.) column module to permit sample collection from between the fabric layers. Fittings were placed in the column to connect the valves and sample ports. A 0.64-cm (1/4-in.) OD

stainless steel tube was connected to the inlet and outlet of the column with fittings. Figures 3.8 and 3.9 illustrate a picture of the column setup and sketch of the column respectively.

### 3.8 Column Studies

Upflow column studies were conducted for copper and Aroclor 1016 to evaluate the feasibility of using the FilterMat™ to treat effluent and runoff passing through the material. The exhaustion time and mass of contaminant absorbed by the FilterMat™ were obtained from the data collected for the Cu column studies. The breakthrough time and mass of contaminant absorbed by the FilterMat™ were obtained from the data collected for the Aroclor 1016 column studies. Only copper and Aroclor 1016 were tested because the sorption behavior of these two contaminants should be generally indicative of other metal and organic contaminants of concern.

The column tests were conducted individually for each of these contaminants using a flow rate and concentration that would be representative of the case study field conditions. The exhaustion time (defined as the time when effluent concentration is approximated to the influent concentration) for copper was predicted based on the activated carbon sorption capacity and the FilterMat® sorption capacity. For Aroclor 1016, breakthrough time (defined as the time when effluent concentration is approximated to the most conservative WQC) was predicted based on the activated carbon sorption capacity since batch sorption tests for this contaminant were only conducted using the activated carbon.

Preliminary tests were conducted to determine appropriate sampling intervals and total operating time for the column tests. The contaminant solutions were pumped into



the column using a Thermo Scientific peristaltic pump model FH-100. Three peristaltic pumps were obtained for this part of the study, and were calibrated prior testing to get a relationship between the pump rotational speed and flow rate. This facilitated the setup of the desired flow rates and estimation of contaminant mass passed through the column over the duration of the tests. The calibration curves for the three pumps are shown in Figure 3.10. A test was conducted using a piece of FilterMat™ with a diameter of 3.8 cm (1.5 in.), the diffuser and a column module with an acrylic circular connector to determine if water would flow around the sides of the FilterMat™ rather than through the entire surface area of the FilterMat™. Through this test we were able to determine that water was not bypassing the FilterMat™.



Figure 3.8 Upflow column setup

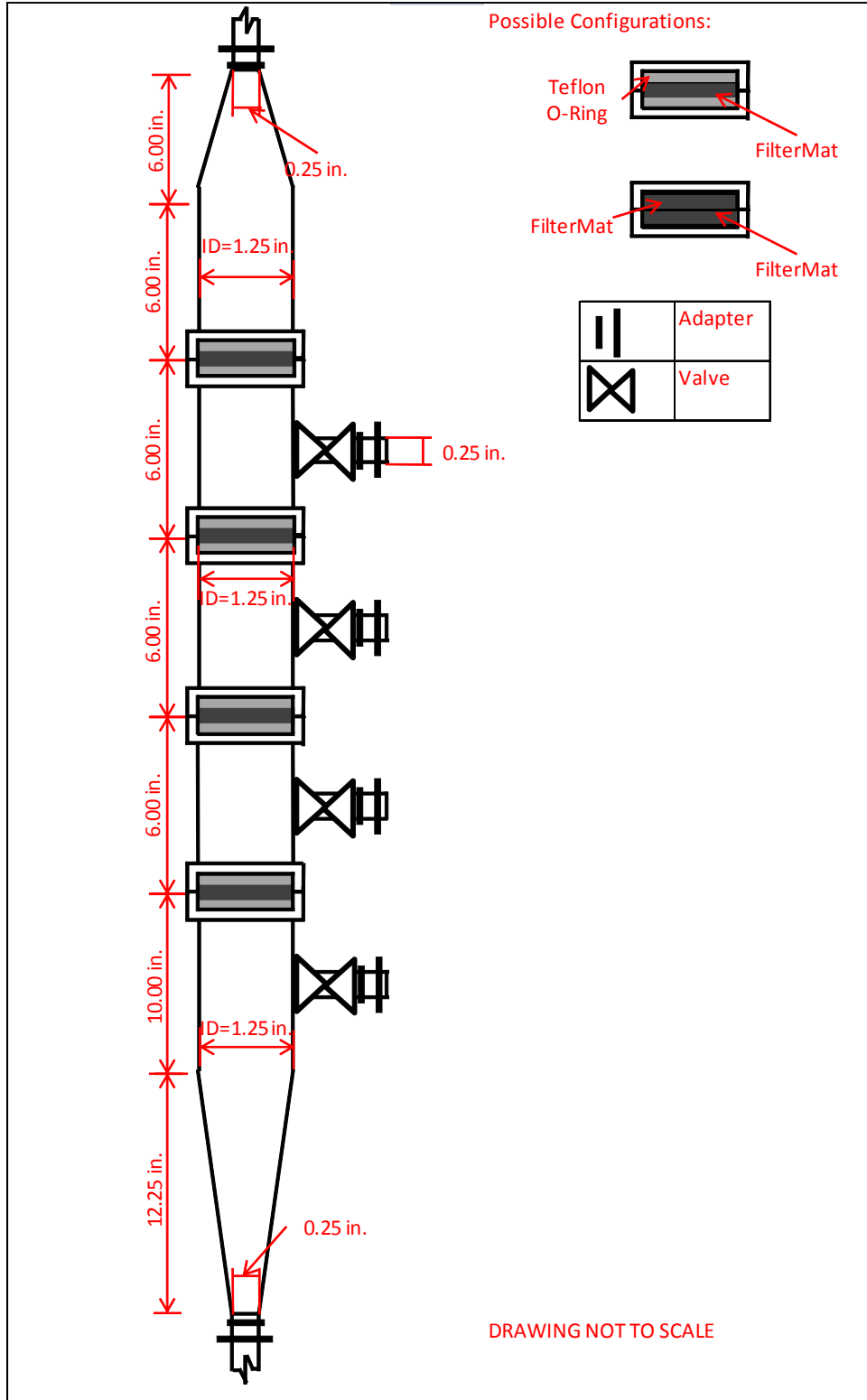


Figure 3.9 Upflow column sketch

### 3.8.1 Copper

The flow rate used for the first column test conducted for copper was approximated to 500 mL/min, which is representative of the case study CDF effluent flow rate. At this flow rate no copper removal was observed (effluent concentrations equaled influent concentrations), therefore the flow rate was reduced to provide greater contact time with the activated carbon in the FilterMat™. A second column test was conducted using a flow rate of approximately 250 mL/min, which represents 54% of the estimated field velocity. For this case contact time between the copper solution and the fabric was also not adequate; therefore, another column test was conducted using a flow rate of approximately 125 mL/min, which represents 27% of the field velocity. For this flow rate a reduction in the contaminant concentration was observed, therefore, this flow rate was used to conduct the remainder of the copper upflow column studies. The final column studies were conducted in triplicate using a flow rate of 125 mL/min and multiple pieces of FilterMat™ 400. A single test was run using the FilterMat™ 800 for comparison purposes. The general procedure followed to run each column test is described below. Table 3.7 shows the parameters and conditions used for each test.

- All the glassware and equipment used for this test was decontaminated as specified in the metals equipment decontamination section (3.3.1).
- Pieces of FilterMat™, also referred as curtains, were cut with a diameter of approximately 3.8 cm (1.5 in.), resulting in an approximate total area of 11.4 cm<sup>2</sup> (1.77in.<sup>2</sup>) and estimated activated carbon content of 0.46 g.
- A synthetic solution was prepared for copper as described in the synthetic solutions section (3.2). For the first two preliminary tests, which did not require a large sample volume, the solution was prepared using a

volumetric flask and stored in a 3.78-L (1-gal) glass jar. For the rest of the column tests the solutions were prepared in an 83-L (22-gal) HDPE rectangular tank. The concentrations used for each column test are shown in Table 3.7. A sample of the solution was collected to get the initial solution concentration.

- The column was assembled with the necessary fittings (see Figure 3.11 for a general schematic of the fittings that were used) and the setup specified in Table 3.7, and connected to a peristaltic pump with 0.64 cm (1/4-in.) ID Tygon® tubing R-1000. Figure 3.11 shows the column setup used for the final column tests including fittings and location of the pieces of fabric.
- The synthetic solution was pumped into the column using the peristaltic pump at the flow rate shown on Table 3.7
- The sample collection process started 5 minutes after the solution began discharging from the outlet in order to flush any residuals that may be present in the column due the cleaning process. During sampling, approximately 20-50 mL of treated water were collected from each sample port. Table 3.7 shows the sampling intervals and total operating time used for each test. For column tests 5-7, there was a lag time of approximately 1 minute and 30 seconds between sampling from each port in order to facilitate orderly sample handling. Note that the sample ports were flushed before each sample collection interval in order to discharge residuals from the previous sample collection. Each sample was collected in a 125-mL Nalgene® HDPE sample bottle, preserved with nitric acid and submitted for copper analysis. For the first preliminary column test, a copper

electrode was used to measure copper concentrations since only approximately values were required in order to evaluate operating parameters and optimum sampling times prior to taking samples for chemical analysis.

- The column effluent was collected in a discharge reservoir for appropriate disposal.

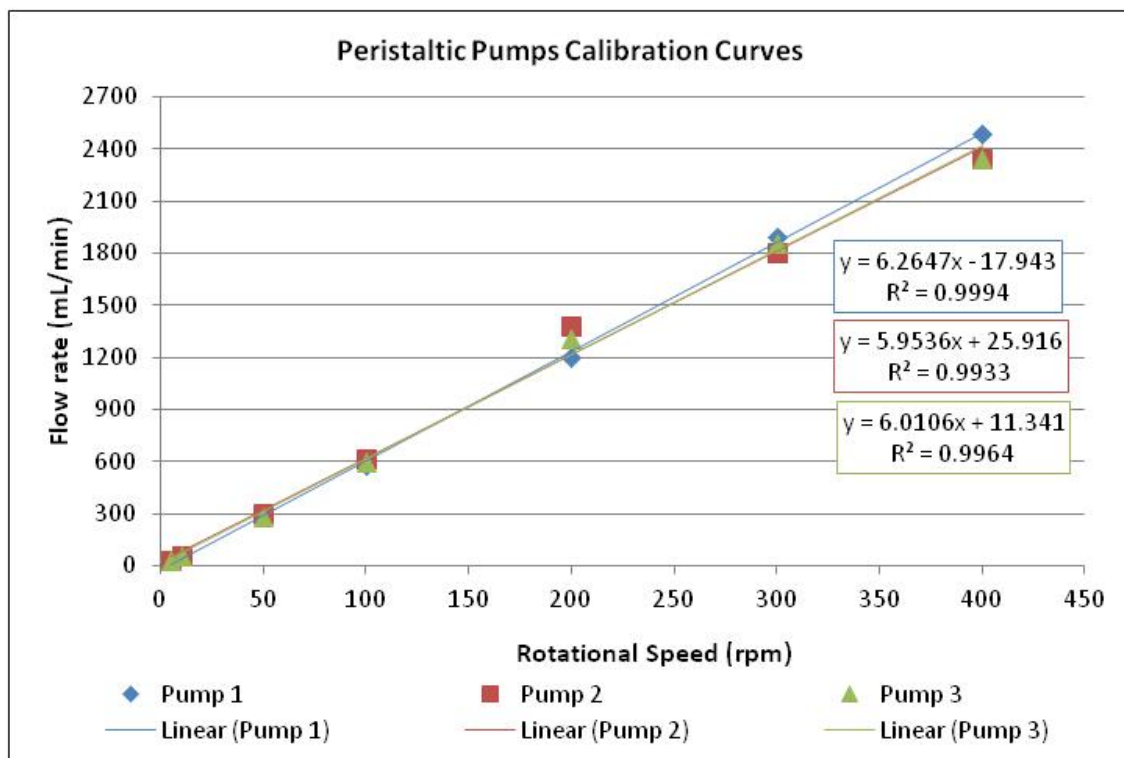


Figure 3.10 Calibration curves of the peristaltic pumps that were used for the column tests

Note that for column tests 2-7 a concentration approximated to the maximum predicted field concentration for the case study was used. A significantly higher concentration was used for preliminary test 1 since for that test concentrations were measured with a copper electrode. The copper electrode measures the conductivity of

copper in mV and requires concentrations of at least 1 mg/L for reliable measurement. This method was not used for the other column tests due to the minimum concentration requirements.

### 3.8.2 Aroclor 1016

A flow rate approximated to 125 mL/min was used for the Aroclor 1016 column tests, based on the results obtained for the copper column test for which flow rates higher than 125 mL/min did not provide adequate contact time between the curtain and the contaminant of concern. As mentioned in the previous section, a flow rate of 125 mL/min represents 27% of the case study field velocity. Two preliminary column tests were conducted to determine the sampling intervals and column operating time. The final column studies were conducted in triplicates using the pieces of FilterMat™ 400. The general procedure followed to run each column test is described below. Table 3.8 shows the parameters and conditions used for each test.

- All the glassware and equipment used for this test was decontaminated as specified in the organics equipment decontamination section (3.3.2).
- Pieces of FilterMat™, also referred as curtains, were cut with a diameter of approximately 3.8 cm (1.5 in.), giving an area of 11.4 cm<sup>2</sup> (1.77 in.<sup>2</sup>) and approximate activated carbon content of 0.46 g.
- A synthetic solution was prepared for Aroclor 1016 as described in the synthetic solutions section (3.2). The synthetic solutions were prepared in 322-L (85-gal) stainless steel drums to minimize losses of the Aroclor through sorption to the container. The concentrations used for each column test are shown in Table 3.8.

- The column was assembled with the necessary fittings (see Figure 3.12 for a general schematic of the fittings that were used) and the setup specified in Table 3.8, and connected to a peristaltic pump with a 0.64-cm (1/4-in.) ID Tygon<sup>®</sup> tubing R-1000. Figure 3.12 shows the column setup used for the final column tests including fittings and location of the pieces of curtain.
- The synthetic solution was pumped into the column using the peristaltic pump upon the completion of the column setup.
- The sample collection process started 5-10 minutes after the solution began discharging from the outlet in order to flush any residuals that may be present in the column due the cleaning process. For each sampling interval, a sample was collected from the inlet and the outlet to get the influent and effluent concentration. A sample was collected from the influent at each sampling interval since the initial concentration could potentially vary due to volatilization of the Aroclor 1016 and analytical variability. For the preliminary test, a sample with an approximate volume of 1 L was collected from the influent and effluent. For the three final tests, a sample with an approximate volume of 1 L was collected from the influent and 2 L from the effluent to ensure that the expected low concentrations in the treated water could be detected. Note that the sampling port was flushed before each sample collection interval in order to discharge residuals from the previous sample collection. Each sample was collected in a 1-L amber glass bottle, preserved at 4°C and submitted for Aroclor 1016 analysis.



- The column effluent was collected in a discharge reservoir for appropriate disposal.

The approach of the column test was changed after obtaining the results from the preliminary test. For the preliminary test, an Aroclor 1016 concentration approximated to the maximum predicted field concentration was used and the test objective was to determine optimum sampling intervals and the time of exhaustion of the carbon in the curtain. During the length of the test (96 hrs) exhaustion time (defined as the time when the effluent concentration is approximated to the influent concentration) was not reached and the data trend suggested that exhaustion time would occur around 8 days. The required volume for running the test for 8 days was very large; therefore, it was unfeasible to follow this approach for the other tests.

For the final tests, the Aroclor 1016 concentration was reduced to a level predicted to achieve breakthrough within 2.5 days; the test objectives were also modified to determine breakthrough rather than carbon exhaustion. Breakthrough would be defined as the time when effluent concentrations are measurable and approximate to the most conservative WQC.

### **3.9 Data Analysis**

Statistical parameters including mean, standard deviation, and coefficient of variation were estimated for those tests that were run in more than one replicate to capture procedural variability and for samples analyzed in triplicates to capture analytical variability. Plots of the equilibrium, batch and column study data were prepared for evaluation of data trends and determination of relevant parameters. Plots of the final concentration as a function of time were created to determine contact time for batch

sorption testing, using the data obtained from the batch equilibrium test. Sorption capacity and contaminant removal percentage were calculated using the data obtained from the batch sorption tests. Isotherm plots were generated from the batch sorption data, and the trends were evaluated with two different models (Freundlich and Langmuir) to determine which model better represented the data trends for each contaminant.

Exhaustion curves were generated for the data obtained from the Cu column tests and breakthrough curves were generated for the data obtained from the Aroclor 1016 column tests. Parameters estimated included overall contaminant removal percentages, relative contaminant removal percentages occurring at each port, and cumulative contaminant mass absorbed by the FilterMat™ in the column. A mass balance was performed to determine the overall removal capacity of the system, which was compared to the predictions made using the carbon capacity estimated from the batch sorption tests. Plots were generated for each of the calculated parameters.

Table 3.7 Matrix of the preliminary and final column tests conducted for copper

Column Test ID	Column Test Type	Target Initial Conc. (mg/L)	Flow Rate (mL/min)	Sampling Interval (mins)	Total Operating Time (min)	FilterMat™ type	Setup Type
1	Preliminary	5	500	1	7.5	400	Single curtain with 2 Teflon® O-rings in 1 module
2	Preliminary	0.5	250	1	13	400	Single curtain with 2 Teflon® O-rings placed in 2 modules
3	Preliminary	0.3	125	1.5	25	400	Double curtains in 2 modules
4	Preliminary	0.3	125	1.5	25	800	Double curtains in 2 modules
5	Final_Rep1	0.3	125	4	180	400	Double curtains in 3 modules
6	Final_Rep2	0.3	125	20	180	400	Double curtains in 3 modules
7	Final_Rep3	0.3	125	20	180	400	Double curtains in 3 modules

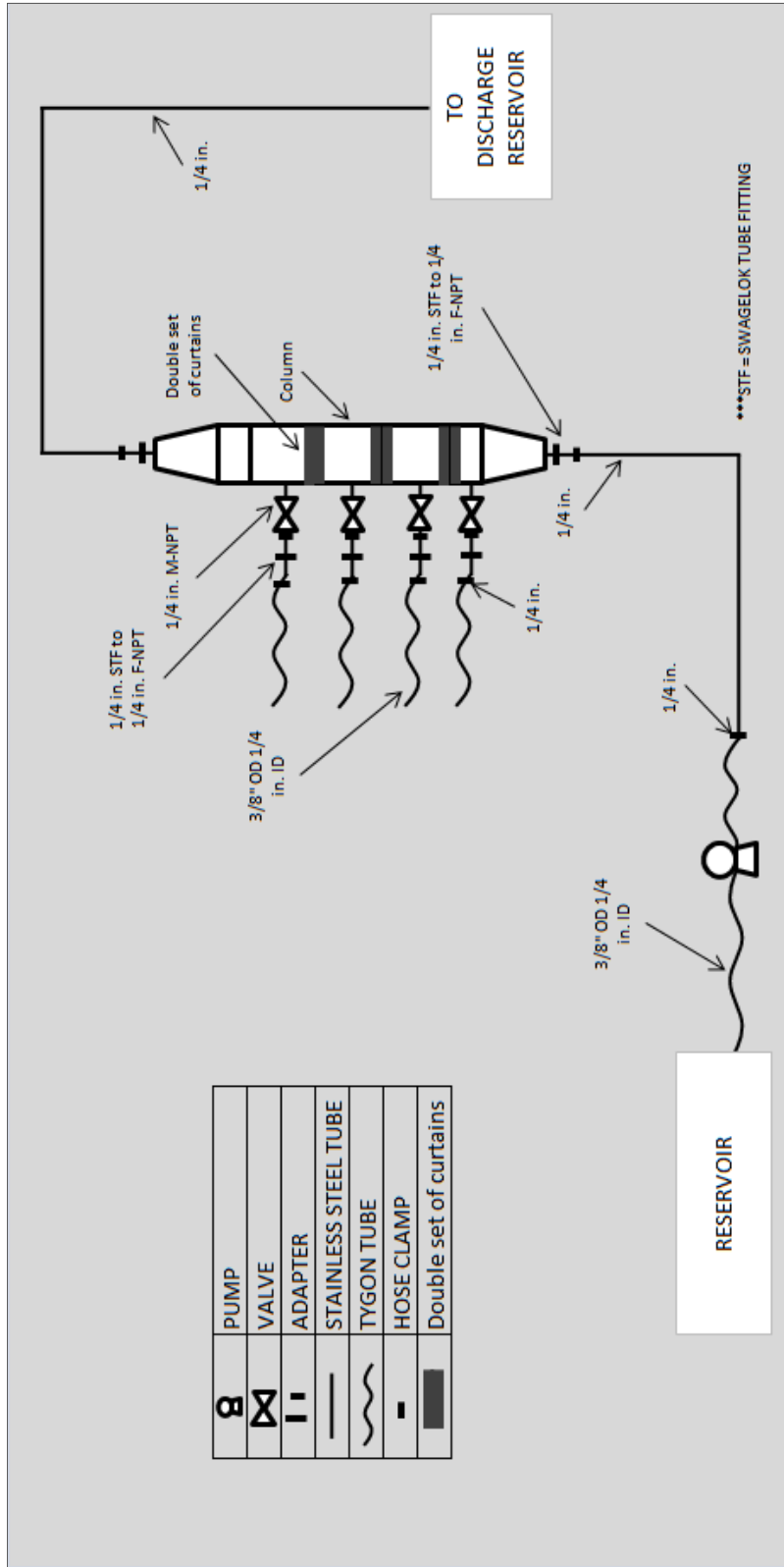


Figure 3.11 General schematic of copper column setup for the final column tests

Table 3.8 Matrix of the preliminary and final column tests conducted for Aroclor 1016

Column Test ID	Column Test Type	Target Initial Conc. (µg/L)	Flow Rate (mL/min)	Sampling Interval (hrs)	Total Operating Time (hrs)	FilterMat™ type	Setup Type
1	Preliminary	0.82	125	24	96	400	Single curtain with 2 Teflon® O-rings in 1 module
2	Final_Rep1	0.1	125	12	60	400	Double curtains in 4 modules
3	Final_Rep2	0.1	125	12	60	400	Double curtains in 4 modules
4	Final_Rep3	0.1	125	12	60	400	Double curtains in 4 modules

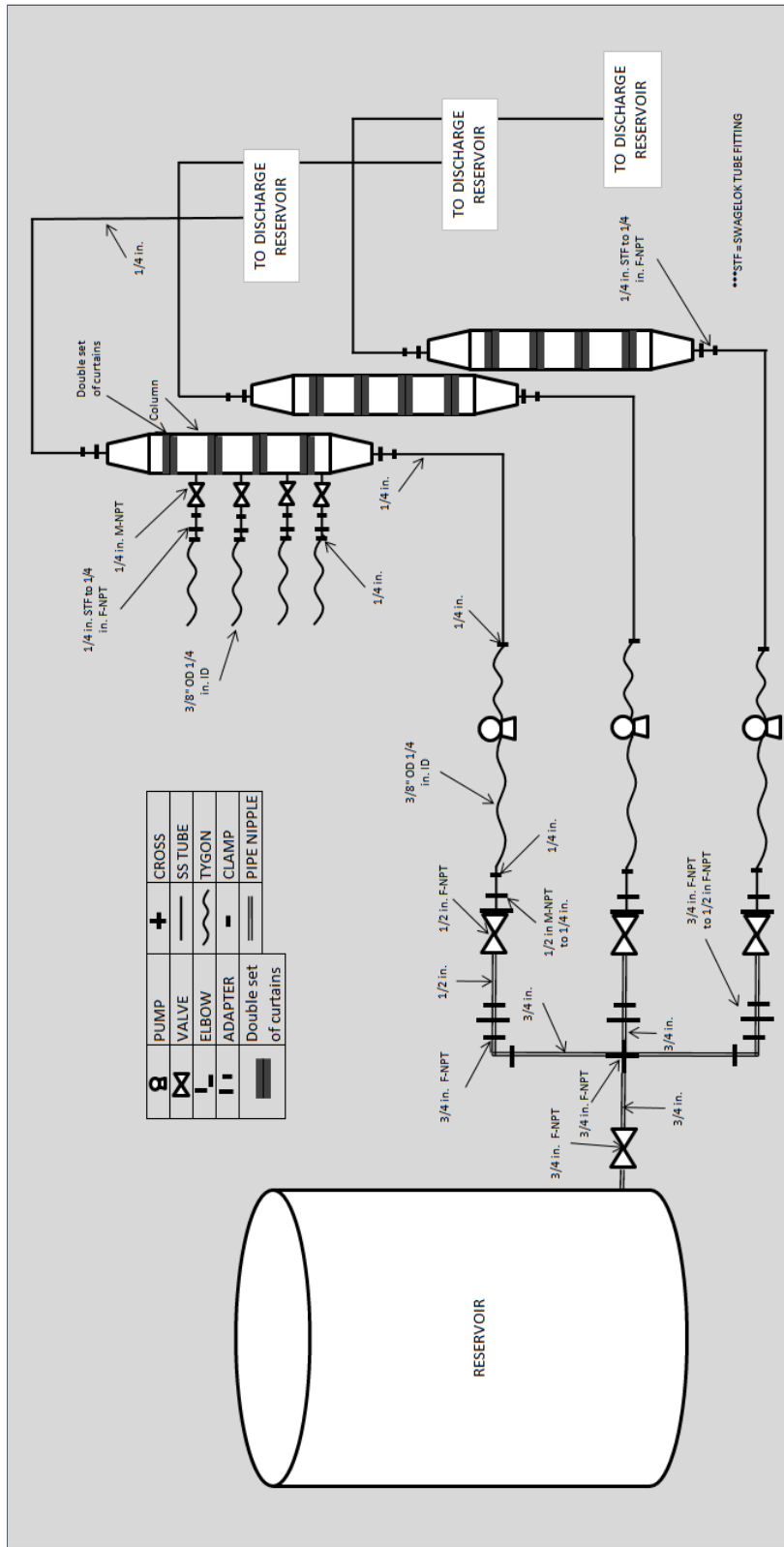


Figure 3.12 General schematic of Aroclor 1016 column setup for the final column tests

## CHAPTER IV

### RESULTS AND DISCUSSION

#### 4.1 Equilibrium Studies

As mentioned in the previous chapter, equilibrium studies were conducted to determine the contact time required to establish equilibrium between the activated carbon contained in the FilterMat™ and the contaminant solutions. The equilibrium time determined for each contaminant was used as the total contact time for the batch sorption tests. The results obtained through the batch equilibrium tests are summarized below.

##### 4.1.1 Metals

The first equilibrium test that was conducted for copper, chromium VI, lead, and silver for which 0.05 g of activated carbon were added to 100 mL solution did not result in sufficient removal to determine equilibrium time. A virtually unchanged concentration was observed for the Cu, Cr VI, Pb and Ag solutions from the beginning (at  $t = 0$  hrs,) until the end of the study (at  $t = 48$  hrs). The contaminant removal percentage was smaller than 3.0% for all the metals with the exception of silver for which the removal percentage ranged from 8.6% to 18%.

A second equilibrium test was therefore conducted by treating 100 mL of the metals solutions (Cu, Cr VI, Pb, and Ag) with 0.25 g of activated carbon. The same approach was also used for the first mercury equilibrium test. A fairly constant concentration was observed from 24 hrs to 72 hrs for all the metals with the exception of silver, for which a minimum value was observed at 48 hrs. Therefore, 48 hrs was

considered to be sufficient to establish equilibrium for all contaminants, and was selected as the contact time for the remainder of the batch studies. This contact time was relatively conservative as compared to equilibrium times reported in the literature, which generally ranged from 105 minutes to 48 hours. Figure 4.1 shows the equilibrium test results obtained for copper, where the final concentration was plotted as a function of time, which is representative of the results obtained for the other tested metals (Pb, CrVI, and Hg). Figure 4.2 shows the equilibrium test results obtained for silver, which were an exception to the results obtained for the other metals because a minimum final concentration was observed at 48 hrs, which suggests that replicates of the test should have been conducted to determine if that point was an outlier. Appendix A shows the data obtained for the equilibrium tests and the plots created for the data analysis for each tested metal.

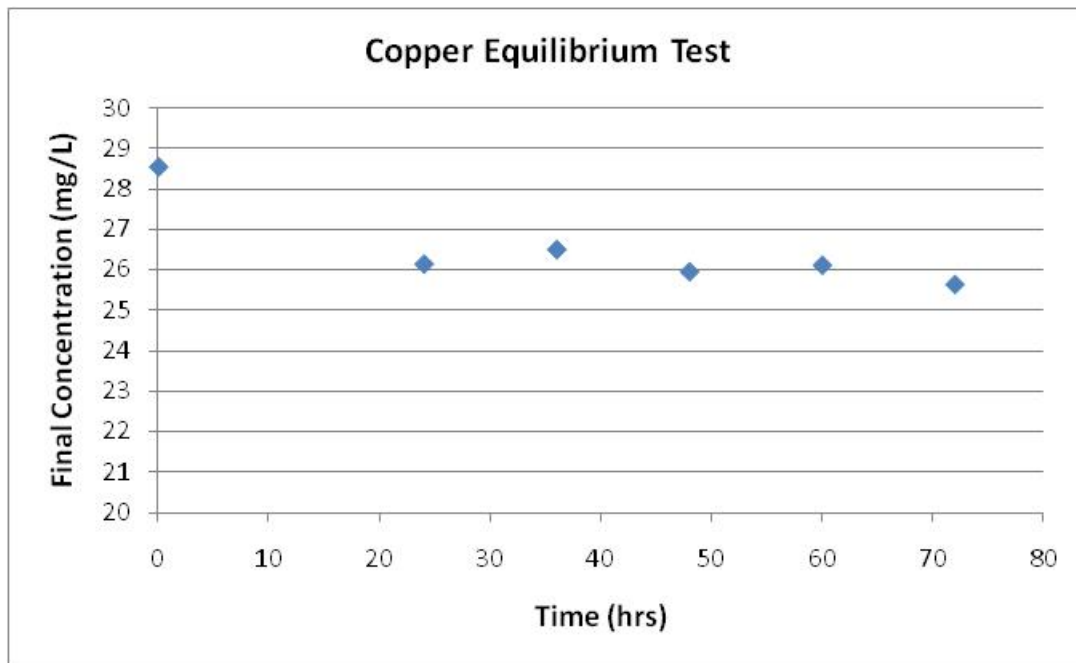


Figure 4.1 Equilibrium test results obtained for Cu (0.25 g of activated carbon in 100 mL of solution)



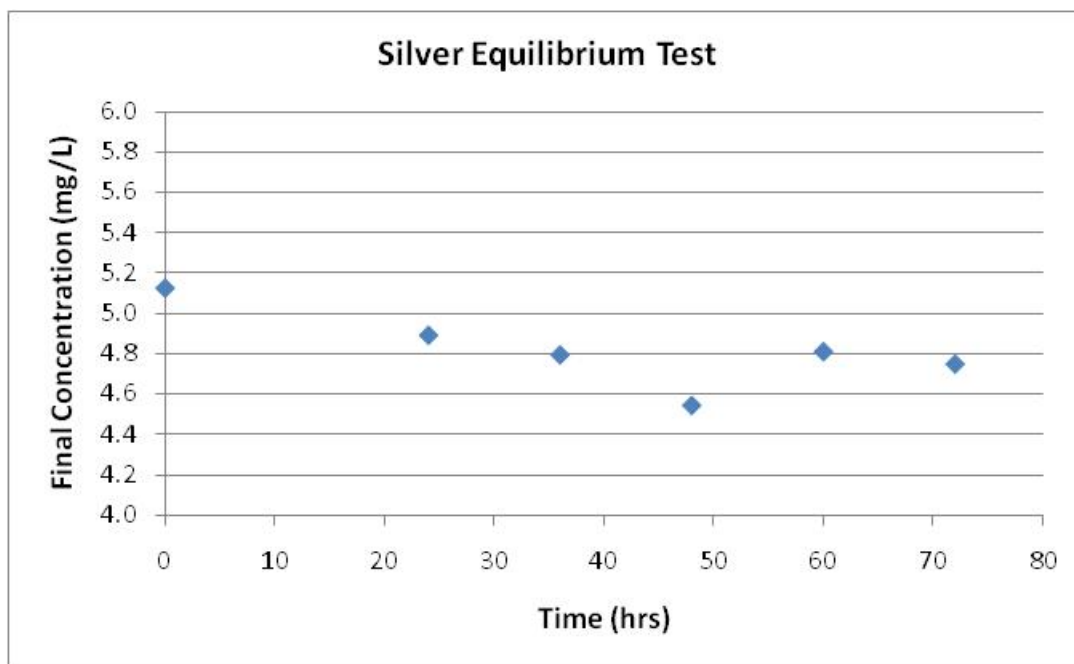


Figure 4.2 Equilibrium test results obtained for Ag (0.25 g of activated carbon in 100 mL of solution)

#### 4.1.2 Organics

Similar to the first equilibrium test conducted for the metals using 0.05 g of activated carbon, the first equilibrium test conducted for DOC (0.05 g of activated in a 100 mL solution) did not result in sufficient removal to determine equilibrium time. The final concentration at all contact times was very similar to the initial concentration from the beginning (at  $t = 0$  hrs) until the end of the study (at  $t = 48$  hrs). The DOC removal percentage estimated for this test was relatively small and variable, thus ranging from 1% to 16%.

A second equilibrium test was conducted for DOC using 0.25 g of activated carbon in 100 mL of solution (Figure 4.3). A minimum concentration was measured at 24 hours, and was similar for all contact times other than  $t=0$ , and  $t=36$  hours. The final concentration for the 36 hour sample was approximately equal to the initial

concentration. The general tendency of the data suggests that equilibrium was likely established at 24 hours, but given the inconsistency observed at 36 hours, a 48 hour contact time was used for the DOC batch sorption tests as well.

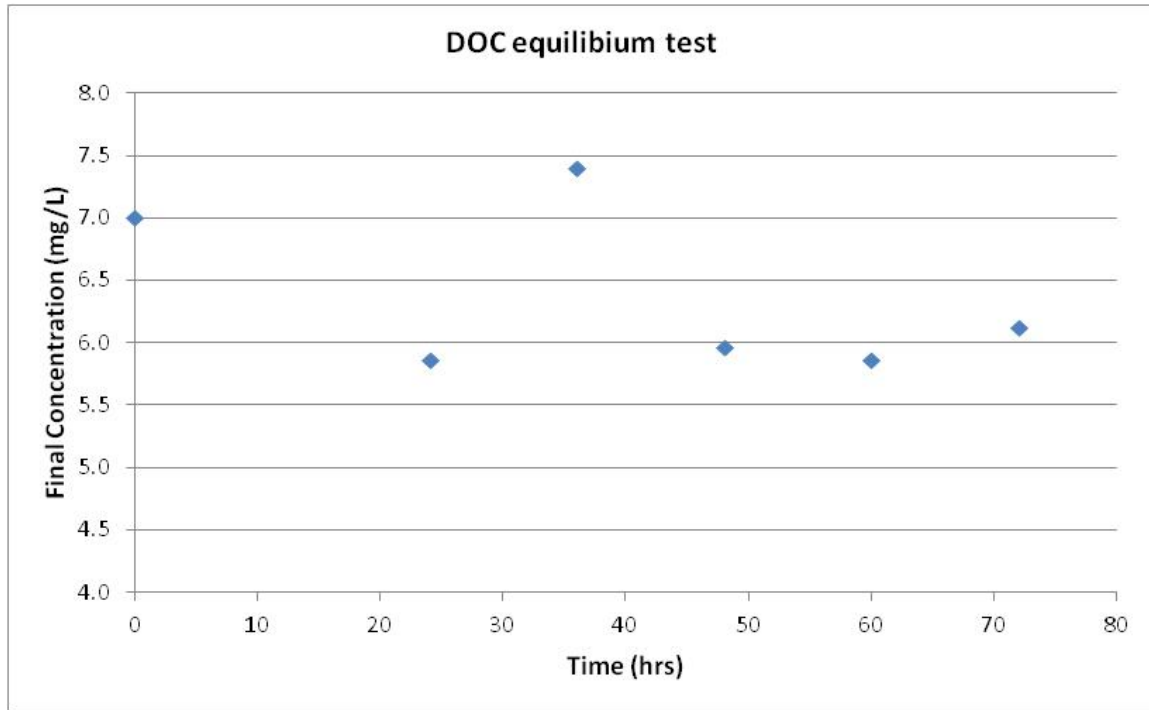


Figure 4.3 Equilibrium test results obtained for DOC (0.25 g of activated carbon in 100 mL of solution)

One equilibrium test was conducted for Aroclor 1016, where 0.05 g of activated carbon were added to 1000 mL of solution. A significant reduction in the contaminant concentration was observed for each of the tested time periods. Some recovery issues were observed for the Aroclor 1016 initial concentration. The initial concentration (0.18  $\mu\text{g/L}$ ) was only 43% of the intended initial concentration (0.42  $\mu\text{g/L}$ ). These differences could be attributed to the extraction process, analytical process, volatilization, sorption to the containers and equipment, or incomplete dilution of the standard in the water. The

final Aroclor 1016 concentration obtained at 24 and 36 hrs had the same order of magnitude (0.00443 and 0.00188  $\mu\text{g/L}$ ), resulting in removal percentages of 97.6 and 98.9% respectively. A minimum concentration of 0.00038  $\mu\text{g/L}$  was observed at 48 hrs, which was an order of magnitude smaller than the final concentrations obtained at 24 and 36 hrs and resulted in a removal percentage of 99.8%. Based on these results a total contact time of 48 hrs was used for the Aroclor 1016 batch sorption tests. Figure 4.4 shows the equilibrium test results obtained for Aroclor 1016, where the final concentration was plotted as a function of time. The data obtained for the Aroclor 1016 and DOC equilibrium tests is shown in Appendix A.

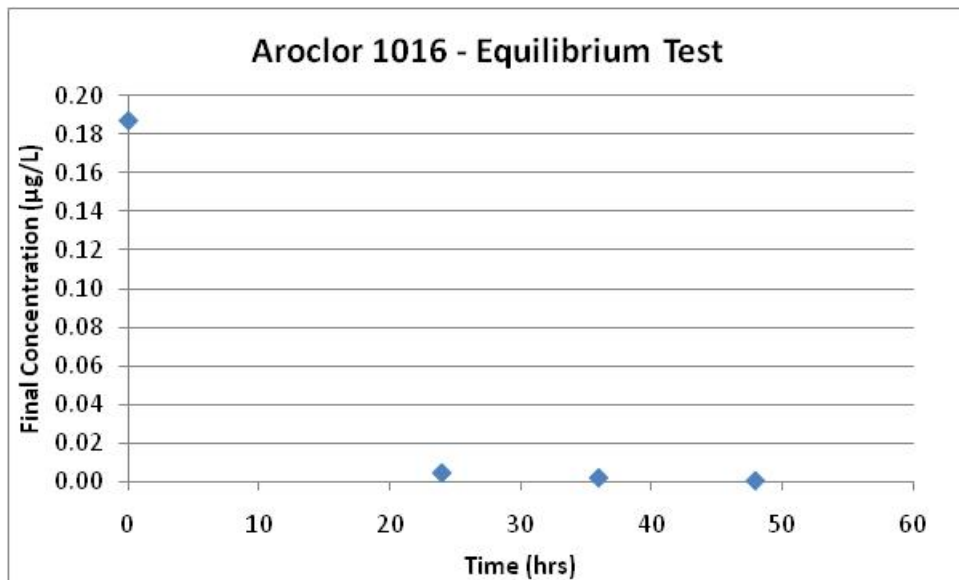


Figure 4.4 Equilibrium test results obtained for Aroclor 1016 (0.05 g of activated carbon in 1000 mL of solution)

#### 4.2 Batch Sorption Studies

Batch sorption tests were conducted using the activated carbon impregnated in the FilterMat™ and pieces of FilterMat™. The sorption capacity of these two materials was obtained for each tested metal and organic contaminant, thus assessing the impact in the

carbon capacity that may be caused by the packaged pieces of curtain (i.e. nonwoven fabric and activated carbon). Preliminary tests were conducted to determine the concentration range and carbon dosages to be used for the batch sorption tests, and whether or not buffering would be necessary for the metals tests. Three buffering tests were conducted to determine the optimum acid buffer strength that would maintain constant pH and prevent precipitation of the tested metals. The results obtained from the buffering tests and batch sorption tests are summarized in the following sub-sections.

Different parameters were also evaluated from the data including sorption capacity and removal percentage. The following expressions were used to estimate these two parameters.

- Sorption capacity

$$\frac{X}{M} = \frac{(C_i - C_e)V}{M} \quad (4.1)$$

where,

$X/M$  = sorption capacity (amount of contaminant sorbed per unit weight of carbon)

$C_i$  = contaminant initial concentration

$C_e$  = contaminant equilibrium concentration

$V$  = total volume of solution in the flask/container

$M$  = weight of activated carbon in the flask/container

- Removal percentage

$$\text{Removal percentage} = \left[ \frac{(C_i - C_e)}{C_i} \right] * 100 \quad (4.2)$$

#### 4.2.1 Buffering

Buffering needs were determined by monitoring the pH of a 30 mg/L Cu solution following the addition of 3.0 g of activated carbon to 100 mL of solution, the highest carbon dosage used in the batch testing. The solution pH increased from 2.69 to an average of 6.59 upon the carbon addition. The pH change in DDI was also monitored for the same carbon dosage in order to assess the impact of the carbon on pH in the absence of copper; the pH increased from 5.54 to 9.27. An additional test was conducted with different carbon amounts (0.01 g, 0.02 g, 1.0 g, 2.0 g, 4.0 g and 6.0 g) added individually to 100 mL of a 50 mg/L Cu solution. The results obtained from this test suggest a linear relationship between pH and carbon dosage (Figure 4.5). Based on these results, buffering was determined to be necessary to maintain a constant pH and prevent precipitation of the metals during sorption testing.

Acetic acid (glacial, 100%) and sodium acetate were selected for buffering the solutions, as previously discussed in Chapter III. A preliminary batch sorption test was conducted for copper, lead and silver using an acetic acid concentration of 0.002 M. The test showed very variable pH; in general, it ranged from 2.61 to 7.38. A measurable linear trend with a direct relationship was observed for the Cu and Pb adsorption isotherms (see Figure B.1 for Freundlich and Figure B.2 for Langmuir in Appendix B); however, a trend could not be established for Ag (0.002 M acetic acid buffer). Three tests were conducted to determine the lowest effective acetic acid concentration that would maintain the pH near 4.75 due to the inconsistencies observed in the preliminary batch sorption test. The acetic acid concentration that maintains a fairly constant pH (near 4.75) would be used as the buffer strength for the activated carbon and FilterMat™ batch sorption tests.

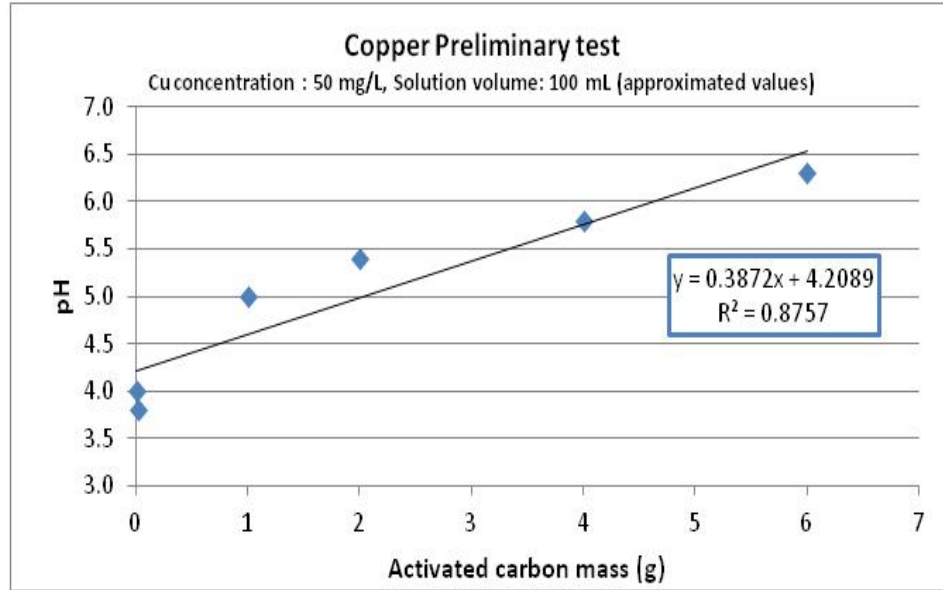


Figure 4.5 Copper preliminary test – pH vs. Activated carbon mass (Cu concentration: 50 mg/L, Solution volume: 100 mL, contact time 48 hrs)

The first test that was performed consisted of titrating 100 mL of a 30 mg/L copper solution with 17.5 M acetic acid, over a period of 48 hrs. The Cu solution contained the maximum amount of activated carbon (3.0 g) used for the batch sorption tests and was titrated initially by adding 5 $\mu$ L of acetic acid periodically until the pH was near 4.75, which is the pKa of acetic acid. The solution was titrated again at 24 and 48 hrs following the same procedure in order to maintain a constant pH. The results obtained through this test, which was conducted in triplicate, are shown in Figure 4.6.

The results show that the pH of the solution is fairly constant and below 5.0 upon the addition of 30  $\mu$ L of acetic acid, which results in an acetic acid concentration of 0.005M. After 24 hrs, the pH increased from 4.43 to 4.71. After 48 hrs, the pH did not rise significantly (from 4.22 at 24 hrs to 4.37 at 48 hrs); however, acetic acid was added to maintain constant pH. An average cumulative volume of 50  $\mu$ L of acetic acid were added to the solution in order to reduce the pH to between 4.0 and 5.0 (i.e. near 4.75) over a 48

hrs period, thus resulting in an acetic acid concentration of approximately 0.009 M. The order of magnitude of the acetic acid concentration that resulted from this test (0.009 M) was the same as the one used for the preliminary batch sorption test (0.002 M). The coefficient of variation between replicates of the copper titration test was smaller than 0.08. Therefore, the pH measurements were not variable, which suggests that the carbon-solution response to the acetic acid addition was consistent. Also, the data trend shown in Figure 4.6 is very similar for the triplicates.

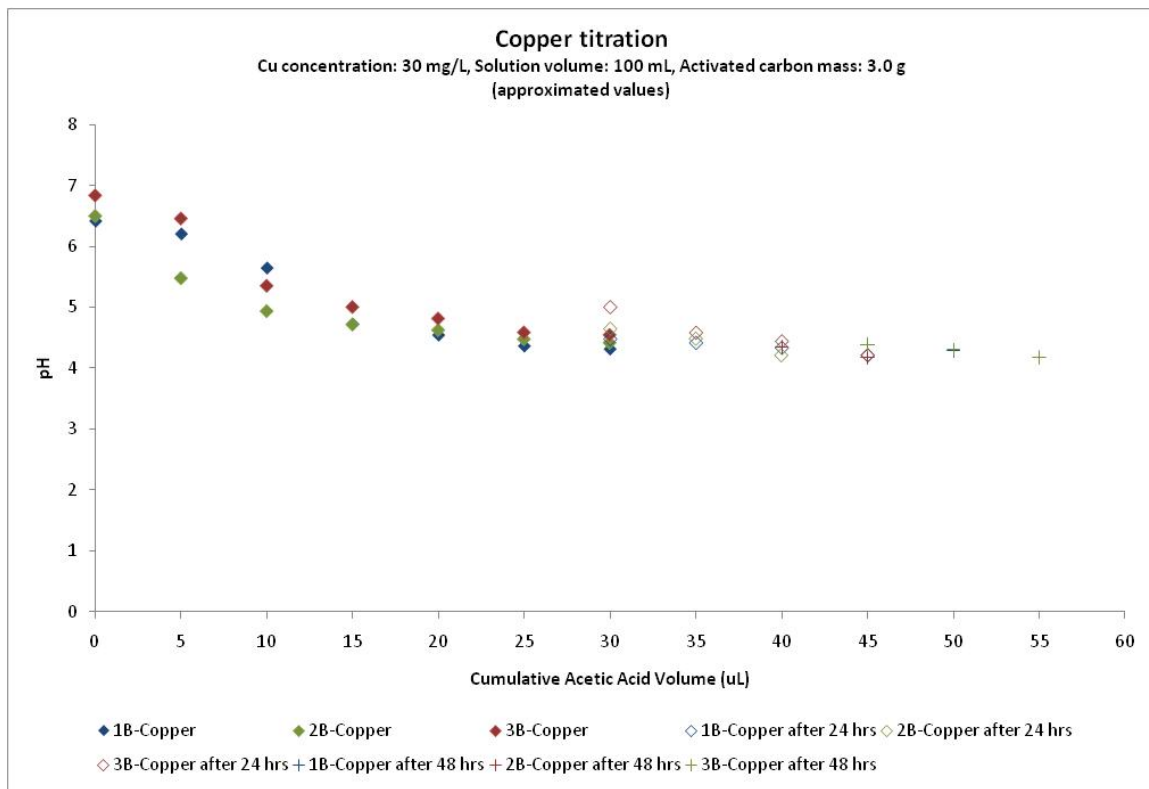


Figure 4.6 Copper solution titration curve – pH vs. Volume of 17.5M acetic acid added (Cu concentration: 30 mg/L, initial solution volume: 100 mL, activated carbon mass: 3.0g)

For comparison, a second titration test was conducted by titrating 100 mL of DDI water containing 3.0 g of activated carbon with acetic acid every 24 hours over a 48 hr

period in order to keep the pH near the pKa of acetic acid (4.75). Figure 4.7 shows the results obtained through the DDI water titration test. The pH of the solution is fairly constant and near 4.75 upon the addition of 35  $\mu\text{L}$  of acetic acid, which results in an acetic acid concentration of 0.006M. An average of 55  $\mu\text{L}$  of acetic acid were added to the solution after 48 hrs in order to reduce the pH to approximately 4.59, thus resulting in an acetic acid concentration of approximately 0.010 M. The coefficient of variation was evaluated between replicates of the DDI water titration test. The pH measurements obtained for each acetic acid volume addition were not variable since the coefficient of variation was smaller than 0.06, which suggest that the carbon-solution response to the acetic acid addition was consistent. Also, the data trend shown in Figure 4.7 is very similar for the three replicates.

Given the inconsistency observed in the pH for the preliminary batch sorption test as compared to the pH of the copper titration test, determining the impact on the sorption behavior and pH using different buffer strengths was obviously important. A sorption test was conducted separately on four Cu solutions with different acetic acid buffer strengths including 0.002 M, 0.02 M, 0.2 M and 0.009 M (Cu solution titrated with acetic acid from aforementioned test). The solutions had a Cu concentration of 30 mg/L and contained 3.0 g of activated carbon in 100 mL of solution. The pH of the samples was measured upon the completion of the test (at t=48 hrs). The mean sorption capacity and removal percentage were obtained for each buffer strength to assess the impact of increasing buffer strength on sorption behavior.



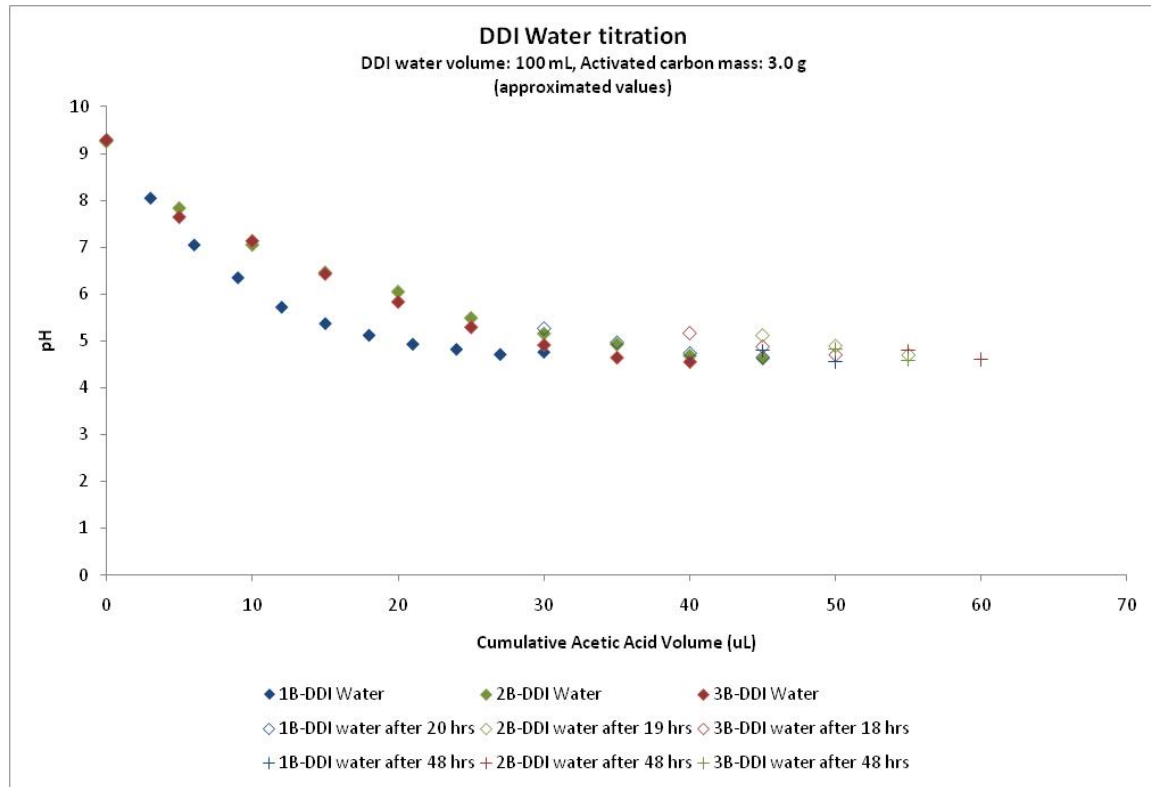


Figure 4.7 DDI water titration curve – pH vs. Volume of acetic acid added (DDI water volume: 100 mL, activated carbon mass: 3.0g)

The results obtained, shown in Table 4.1, demonstrate that the mean sorption capacity and the removal percentage are not impacted significantly by the acetic acid concentration. The coefficient of variation was evaluated between the capacities and removal percentages obtained for the different buffer strength, resulting in 0.11 and 0.024 respectively. For the different acid buffer strengths, the sorption capacity was near 1 mg/g and the contaminant removal percentage was greater than 95%. The results also show that the pH was significantly affected by the buffer strength.

Table 4.1 Batch sorption tests with different buffer strengths results

Mean acetic acid concentration (M)	Mean sorption capacity (mg/g)	Mean removal percentage	Mean final pH
0.002	1.14	99.9	6.14
0.02	0.98	99.5	5.27
0.2	0.87	95.5	4.72
0.009 (titrated solution)	0.92	95.7	4.22

The weaker buffered solutions (0.002 M and 0.02 M) resulted in a final pH higher than 4.75, whereas, the strongest buffered solution (0.2 M) resulted in a final pH of 4.72, very near the target pH of 4.75. The Cu titrated solutions behaved differently than the buffered solutions; the final pH averaged 4.22, which was lower than the final pH for the other acid buffer strengths. Also, the removal percentage for the titrated solution was inconsistent with that obtained for the other buffer strengths, being comparable to that achieved with the 0.2M buffer, rather than lying somewhere in between the results obtained for the 0.02 M and 0.002 M buffers. This difference could be attributed to the periodic addition of acetic acid over a 48 hrs period as compared to adding the needed volume of acetic acid initially as was done for the other buffer strengths. This difference could also be attributed to variability in the carbon physical and chemical properties which may result in differences in the required buffer strength.

The results of the copper titration test were disregarded because of the observed inconsistencies. Also, the manner in which the solutions with the other buffer strengths (0.002 M, 0.02 M, and 0.2 M) were prepared is more representative of the solution preparation process. The mean sorption capacity and removal percentage slightly increased as the acetic acid concentration decreased, which suggests that Cu precipitation might be occurring at lower buffer concentrations. However, the differences between the capacity and removal percentage obtained for the different buffer strengths did not appear

to be appreciable as evidenced by the coefficient of variation (0.11 and 0.024). Therefore, a buffer with an acetic acid concentration of 0.2 M was selected for the remaining batch testing in order to maintain a constant pH and prevent precipitation of the metals.

#### 4.2.2 Activated Carbon

The activated carbon batch sorption tests were conducted for each metal and organic contaminant by varying the dose of activated carbon and using a fixed contaminant concentration and solution volume. The samples were shaken for 48 hrs (which was previously determined sufficient for equilibrium to be reached), filtered, and submitted for chemical analysis. The initial concentration was measured for each contaminant as well as the equilibrium concentration for each carbon dosage. The collected data was used to estimate the activated carbon sorption capacity and the contaminant removal percentage. Langmuir and Freundlich adsorption isotherms were developed from the sorption capacity and equilibrium concentrations for each metal and organic contaminant to determine which model provided the best fit. However, the Freundlich adsorption isotherm is expected to show a better representation of the collected data given the test conditions and the pore structure of the GAC. The Freundlich model encompasses the heterogeneity of the activated carbon surface and the exponential distribution of adsorption sites and their energies (Faust and Aly 1987). The Langmuir adsorption isotherm is generated by plotting the inverse of the activated carbon sorption capacity ( $M/X$ ) against the inverse of the equilibrium concentration ( $1/C_e$ ). The following general expression is the linear form of the Langmuir equation, where  $1/X_m$  is the intercept of the line and  $1/(b*X_m)$  is the slope of the line:

$$\frac{M}{X} = \frac{1}{X_m} + \left(\frac{1}{C_e}\right) \left(\frac{1}{b * X_m}\right) \quad (4.3)$$

where,

$M/X$  = inverse of sorption capacity

$1/C_e$  = inverse of equilibrium concentration

$X_m$  = amount of contaminant adsorbed per unit weight of activated carbon required for monolayer coverage of the surface (monolayer capacity)

$b$  = constant related to the heat of adsorption

The Freundlich empirical equation is written in logarithmic form for linearization of the data. The Freundlich adsorption isotherm is obtained by plotting the logarithm of the sorption capacity ( $\log X/M$ ) against the logarithm of the equilibrium concentration ( $\log C_e$ ). Equation 4-4 shows the logarithmic expression, where  $\log K$  is the intercept at  $\log C_e = 0$  ( $C_e = 1$ ), and  $1/n$  is the slope of the line:

$$\log \frac{X}{M} = \log K + \frac{1}{n} \log C_e \quad (4.4)$$

where,

$X/M$  = sorption capacity

$C_e$  = equilibrium concentration

$K$  and  $1/n$  = constants characteristic of the system

A linear form of the Freundlich isotherm could be obtained by plotting the data on log-log paper; alternatively, the data can be linearized by taking the log of Freundlich's empirical equation, as was done here. Appendix B shows the activated carbon batch sorption test data, the evaluated statistical parameters (mean, standard deviation and coefficient of variation), and the Freundlich and Langmuir adsorption isotherm models

for each of the tested metals and organics. A summary of the results obtained for the metal and organic contaminants is presented below.

#### 4.2.2.1 Metals

The Langmuir and Freundlich adsorption isotherm models were developed for each of the tested metals in order to obtain the isotherm constants and determine which model represents better the data trend. Both models represent a good fit for all the tested metals. The regression coefficient of determination was statistically significant ( $R^2 > 0.8$ ) for all metals except silver for which an  $R^2$  of 0.76 was obtained for the Freundlich model (See Table 4.2). Based on the coefficient of determination, Cu and Pb are best represented by Freundlich, and Cr VI, Hg and Ag are best represented by Langmuir (see Table 4.2). Figures 4.8 and 4.9 show the Langmuir and Freundlich adsorption isotherms developed for copper. The Langmuir and Freundlich isotherm models developed for the other metals are shown in Appendix B. The constants obtained from each model for each contaminant are shown in Table 4.2. Figure 4.10 shows a plot of the Cu removal percentage as a function of the activated carbon mass, where it can be seen that the contaminant removal percentage is greater than 99% if more than 2.0 g of carbon are added to the batch system. The relationship between the contaminant removal percentage and activated carbon mass was logarithmic for all the tested contaminants. Similarly, removal percentages greater than 90% resulted from the Cr VI and Hg batch systems with a carbon mass greater than 2.0 g, and from the Pb batch system with a carbon mass greater than 1.0 g. For silver, the maximum removal percentage that was obtained for the batch system was approximated to 68%.

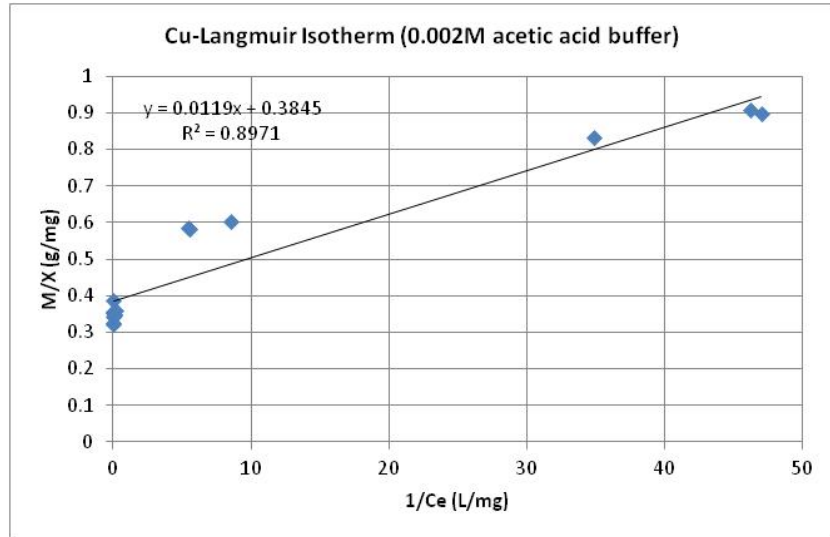


Figure 4.8 Cu - Langmuir isotherm for activated carbon batch sorption test (0.002 M acetic acid buffer concentration)

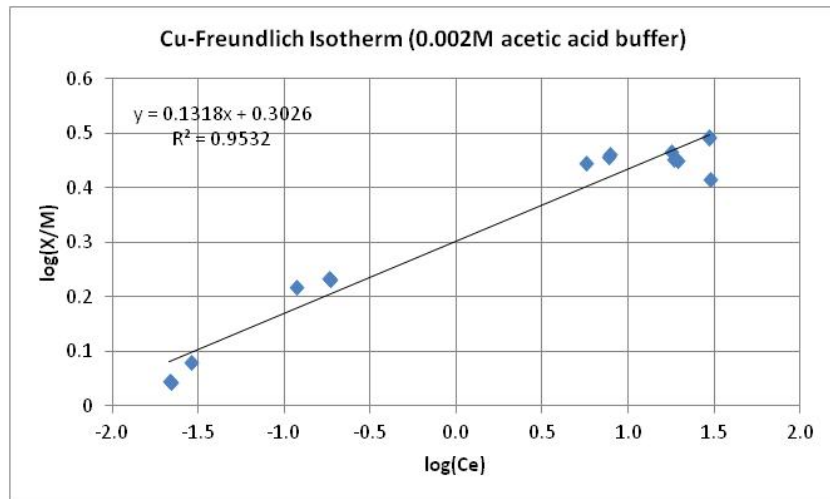


Figure 4.9 Cu - Freundlich isotherm for activated carbon batch sorption test (0.002 M acetic acid buffer concentration)

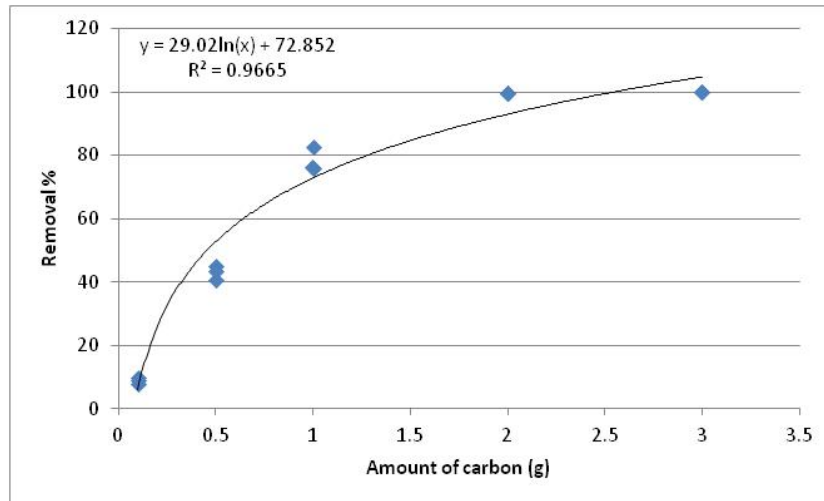


Figure 4.10 Cu - Contaminant removal percentage vs. amount of carbon plot for activated carbon batch sorption test (0.002 M acetic acid buffer concentration)

The initial and equilibrium concentrations obtained for each metal evidence very little analytical variability as reflected by the coefficient of variation for the analytical triplicates, which was much smaller than 0.1. The procedural replicates of the data and results (solution volume, amount of carbon, equilibrium concentration, pH, sorption capacity, removal percentage), also showed very little variability, having a coefficient of variation much smaller than 0.1, with some exceptions. The highest coefficient of variation obtained was around 0.3, however, this is considered acceptable for data quality objectives (Acevedo and Estes 2011). The final pH of the Cu and Pb sorption tests conducted with 1.0 g, 2.0 g and 3.0 g of carbon was not consistent and was greater than 4.75 (as high as 7.38), due to the weak buffer utilized (0.002 M acetic acid buffer) for these batch sorption studies. However, the isotherm data showed a measurable linear trend with a direct relationship and significant regression coefficients of determination.

Table 4.2 Langmuir and Freundlich isotherm constants obtained for the metals (activated carbon batch sorption tests)

Contaminant	Acetic acid buffer concentration	Langmuir Isotherm					Freundlich Isotherm				
		$1/X_m$	$1/(b \cdot X_m)$	Coefficient of determination ( $R^2$ )	$X_m$	B	log K	$1/n$	Coefficient of determination ( $R^2$ )	K	n
Copper	0.002 M	0.3845	0.0119	0.8971	2.6008	0.004576	0.3026	0.1318	0.9532	2.007	7.587
Chromium VI	0.2 M	1.3456	1.3572	0.9683	0.7432	1.8262	-0.428	0.7178	0.9379	0.373	1.393
Lead	0.002 M	0.2703	0.0022	0.9465	3.6996	0.0005947	0.4613	0.143	0.9513	2.893	6.993
Mercury	0.2 M	0.2501	0.9985	0.9304	3.9984	0.2497	-0.116	1.0457	0.9221	0.77	0.956
Silver	0.2 M	-69.03	37.45	0.9214	-0.01449	-2585	1.2861	6.4616	0.7633	19.32	0.1548



A batch sorption test was conducted using an acetic acid buffer of 0.002 M for Ag as well. A trend could not be established for the data obtained through this test; the coefficient of determination obtained from the adsorption isotherms was not significant ( $R^2 < 0.8$ ). Also, the pH was not consistent and was greater than 4.75 for the samples containing an activated carbon mass of 1.0 g, 2.0 g, and 3.0 g. Therefore, the Ag test was re-run with an acetic acid buffer concentration of 0.2 M, which was also used for the Cr VI and Hg tests, in order to achieve better control of the pH. The Pb and Cu tests were not re-run because the isotherm data showed a linear relationship. Even at the increased pH observed for the Cu and Pb 0.002 M buffered batch sorption tests, the differences in the amount of contaminant sorbed did not appear to be appreciable for the different buffer strengths as evidenced by the results obtained through the buffer strengths test (see Table 4.1). Given the pH changes observed with 1.0 g, 2.0 g and 3.0 g of carbon, precipitation may have been responsible for some removal, but the percentage that could be attributed to this removal mechanism was relatively small (~ 4%).

Very little variability was observed in the procedural replicates of the data and results (solution volume, amount of carbon, equilibrium concentration, pH, sorption capacity, removal percentage) obtained for the metals that were buffered with 0.2 M acetic acid. However, the initial concentrations obtained for Cr VI, Hg and Ag were smaller than the target initial concentrations. Issues with the instrument were encountered when analyzing the Cr VI and Ag samples. The samples were analyzed in the same batch; therefore, the problem was reflected in each analyzed sample, but did not appear to affect the data trends and contaminant sorption behavior. The low initial solution concentration obtained for mercury could possibly be attributed to volatilization losses, but also did not appear to affect the data trends. Although the initial concentration was lower than

anticipated, this would not have affected the relative measurements obtained from the sorption tests.

#### 4.2.2.2 Organics (DOC, Aroclor 1016)

Adsorption isotherms, including Langmuir and Freundlich, were also developed for DOC and Aroclor 1016 in order to obtain the isotherm constants and determine which model shows a better representation of the data trend. The Freundlich model represents better the sorption behavior of Aroclor 1016; the coefficient of determination obtained was statistically significant ( $R^2 > 0.8$ ). The  $R^2$  obtained from the Aroclor 1016 Langmuir model was 0.6185. Figures 4.11 and 4.12 show the Langmuir and Freundlich adsorption isotherm models developed for Aroclor 1016. Figure 4.13 shows the Aroclor 1016 removal percentage as a function of the carbon dosage, this plot shows a significant linear relationship with a removal percentage greater than 99% for all the evaluated carbon dosages. The DOC data could not be fitted with any of the evaluated adsorption isotherm models (Langmuir and Freundlich); no trend was discernible and the coefficient of determination was not significant.

Table 4.3 shows the isotherm constants obtained Aroclor 1016 as well as the models coefficient of determination. The DOC removal percentage was smaller than 31% for all the carbon dosages. The relationship between the DOC removal percentage and the activated carbon mass was not significant and no data trend was discernible. The DOC analytical variability was evaluated by estimating the coefficient of variation for the analytical replicates, which showed very little variability, having a coefficient of variation much smaller than 0.1 for all samples.

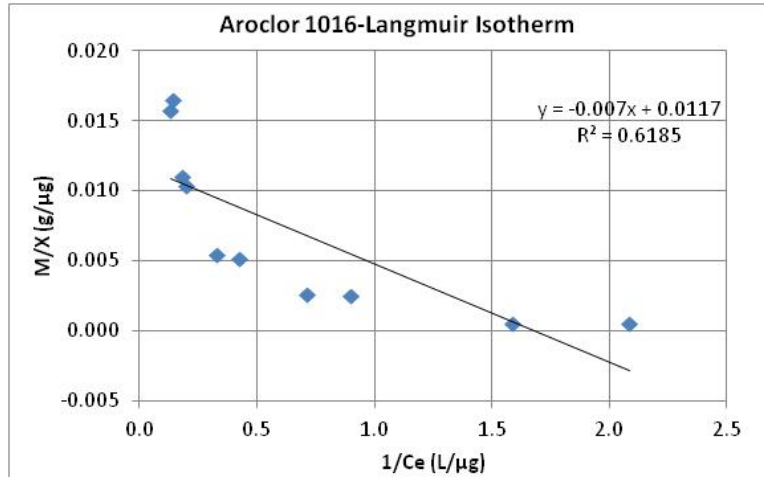


Figure 4.11 Aroclor 1016 - Langmuir isotherm for activated carbon batch sorption test

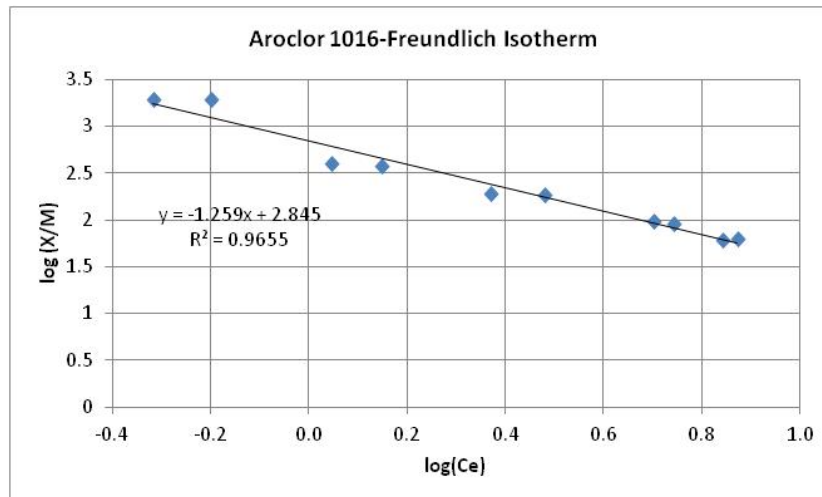


Figure 4.12 Aroclor 1016 - Freundlich isotherm for activated carbon batch sorption test

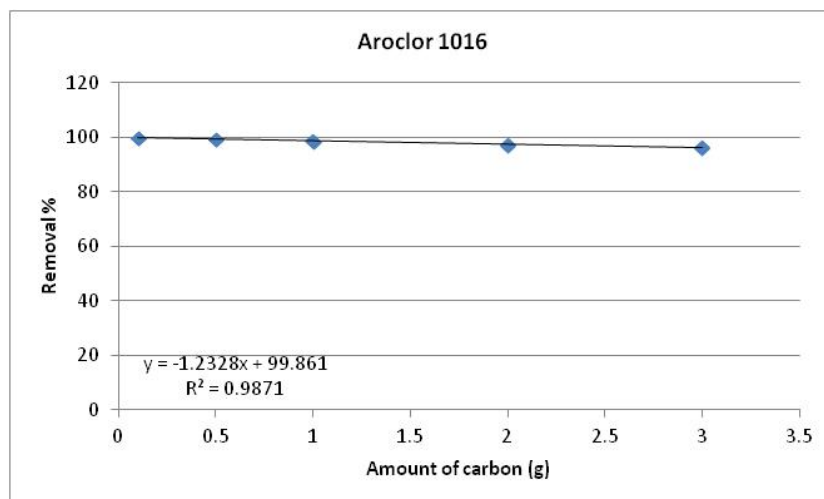


Figure 4.13 Aroclor 1016 - Contaminant removal percentage vs. amount of carbon plot for activated carbon batch sorption test

The analytical variability was not evaluated for the Aroclor 1016 samples because analytical replicates were not analyzed. Note that the final DOC concentrations for the samples containing 2.0 g and 3.0 g of activated carbon were higher than the initial solution concentration. This was attributed to fine carbon particles passing through the filter and increasing the DOC concentration in the filtrates. Therefore, a DDI water batch sorption test was conducted as a control; the sample concentrations for the DOC batch tests were corrected based on the DOC concentrations obtained for the DDI water batch sorption test.

The analytical variability of the corrected DOC concentrations was low, resulting in a coefficient of variation much smaller than 0.1. However, concentrations higher than the initial were observed for the samples associated with 3.0 g of activated carbon even after the correction in the DOC concentration was made. For most of the evaluated parameters (solution volume, amount of carbon, equilibrium concentration, pH, sorption capacity, removal percentage) there was very low procedural variability; resulting in a

coefficient of variation between replicates smaller than 0.3. Exceptions were the sorption capacity and removal percentages estimated for the samples associated with 2.0 g and 3.0 g of activated carbon for which a coefficient of variation greater than 0.3 was observed.

The initial concentration obtained for the Aroclor 1016 sample was smaller than the target initial concentration, suggesting either sample recovery issues, problems with the standard, or errors in making up the solution. The initial concentration (0.192  $\mu\text{g/L}$ ) was about 46% of the target initial concentration (0.42  $\mu\text{g/L}$ ). These differences could be attributed to the extraction process, analytical process, volatilization, sorption to the containers and equipment, or incomplete dilution of the standard in the water. Although the initial concentration was lower than anticipated, this would not have affected the relative measurements obtained from the sorption tests. For most of the evaluated parameters and estimated results (solution volume, amount of carbon, equilibrium concentration, pH, sorption capacity, removal percentage), the coefficient of variation estimated between replicates was much smaller than 0.1, suggesting that procedural variability of the Aroclor 1016 batch sorption tests was very small. A few parameters showed a coefficient of variation ranging from 0.1 to 0.3, which is still within an acceptable range to meet typical data quality objectives.

Table 4.3 Langmuir and Freundlich isotherm constants obtained for the organics (activated carbon batch sorption tests)

Contaminant	Langmuir Isotherm				Freundlich Isotherm					
	$1/X_m$	$1/(b \cdot X_m)$	Coefficient of determination ( $R^2$ )	$X_m$	$b \cdot X_m$	log K	1/n	Coefficient of determination ( $R^2$ )	K	n
Aroclor 1016	0.0117	-0.007	0.6185	85.47	-0.00008	2.845	-1.259	0.9655	699.8	-0.7943

### 4.2.3 FilterMat™

Batch sorption tests were conducted for Cu, Cr VI, Pb, Ag, and DOC using pieces of FilterMat™. The tests were conducted by varying the number of fabric pieces added to the solution (equivalent to varying the carbon dosage) and using a fixed concentration and solution volume, and an acetic acid buffer strength of 0.2M. The samples were mixed for 48 hrs (which was previously determined sufficient for equilibrium to be reached), filtered, and submitted for chemical analysis. Both the initial and equilibrium contaminant concentration were obtained for each FilterMat™ dosage. The collected data was used to estimate the FilterMat™ sorption capacity and the contaminant removal percentage. The Langmuir and Freundlich isotherms were developed using the same approach and expressions that were discussed in section 4.2.2. Appendix C shows the FilterMat™ batch sorption test data, the evaluated statistical parameters (mean, standard deviation and coefficient of variation), and the Freundlich and Langmuir adsorption isotherm models for each tested metal and organic contaminant. A summary of the results obtained for the tested contaminants is presented below.

#### 4.2.3.1 Metals

The Langmuir and Freundlich adsorption isotherms were developed using the capacity and the equilibrium concentrations obtained through the FilterMat™ batch sorption test. For all the tested metals, both models show a good representation of the data trend, resulting in a significant coefficient of determination. Figures 4.14 and 4.15 show the Langmuir and Freundlich adsorption isotherms developed for copper. The Freundlich and Langmuir adsorption isotherm models developed for the other tested metals are shown in Appendix C. The isotherm constants and regression coefficients of determination for each model and tested contaminant are shown in Table 4.4. Based on

the coefficients of determination, the Freundlich model shows a better representation of the data obtained for CrVI and the Langmuir model shows a better representation for Cu, Pb and Ag.

Figure 4.16 shows a plot of the copper removal percentage as a function of the activated carbon mass contained in the pieces of fabric; the relationship between these two parameters is linear and statistically significant. Similarly, the relationship between the contaminant removal percentage and the activated carbon mass (contained in the FilteMat™) was linear and statistically significant for the other tested metals (Cr VI, Pb and Ag). Maximum removal percentages, obtained for approximately 0.41 g of activated carbon contained in the pieces of fabric, were approximated to 79%, 76%, 64% and 91% for Cu, Cr VI, Pb and Ag respectively. Analytical variability was very low, resulting in a coefficient of variation much smaller than 0.1.

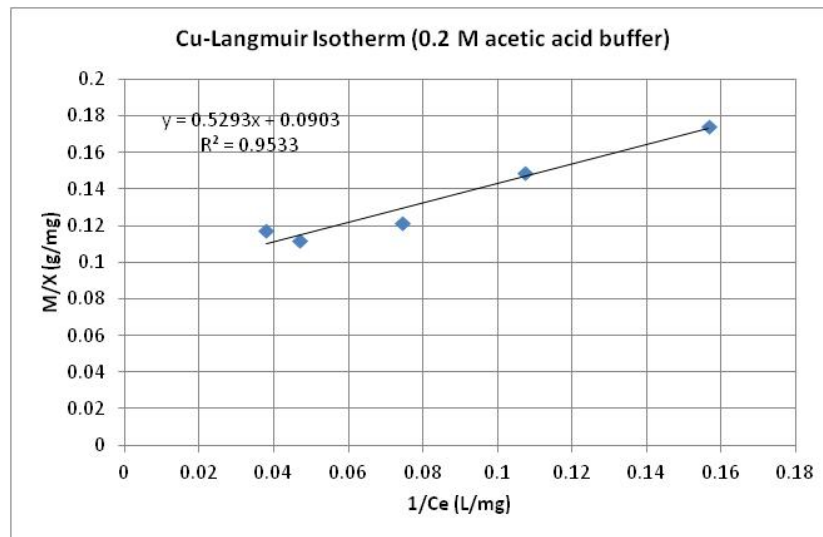


Figure 4.14 Cu - Langmuir isotherm for FilterMat™ batch sorption test (0.2 M acetic acid buffer concentration)



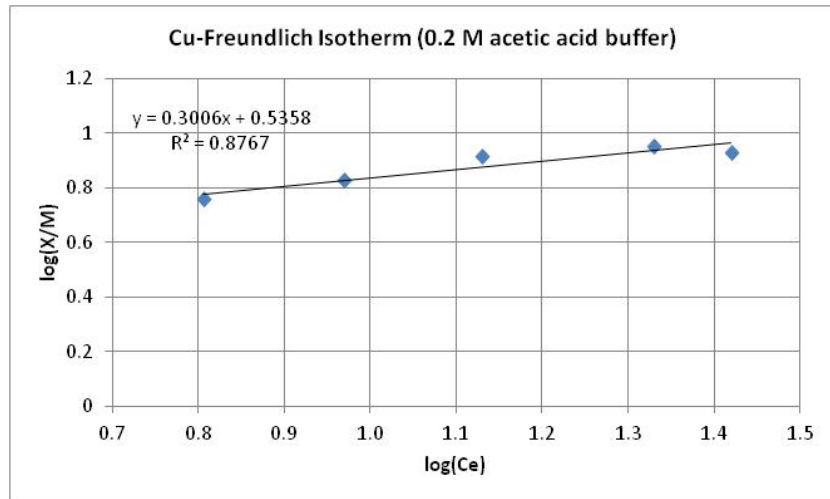


Figure 4.15 Cu - Freundlich isotherm for FilterMat™ batch sorption test (0.2 M acetic acid buffer concentration)

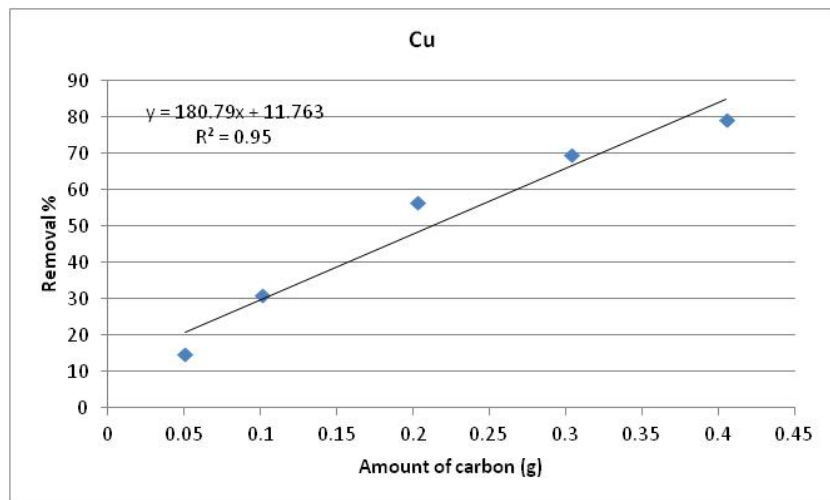


Figure 4.16 Cu - Contaminant removal percentage vs. amount of carbon plot for FilterMat™ batch sorption test (0.2 M acetic acid buffer concentration)

Table 4.4 Langmuir and Freundlich isotherm constants obtained for the metals (FilterMat™ batch sorption tests)

Contaminant	Acetic acid buffer concentration	Langmuir Isotherm				Freundlich Isotherm					
		$1/X_m$	$1/(b \cdot X_m)$	Coefficient of determination ( $R^2$ )	$X_m$	B	log K	$1/n$	Coefficient of determination ( $R^2$ )	K	n
Copper	0.2 M	0.0903	0.5293	0.9533	11.07	0.04780	0.5358	0.3006	0.8767	3.434	3.327
Chromium VI	0.2 M	0.182	1.0343	0.9385	5.495	0.1882	-0.076	0.7276	0.9521	0.840	1.374
Lead	0.2 M	0.0943	1.5617	0.9682	10.60	0.1473	0.0638	0.5387	0.946	1.158	1.856
Silver	0.2 M	-0.899	0.6856	0.9677	-1.112	-1	1.2906	2.9592	0.9557	19.53	0.3379

#### 4.2.3.2 Organics

The capacity and the equilibrium concentrations obtained through the FilterMat™ batch sorption test for DOC were used to develop the Langmuir and Freundlich isotherms. The data trend shown through these two models was not significant ( $R^2 < 0.8$ ) and did not show a discernible trend. Maximum removal percentage obtained for the DOC samples was associated with 0.30 g of activated carbon (amount of carbon contained in the pieces of fabric) and approximated to 26%. Similar to the batch sorption test conducted with activated carbon, the equilibrium concentrations were higher than the initial for the samples containing 0.05, 0.3 and 0.41 g of carbon. This was attributed to particulate carbon passing through the filter and being measured as DOC. Therefore, a batch sorption test was conducted using DDI water in order to verify this and to correct the equilibrium DOC concentrations.

The relationship between the carbon amount and the DOC equilibrium concentrations obtained through the DDI water batch sorption test increases linearly, supporting the assertion that fine carbon particles were passing through the filter and artificially increasing the final solution DOC concentration. Even after correcting for this factor, the concentration of the 0.05 g of activated carbon (1 piece of fabric) was still three times higher than the initial solution concentration. Therefore, this point was eliminated from the data analysis as a data outlier. Low analytical variability was observed in the corrected DOC concentrations, resulting in a coefficient of variation much smaller than 0.1.

#### 4.3 Column Studies

Column tests were conducted in order to evaluate the efficiency of the FilterMat™ in treating a synthetic effluent in a flow through regime. In a flow through regime,

contact time between adsorbate and adsorbent is expected to be much less than that required for establishing equilibrium, making performance difficult to predict on the basis of equilibrium batch testing. Studies were conducted for synthetic effluents containing copper and Aroclor 1016, in order to evaluate performance for a representative metal and organic contaminant from the previously identified constituents of concern. Through this study the expected life of the curtains was estimated. The exhaustion time (Cu column tests), breakthrough time (Aroclor 1016 column tests), and mass of contaminant absorbed by the FilterMat™ were obtained for each contaminant using the collected data, and the following parameters were estimated in order to enable the performance prediction of using multiple curtains in a flow through regime.

- Detention time ( $T_d$ ) for each curtain layer was estimated in order to determine how long the pieces of fabric are in contact with the synthetic solution. The following equation was used to estimate the detention time:

$$T_d = \frac{A_c * t_c * n_c * \varphi_c}{Q} \quad (4.5)$$

where,

$A_c$  = area of the curtain (7.94 cm<sup>2</sup>, 1.23 in.<sup>2</sup>)

$t_c$  = thickness of the curtain (~1.0 mm, ~0.4 in.)

$n_c$  = total number of curtains per module

$Q$  = flow rate

$\varphi_c$  = curtain porosity ( $V_v/V_T = 0.5$ )

- Overall removal percentage for each curtain layer in the column:

$$\text{Overall removal percentage} = \left[ \frac{(C_{inf} - C_{eff})}{C_{inf}} \right] * 100 \quad (4.6)$$

where,

$C_{inf}$  = column influent concentration (concentration entering the column, upstream of all curtain layers)

$C_{eff}$  = curtain layer effluent concentration (concentration at the sampling port downstream of a specific curtain layer)

- Relative removal percentage for each curtain layer (expressed as % of layer influent concentration)

$$\text{Relative removal percentage (as \% of } C_{inf,layer}) = \left[ \frac{(C_{inf,layer} - C_{eff})}{C_{inf,layer}} \right] * 100 \quad (4.7)$$

where,

$C_{inf,layer}$  = curtain layer influent concentration (concentration measured just upstream of each curtain layer, and equal to the previous layer effluent concentration)

- Column effluent concentration (expressed as % of column influent concentration)

$$\text{Effluent conc. (as \% of } C_{inf}) = \left[ \frac{C_{eff}}{C_{inf}} \right] * 100 \quad (4.8)$$

- Contaminant mass passing each curtain layer as a function of time:

$$M_{eff,layer} = Q * \int_{t_{i-1}}^{t_i} C_{eff}(t) dt \quad (4.9)$$

where,

$M_{eff,layer}$  = contaminant mass passing curtain layer effluent over a specified time interval

$Q$  = column flow rate

$C_{eff}(t)$  = effluent concentration as a function of time (expression obtained from column exhaustion curve ( $C_u$ ) or breakthrough curve (Aroclor 1016) for each curtain layer)

- Contaminant mass in column influent as a function of time:

$$M_{inf} = Q * C_{inf} * (\Delta t) \quad (4.10)$$

where,

$M_{inf}$  = contaminant mass entering column through influent over a specified time interval

$\Delta t$  = time interval

- Contaminant mass sorbed by each curtain layer as a function of time as reflected by concentrations measured at sampling ports upstream (influent port) and downstream (effluent port) of each curtain layer:

$$M_{sorbed,layer_i} = M_{inf,layer_i} - M_{eff,layer_i} \quad (4.11)$$

where,

$M_{sorbed,layer_i}$  = contaminant mass sorbed by curtain layer  $i$  (for a specified time interval)

$M_{inf,layer_i}$  = contaminant mass entering curtain layer through influent over a specified time interval ( $M_{inf}$  for port 1, and  $M_{eff\ i-1}$  for the remaining ports)

$M_{\text{eff,layer } i}$  = contaminant mass in curtain layer effluent over a specified time interval

- Cumulative mass sorbed by curtain layer:

$$M_{\text{cumulative,layer } i} = \sum_{t=0}^n M_{\text{sorbed,layer } i} \quad (4.12)$$

where,

$M_{\text{cumulative,layer } i}$  = cumulative contaminant mass sorbed by curtain layer  $i$

Figure 4.17 illustrates a schematic of a section of the column that shows the influent and effluent from port  $i$  also referred to as curtain layer  $i$  along the text. Note that curtain layer  $i$  may have a single fabric layer or multiple fabric layers together as shown in the figure. Appendix D shows the data obtained for the copper and Aroclor 1016 column tests. The results obtained through the column tests are summarized in the following sections.

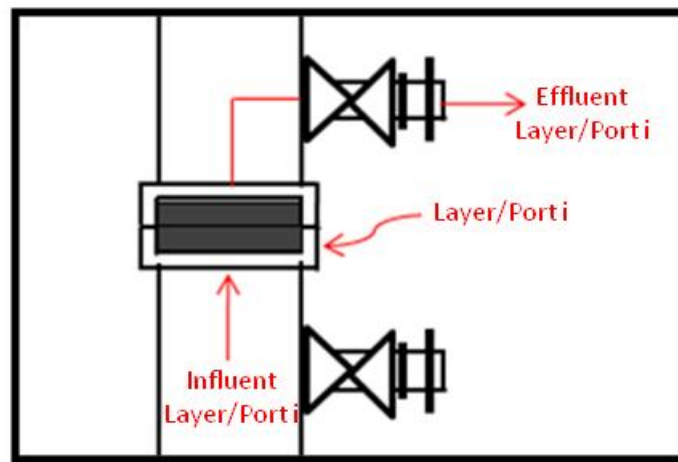


Figure 4.17 Column section showing influent and effluent from port/layer  $i$

### 4.3.1 Copper

Preliminary column tests demonstrated that a flow rate of 125 mL/min with two curtain layers between each sampling port provided sufficient detention time to achieve the required removal of copper from the synthetic effluent, for a period of time.

Preliminary tests were conducted to identify appropriate sampling intervals for definition of an exhaustion curve for Cu, and to evaluate operating conditions that would reduce contaminant concentrations below a specified threshold while achieving exhaustion in a reasonable period of time. No copper removal resulted from the first preliminary test for which a flow rate of 500 mL/min and a single piece of curtain were used, with a resulting detention time of approximately 0.48 seconds.

Detention time was therefore increased by decreasing the flow rate and adding a second single curtain to increase removal. For the second preliminary test, a single curtain was placed in two separate modules (in series) and a flow rate of 250 mL/min was used, which resulted in a detention time per curtain of 0.95 seconds and overall removal percentages smaller than 7.3%. A third and fourth preliminary test was conducted using double curtains in two separate modules (in series) and a flow rate of 125 mL/min, resulting in a detention time for each double curtain of 3.80 seconds. Overall copper removal percentage ranged from 34% to 89% with the FilterMat™ 400 and from 0.5% to 11.7% with the FilterMat™ 800 (which contains a higher mass of carbon than FilterMat™ 400, but of larger particle size).

This information was crucial for the design of the final column tests for which a flow rate of 125 mL/min was selected. Double FilterMat™ 400 curtains in 3 modules were used, in order to reduce the Cu concentration (300 µg/L) to a level below the lowest allowable concentration (33.9 µg/L) (see Table 1.1 in Chapter I). The column system and



the individual curtain layer capacities were initially estimated using the maximum capacity obtained from the batch sorption tests, expressed in terms of the total contaminant mass sorbed.

The column capacity predicted using the results from the activated carbon batch sorption tests corresponded more closely than the results from the FilterMat™ batch sorption tests, although observed capacity was lower in the column than predicted for all ports and all configurations, with the exception of the layers located in port 2-columns 5 and 6 (see Table 4.6). The copper effluent concentration obtained for each layer as a function of time was generally higher than predicted (see Figure 4.18, data obtained for column test 5). Exhaustion time occurred at approximately 146 minutes for column test 4, and was projected to occur at 198, and 183 minutes, for column tests 5 and 6 respectively.

Figure 4.19 shows the cumulative Cu mass sorbed by the pieces of fabric as a function of time obtained for column test 5, this plot includes the cumulative Cu mass sorbed by each layer and by the system, cumulative Cu mass in the influent, and the layers and system predicted capacity. This plot clearly shows that the predicted capacities were higher than the observed capacities for both the individual curtain layers and for the column as a whole. The column systems 4, 5, and 6 sorbed about 37%, 48%, and 53% of the total Cu mass that was input into the system. For about 20 minutes, the three column systems maintained effluent concentration levels below the allowable concentration.

As expected, the overall copper removal percentage and relative copper removal percentage (expressed as % of curtain layer influent) show an inverse relationship with time, decreasing as time increases. The effluent concentration (expressed as % of influent) increases as time increases and shows a similar behavior to the exhaustion

curves. The column influent and effluent concentrations measured for the three column tests show little variability resulting in a coefficient of variation generally smaller than 0.3 for each time interval and port. Similarly, the cumulative mass sorbed for each time interval and curtain layer calculated for the three column tests showed very little variability, with a resulting coefficient of variation always smaller than 0.3.

The data obtained from the three final column tests was compared by plotting the exhaustion curves and the cumulative mass sorbed (by layer) as a function of time for each column test in the same series (Figures 4.20 and 4.21). A plot of the copper mass sorbed as a function of time suggests that desorption of Cu occurred from the pieces of fabric located in port 1 of column 4, at 110 minutes, ports 2 and 3 of column 4 at 160 minutes, and port 3 of column 5 at 170 minutes. Note that some of the data had to be interpolated for comparison purposes since samples from ports and columns were not taken at the same time. The data interpolation did not affect the outcome of this comparison, very little variability was observed in the interpolated data as reflected by the coefficient of variation evaluated between replicates.

Table 4.5 Observed capacities as a percentage of predicted capacities

Column Test number	Port Capacity (as % of curtain layer predicted capacity)			System Capacity (as % of system predicted capacity)
	1	2	3	
4	28.0%	61.4%	29.4%	39.6%
5	46.6%	100%	22.7%	57.4%
6	49.4%	100%	36.4%	62.7%

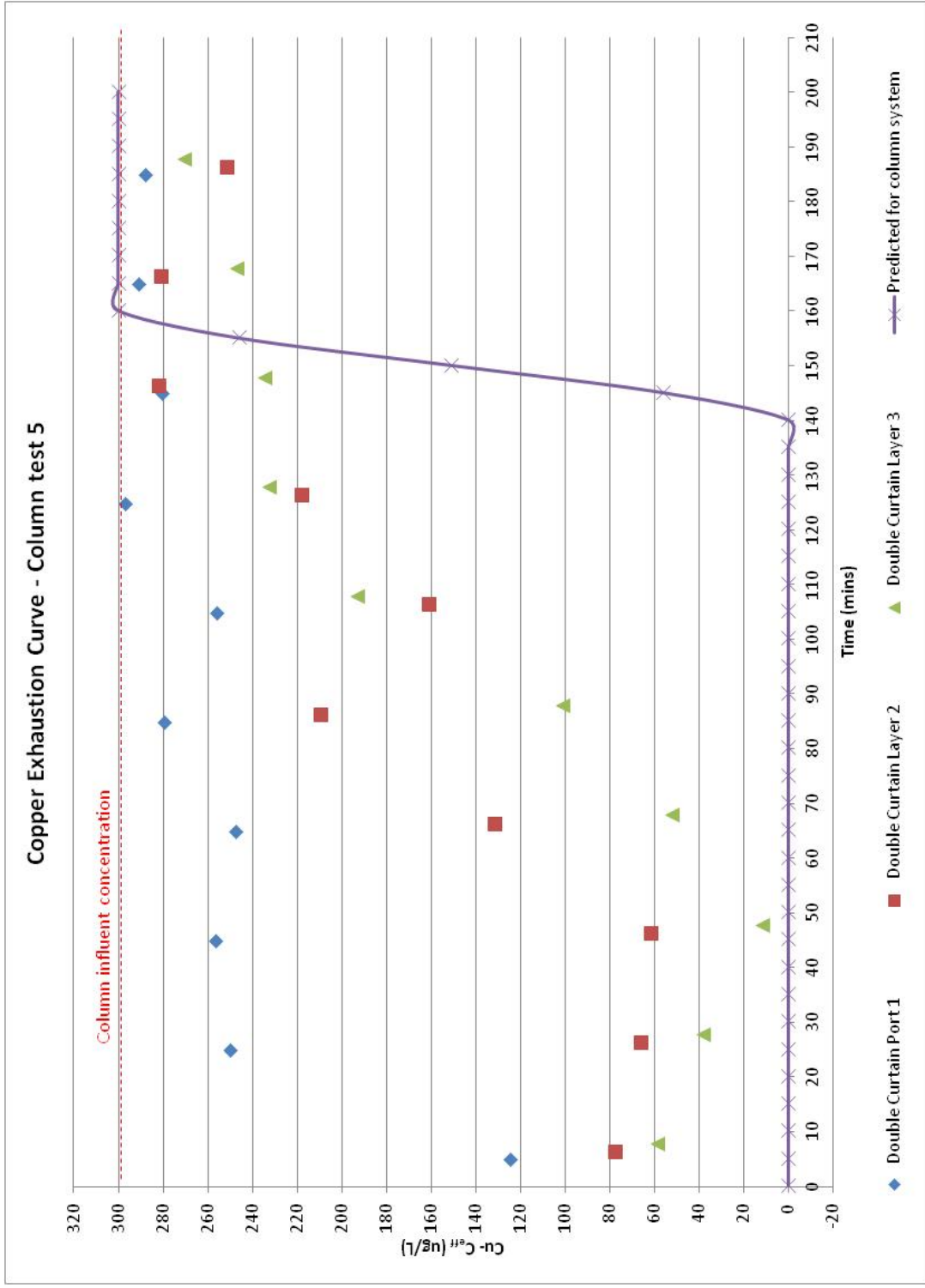


Figure 4.18 Cu column test 5 - Effluent concentration as a function of time (exhaustion curve)

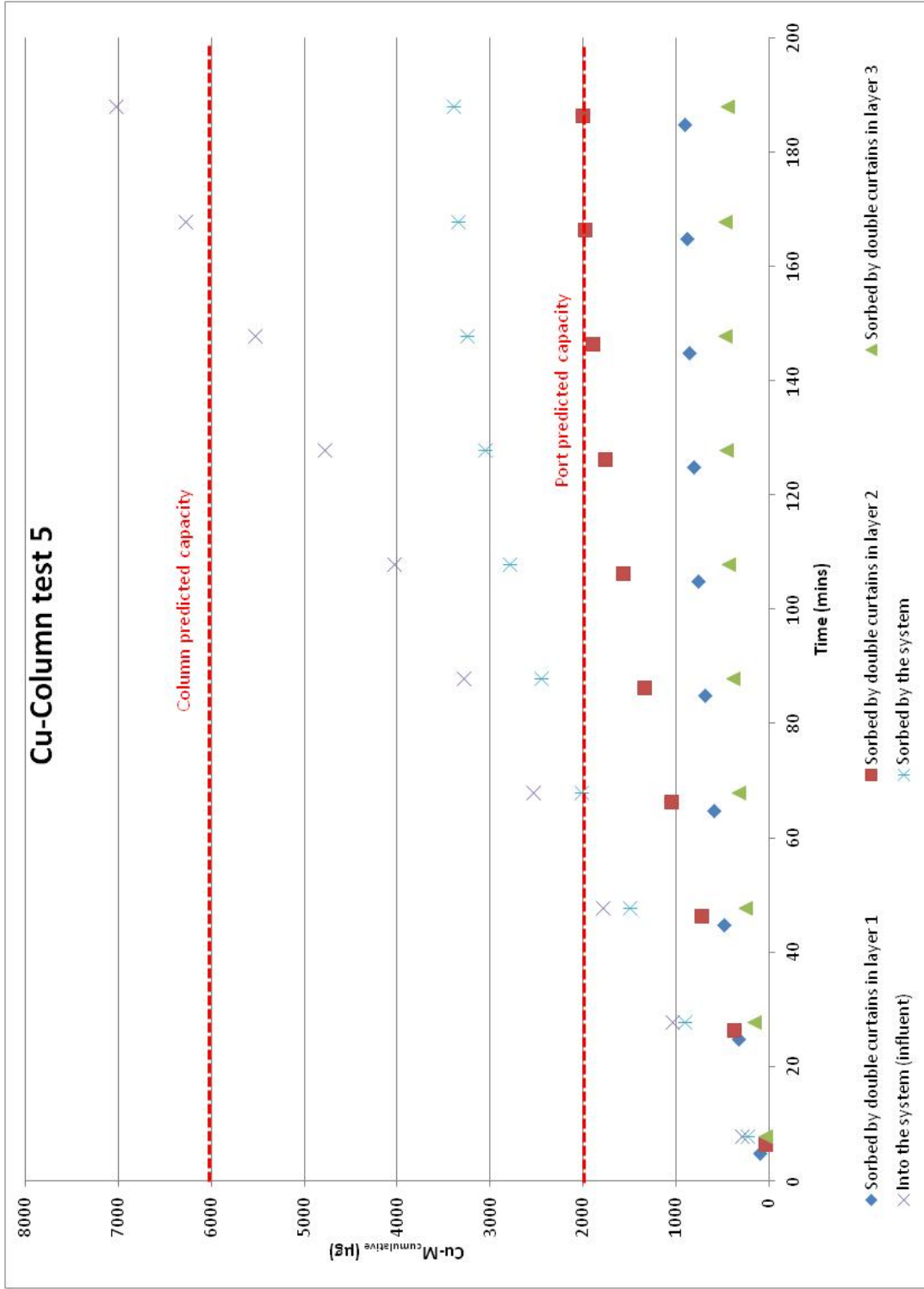


Figure 4.19 Cu column test 5 - Cumulative copper mass sorbed as a function of time

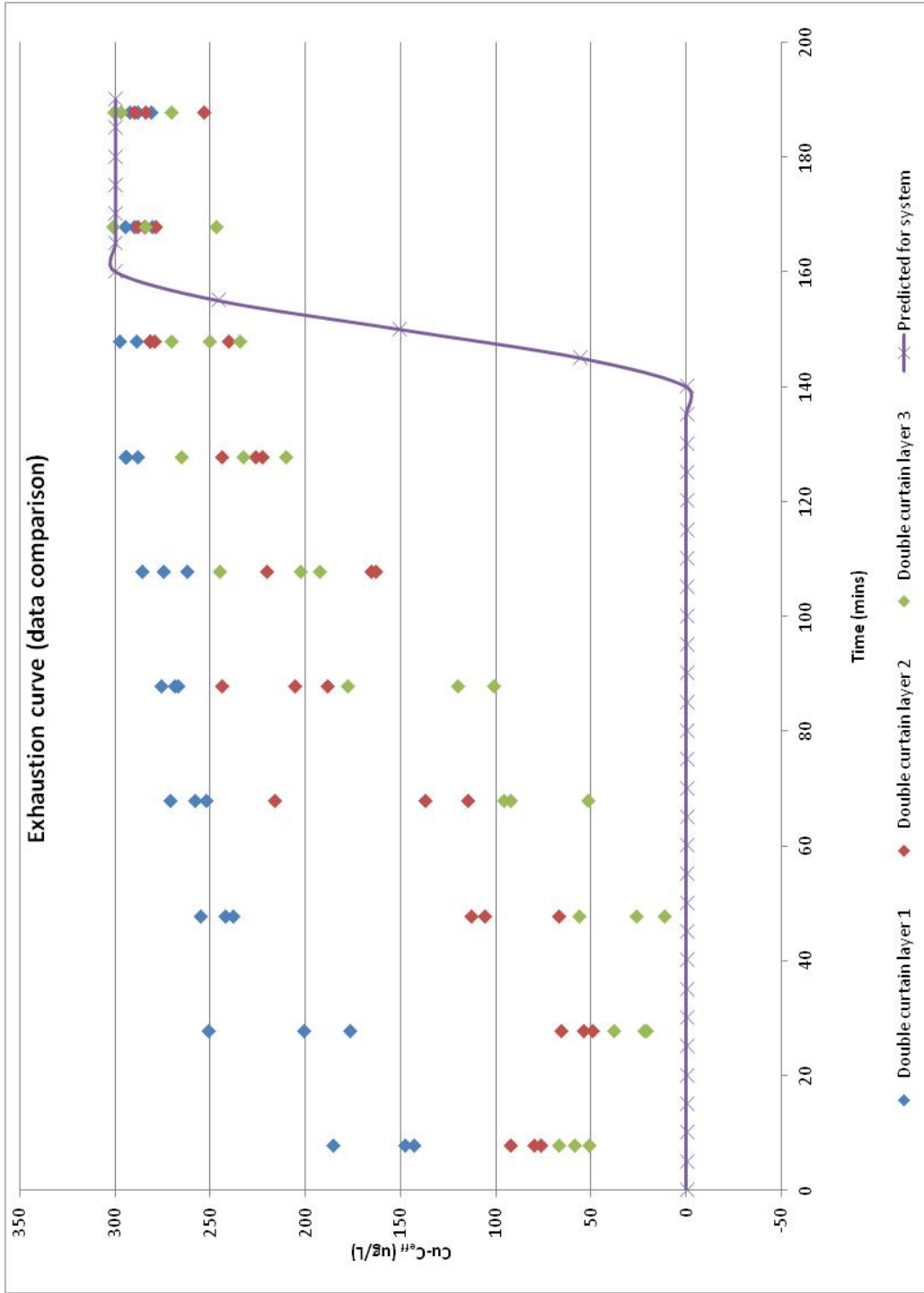


Figure 4.20 Replicate data comparison for column tests 4, 5 and 6 - Effluent concentration as a function of time (exhaustion curve)

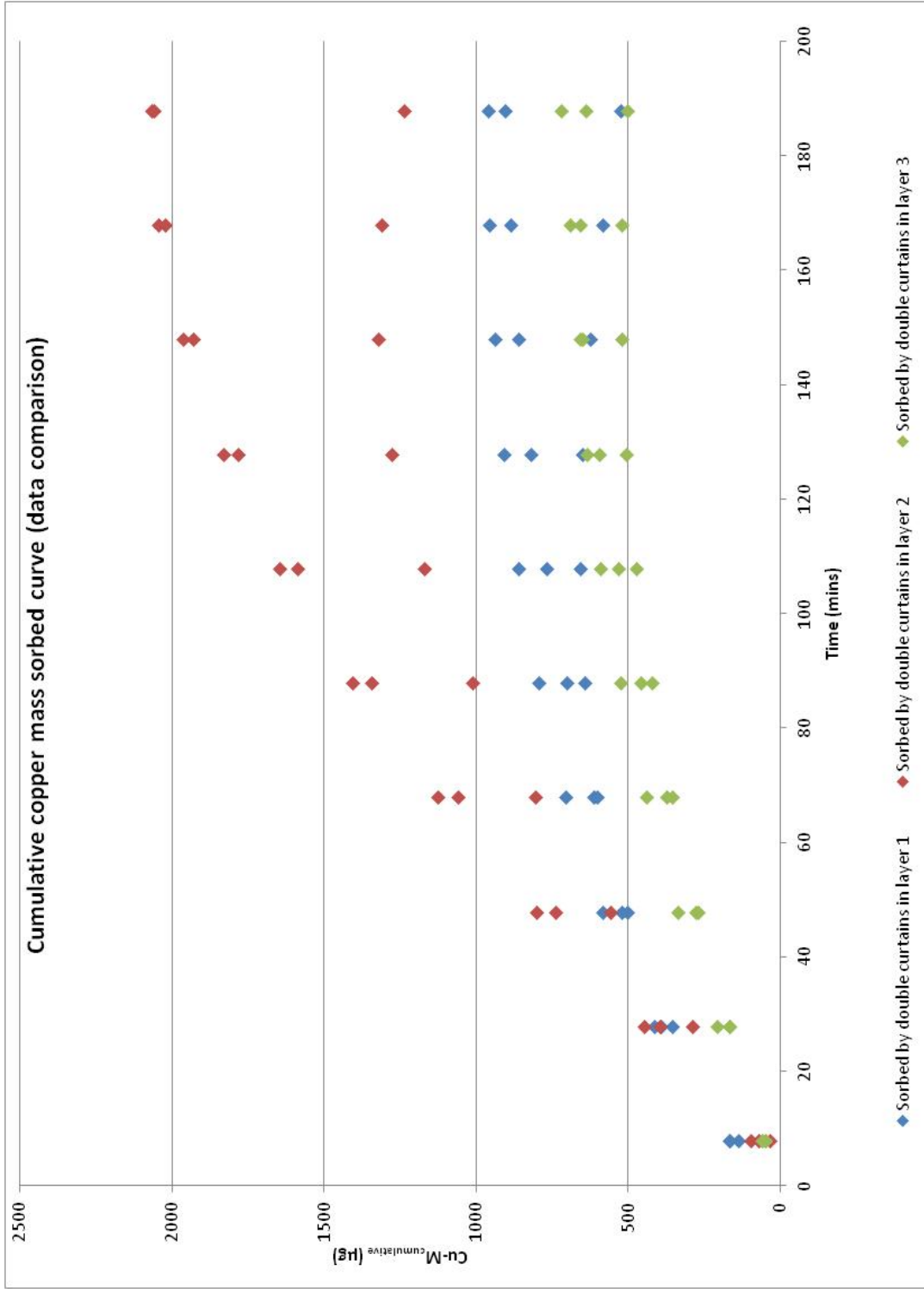


Figure 4.21 Replicate data comparison for column tests 4, 5 and 6 - Cumulative copper mass sorbed as a function of time

### 4.3.2 Aroclor 1016

Based on the results obtained from the preliminary Cu column tests, a flow rate of 125 mL/min and one curtain were used for the preliminary test to treat a synthetic solution with an Aroclor 1016 concentration of approximately 0.82 µg/L. This results in a detention time of 1.90 seconds. Exhaustion time for Aroclor 1016 (defined as the time when the effluent concentration is approximately equal to the influent concentration) was expected to occur at approximately 90 hrs, based on the activated carbon sorption capacity determined from the batch testing and the column setup. Exhaustion was not achieved in 90 hours however, and the observed data trend suggested that exhaustion would not occur until around 8 days; therefore, the test approach was changed to be able to obtain relevant data within a shorter timeframe. Running a column test for 8 days would require an impractical volume of the synthetic solution.

The final column test approach consisted of changing the Aroclor 1016 concentration to a level predicted to achieve breakthrough within 2.5 days. The prediction was based on the results obtained from the first Aroclor 1016 column test. The test objectives were also modified to determine the time that the most conservative water quality criteria would be exceeded (breakthrough), rather than exhaustion as previously defined for Cu. For the final column tests, an Aroclor 1016 concentration of approximately 0.1 µg/L was used, a flow rate of 125 mL/min, and double curtains were placed in 4 modules resulting in a detention time per layer of 3.80 seconds. Breakthrough was not achieved during the 2.5 day period that was used to run the final column tests (column tests 2-4), however. For column test 2, the effluent concentration levels at 2 and 2.5 days were 0.006 and 0.0037 µg/L, respectively, which results in a concentration reduction of approximately 90% for both time periods (see Table 4.6).

Table 4.6 Aroclor 1016 column test 2 data

Time (mins)	Influent Concentration ( $\mu\text{g/L}$ )	Effluent Concentration ( $\mu\text{g/L}$ )	Overall Removal %	Effluent concentration (as % of column influent)
10	0.093	0	100	0
720	0.081	0	100	0
1440	0.095	0	100	0
2160	0.095	0	100	0
2880	0.059	0.006	89.8	10.2
3600	0.044	0.0037	91.6	8.4

Figure 4.22 shows the Aroclor 1016 influent and effluent concentrations measured for column tests 2 as a function of time. The Aroclor 1016 overall removal percentage obtained by comparison of the influent and effluent concentrations (see Equation 4.6) of column system 2 as a function of time is shown in Figure 4.23. Note that the influent concentration was also quite variable and that is why both time periods resulted in the same reduction percentage (see Table 4.6 and Figure 4.22). The reduction percentage required for reducing the target initial influent concentration from 0.1  $\mu\text{g/L}$  to an effluent concentration of 0.01  $\mu\text{g/L}$  was 90%, therefore the observed reduction was appropriate for the test objectives. However, though the operating parameters for column tests 3 and 4 were based on the success of column test 2, the effluent concentrations were non-detect during the 2.5 day period that was used to run column tests 3 and 4. Therefore, column test 3 was run for 3.5 additional days in order to determine the breakthrough time of the pieces of fabric. During this period of time the Aroclor 1016 concentration in the column effluent was not detected, therefore, the pieces of fabric were not exhausted. This phase of the study is being continued to achieve breakthrough of the column system. If



the column system is not exhausted during a reasonable period of time, the Aroclor 1016 will be extracted from each curtain layer to determine the amount of Aroclor 1016 that has been sorbed by each layer and which layers have been exhausted. This information could be used to extrapolate the breakthrough time of the column system and design an effective system for treatment of CDF effluent. Given the failure of the replicate Aroclor 1016 column tests to show breakthrough, the sorption capacity of the column system was recalculated based on the results of the the Aroclor 1016 batch sorption test, which results in a projected breakthrough time of 247 days. There is a significant difference between the two predictions that were made for the breakthrough time of the Aroclor 1016 column tests (2.5 days vs. 247 days). The prediction made based on the batch sorption capacity does not seem like a viable estimate because it is expected that the most favorable sorption sites are occupied in the flow-through regime and then no further sorption takes place as shown by the Cu column test results. However, a higher percentage of the column system capacity is expected to be utilized for Aroclor 1016 as compared to Cu. For the Aroclor 1016 column tests, the influent concentration was also quite variable, making mass balance difficult to develop. To estimate the total mass sorbed by the column system, the average of the influent concentration was therefore used as the baseline for the mass balance. For column test 2, approximately 94% of the contaminant mass passing through the column was sorbed over a period of 2.5 days.

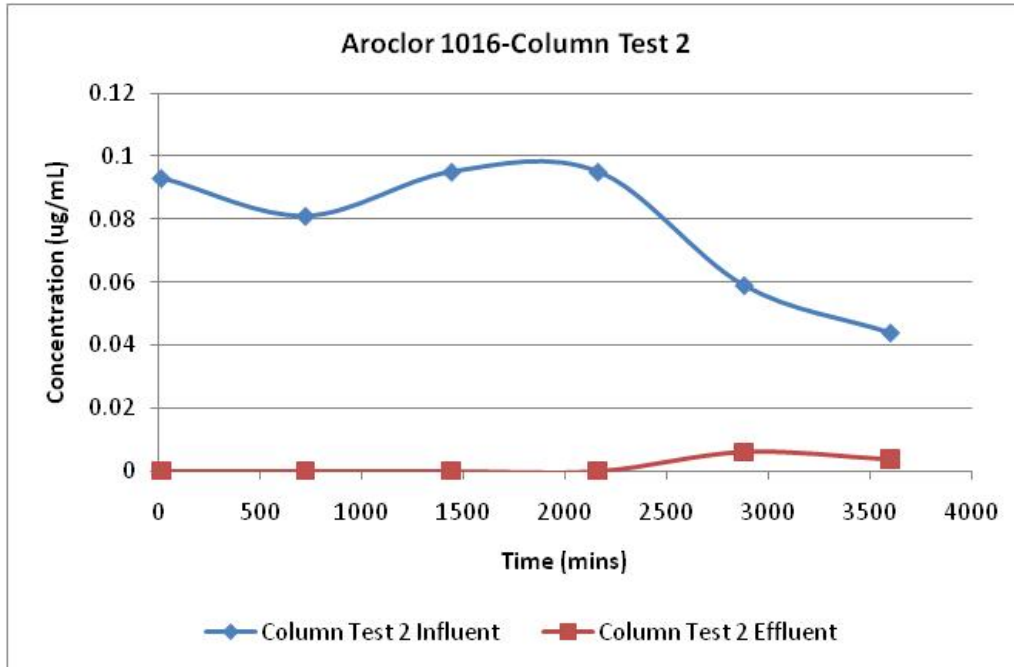


Figure 4.22 Aroclor 1016-Column Test 2: Concentration vs. Time

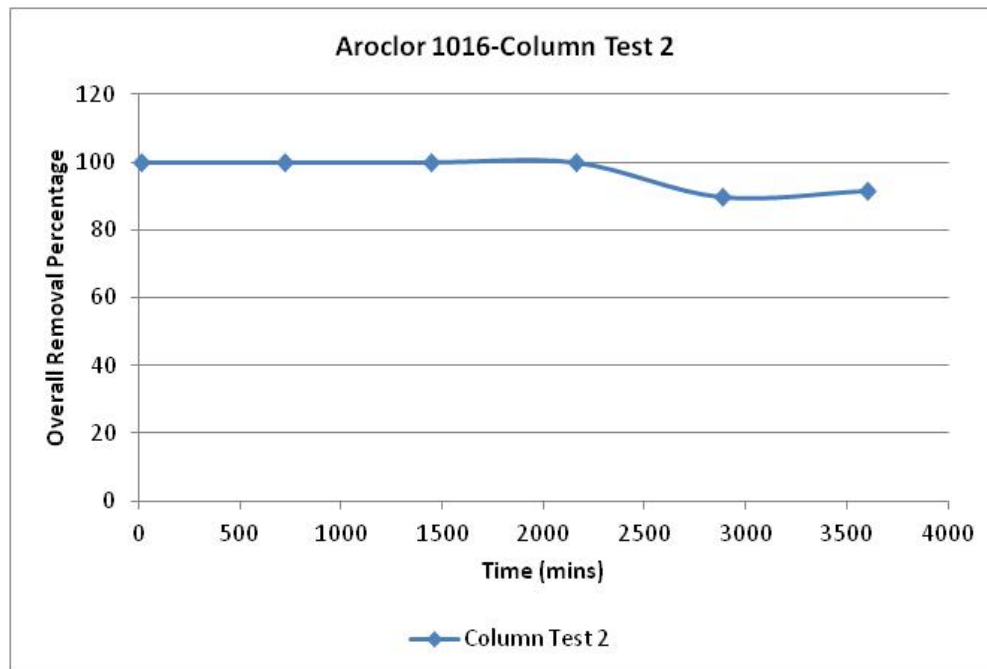


Figure 4.23 Aroclor 1016-Column Test 2: Overall removal percentage obtained by comparison of the influent and effluent concentrations (see Equation 4.6) of the column as a function of time

#### 4.4 Discussion

The objective of conducting the equilibrium studies was to determine the contact time considered to be sufficient to establish equilibrium between the activated carbon and the tested contaminants. This contact time was then selected to conduct the batch sorption studies. A contact time of 48 hrs appeared to be sufficient to reach equilibrium state for all the contaminants. This value was considered relatively conservative given the equilibrium times reported in the literature, which generally ranged from 105 minutes to 48 hours.

The Freundlich and Langmuir adsorption isotherms were developed using the data collected from the activated carbon and FilterMat™ batch sorption tests in order to determine which model best represented the data. The Freundlich model developed using the activated carbon batch sorption data best represents the sorption of Cu, Pb, and Aroclor 1016 (see Appendix B). The Langmuir model developed using the activated carbon batch sorption data best represents the sorption of CrVI, Hg, and Ag (see Appendix B). The coefficients of determination obtained from the Freundlich model were significant ( $R^2 > 0.8$ ) for all the tested constituents with the exception of DOC and Ag. The coefficients of determination obtained from the Langmuir model were significant ( $R^2 > 0.8$ ) for all the tested constituents except for DOC and Aroclor 1016. The isotherm constants obtained from the two models were different for each tested contaminant. Mercury showed the largest monolayer capacity ( $X_m$ ) followed by lead, copper, chromium VI, and silver. The monolayer capacity obtained for silver was not reasonable since a negative value was obtained. Therefore, the data does not show conformity to the ideal localized monolayer model.

The shape of the silver isotherm is characteristic of a type III isotherm, and not type I isotherm, which is represented through the Langmuir and Freundlich models (Brunauer et al. 1940). This suggests that multilayer adsorption might be occurring rather than monolayer adsorption. The BET isotherm is used to represent systems that show multilayer adsorption, however, it was not possible to develop this isotherm using the collected data because the model is not applicable to the adsorption of solutes from liquid solutions. The BET equation is useful for determining the surface areas from multilayer adsorption of activated carbon (Cooney 1994).

The largest Freundlich adsorption constant  $K$ , defined as the capacity when the equilibrium concentration is equal to 1, was obtained for Aroclor 1016, followed by lead, copper, mercury and chromium VI. For Aroclor 1016, the  $K$  value was three orders of magnitude larger than the  $K$  obtained for lead and copper; as expected; reflecting the higher affinity of the activated carbon for sorption of Aroclor 1016 as compared to the metals. Aroclor 1016 showed an inverse relationship between the sorption capacity and the equilibrium concentration, which resulted in a negative  $1/n$  (see Figure 4.12). The Aroclor 1016 Freundlich isotherm had a slope ( $1/n$ ) close to -1, which indicates high sorption capacity at low equilibrium concentrations that rapidly diminishes at higher equilibrium concentrations. A relatively similar Aroclor 1016 removal, ranged from 96.11 to 99.75, was observed for all the amounts of carbon that resulted in a reduction in the capacity as the amount of carbon increased. Chromium VI and mercury Freundlich isotherms had a slope ( $1/n$ ) close to 1, which indicates a high sorption capacity at high equilibrium concentrations that rapidly decreases at lower equilibrium concentrations. Copper and lead Freundlich isotherms had a slope ( $1/n$ ) much smaller than one, which

indicates that the sorption capacity is only slightly reduced at the lower equilibrium concentrations.

The Freundlich model developed using the FilterMat™ batch sorption data best represents the sorption of CrVI (see Appendix C). The Langmuir model developed using the FilterMat™ batch sorption data best represents sorption of Cu, Pb and Ag (see Appendix C). The coefficients of determination obtained from the Freundlich and Langmuir models were significant ( $R^2 > 0.8$ ) for each tested metal. The largest monolayer capacity ( $X_m$ ) was obtained for copper, followed by lead, chromium VI and silver. Similar to the results obtained from the activated carbon batch sorption tests, the monolayer capacity obtained for silver was negative, which is not reasonable. The data does not show conformity to the ideal localized monolayer model (type I isotherm). The silver isotherm shape is characteristic of a type III, which suggests that multilayer adsorption might be occurring and is better represented by the BET isotherm. This isotherm could not be developed with the data collected for this part of the study.

The largest Freundlich adsorption constant  $K$  was obtained for silver, followed by copper, lead and chromium VI. The slope obtained through the Freundlich isotherm ( $1/n$ ) was close to 1 for chromium VI and much greater than 1 for silver, which indicates a high sorption capacity at high equilibrium concentrations that rapidly diminishes at lower equilibrium concentrations. The copper Freundlich isotherm has a slope ( $1/n$ ) much smaller than 1, which indicates that the sorption capacity is only slightly reduced at the lower equilibrium concentrations.

The FilterMat™ monolayer capacity ( $X_m$ ) obtained for copper, chromium VI, lead, and silver was larger than the activated carbon  $X_m$ . Similarly the FilterMat™ Freundlich adsorption constant,  $K$ , obtained for copper, chromium VI and silver was

larger than the activated carbon K. This information suggests that the FilterMat™ nonwoven fabric may be contributing to the sorption of metals, resulting in a higher affinity as compared to the activated carbon alone.

This is more clearly shown by the computed capacities, which were always larger for the FilterMat™ even though smaller amounts of carbon were contained in the pieces of fabric used for the FilterMat™ batch sorption tests, as compared to the amounts of activated carbon used for the activated carbon batch sorption tests. The FilterMat™ monolayer capacity (11.07 mg/g) obtained for copper is comparable to the activated carbon cloth capacity reported in the literature for copper (11.05 mg/g, Faur-Brasquet et al. 2002). Activated carbon capacities reported in the literature for the different tested contaminants (see Table 2.1 in Chapter II) were larger than the capacities obtained for the Aquasorb® activated carbon (see data shown in Appendix B and C).

The maximum capacity obtained for copper through the FilterMat™ and activated carbon batch sorption tests was used to make predictions of the exhaustion time and capacity of the curtains (expressed as contaminant mass sorbed). After obtaining the column results it was determined that the activated carbon sorption capacity was more representative of the sorption behavior obtained for the column system, than the capacity obtained for the FilterMat™ which was higher.

The copper column tests showed that the curtain is not efficient in the removal of copper in a flow through configuration and exhaustion time is achieved very quickly, which was consistent with the exhaustion predictions based on the capacity obtained through the activated carbon batch sorption tests. For only 20 minutes, the copper concentration in the effluent was reduced to the desired levels (allowable concentration). Based on the data, copper exhaustion time could potentially occur between 2.4 and 3.3

hrs if six curtains are used in series for treatment. The data trend demonstrates that the use of more curtains is not expected to extend the curtain life significantly because the fabric layers become exhausted in a relatively short period of time (see Figures 4.18 and 4.20).

The total percentage of copper mass sorbed by the column system was relatively low, ranging from 37% to 53%, which is considered inefficient since more than half of the contaminant mass is not being sorbed by the system and the treatment objective was only met for a short period of time (20 mins). A similar behavior is expected for the other metals since all of those had a low sorption capacity in the batch testing. Therefore, another alternative is needed for the treatment of metals in CDF effluent. One alternative is to fabricate a FilterMat™ impregnated with a type of carbon that has a larger sorption capacity for metals or with another type of material that has been proven to have large affinity for sorption of metals, such as zeolite, apatite, or perhaps a synthetic ion exchange resin.

The column system used for the Aroclor 1016 column tests was more efficient in the concentration reduction of Aroclor 1016. Breakthrough, the time when the effluent concentration exceeds the WQC, did not occur for column systems 2, 3, and 4. For column system 2, measurable effluent concentrations were obtained at 2.0 and 2.5 days, which resulted in an overall removal percentage obtained by comparison of the influent and effluent concentrations of approximately 90% for those periods of time. The total percentage of Aroclor 1016 mass sorbed by column 2 was approximated to 94%. An overall removal percentage of 90% is required to reduce the Aroclor 1016 concentration from 0.1 µg/L to 0.01 µg/L, therefore the results obtained through column test 2 were considered acceptable and two replicates of the test were conducted. For two replicates of

column test 2, column tests 3 and 4, the effluent concentration was not detected at 6.0 and 2.5 days respectively. This evidences that the breakthrough time prediction did not work for column tests 3 and 4, which could be attributed to variation in the carbon amount contained in the fabric pieces and variability in the physical and chemical properties of the carbon. Column test 3 is being continued to determine breakthrough time of the column system. Based on the sorption capacity obtained through the Aroclor 1016 batch sorption test, the breakthrough time is now projected to be 247 days in the future. There is a significant difference between the two predictions that were made for the breakthrough time of the Aroclor 1016 column tests (2.5 days vs. 247 days). The prediction made based on the batch sorption capacity does not seem like a viable estimate because it is expected that the most favorable sorption sites are occupied in the flow-through regime and then no further sorption takes place as shown by the Cu column test results. However, a higher percentage of the column system capacity is expected to be utilized for Aroclor 1016 as compared to Cu. Conducting the Aroclor 1016 column test for 247 days is unfeasible due to the water volume requirements. In order to extrapolate the breakthrough time of the pieces of fabric, the Aroclor 1016 could be extracted from the fabric pieces to determine if some of them have reached breakthrough. A system breakthrough time could be extrapolated using this information. Based on the results obtained thorough the Aroclor 1016 column tests, the FilterMat™ 400 could be potentially used as a treatment alternative for removal of organic contaminants present in CDF effluent and runoff, although the economics of the treatment system require further analysis. Further, effluents generally contain a mixture of contaminants, which may require additional testing. The expected life of this treatment alternative has not been defined at this point of the study; however, breakthrough time is expected to be longer



than 6.0 days which seems practical for treatment of CDF effluent and runoff. Further testing is needed to better understand the variability observed in the Aroclor1016 column testing and to enable performance predictions.

## CHAPTER V

### SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

#### 5.1 Summary and conclusions

For this study a passive, low-tech, low-cost water treatment technology was considered for the removal of metal and organic contaminants from CDF effluent and runoff in order to reduce contaminant concentrations to meet WQC after dilution. Layers of Huesker's FilterMat™400, which consists of two layers of PP nonwoven geotextile impregnated with two layers of Aquasorb® activated carbon, could be hung as a curtain along the weir in order to reduce contaminants concentration. The main objectives of the study were to evaluate the efficiency of the curtain in removing contaminants from a synthetic effluent in a flow through regime and to estimate the expected life of the curtains.

Three different laboratory tests were designed and conducted for this study including batch equilibrium tests, batch sorption tests, and upflow column tests. Important parameters were obtained from a case study to design the laboratory tests conducted for this study, including field approach velocity, contaminants of concern and their maximum predicted concentrations, and treatment targets (WQC or allowable discharge concentrations). The constituents evaluated in this study included copper, chromium VI, lead, mercury, silver, DOC, and Aroclor 1016.

The metals and DOC final equilibrium tests were conducted by contacting 100 mL of the solution with 0.25 g of activated carbon, and measuring the final

concentrations individually at 24, 36, 48, 60, and 72 hrs. The Aroclor 1016 equilibrium test was conducted by contacting 1000 mL of the solution with 0.05 g of activated carbon, and measuring the final concentrations individually at 24, 36, and 48 hrs. This test was conducted to determine the contact time considered to be sufficient to establish equilibrium between the activated carbon and the contaminants of interest. Based on the results obtained through these tests, it was concluded that using a contact time of 48 hrs was sufficient to establish equilibrium state between the adsorbent and the solutions. Equilibrium times reported in the literature generally ranged between 105 minutes to 48 hrs; therefore, the selected contact time was considered relatively conservative. The selected contact time was used to conduct the batch sorption studies.

Batch sorption tests were conducted using the activated carbon contained in the FilterMat™ and pieces of FilterMat™, which were designed based on preliminary tests and relevant information obtained from the literature review. The sorption capacity of these two materials was obtained for each tested contaminant, thus assessing the impact in the carbon capacity that may be caused by the packaged pieces of curtain (i.e. nonwoven fabric and activated carbon). The batch sorption tests were conducted by varying the carbon dosage and using a fixed contaminant concentration and solution volume, and shaking the samples for 48 hrs in order to obtain the equilibrium concentration. The sorption capacity and the removal percentage were evaluated for each conducted test.

Preliminary tests conducted for copper indicated that buffering would be necessary for the metals because pH was very variable upon the addition of the activated carbon. The literature review suggested that maintaining a fairly constant pH (between 4 and 5) during the performance of the batch sorption tests might be necessary to achieve

greater adsorption and prevent precipitation of the metals. Therefore, acetic acid, which has a pKa of 4.75, and sodium acetate were selected to buffer the metals solution. A preliminary batch sorption test was conducted for Cu, Pb and Ag using an acetic acid concentration of 0.002 M to buffer the solutions. The pH was variable and greater than 4.75 for the sorption tests conducted with 1.0 g, 2.0 g, and 3.0 g of activated carbon.

The adsorption isotherms data trend obtained for Cu and Pb showed a direct linear relationship (i.e. sorption capacity increased as equilibrium concentration increased) and resulted in a coefficient of determination greater than 0.8; however, no data trend could be established for Ag. Therefore, three different buffer tests were conducted to determine the lowest effective acetic acid concentration that would maintain the pH near 4.75. The tests consisted of titrating a Cu solution and DDI water separately with acetic acid, and evaluating sorption capacity and removal percentage of Cu at different buffer strengths. These tests were conducted using 3.0 g of activated carbon, which is the largest carbon amount used for the batch test.

From these tests, it was concluded that an acetic acid concentration of 0.2 M is expected to maintain a constant pH throughout the batch sorption tests and would prevent precipitation of the metals. However, sorption capacity and removal percentage were not significantly affected at lower buffer strengths for Cu and Pb. The data suggests that precipitation of Cu might be taking place as the buffer strength decreases; however, the difference in Cu removal percentage was not significant (~4 % between 0.2 M and 0.002 M) suggesting that precipitation did not impact the results greatly. The Ag batch sorption test was re-run using a buffer strength of 0.2 M in order to maintain constant pH and obtain a measurable adsorption data trend. The remaining batch sorption tests were also conducted with a 0.2 M acetic acid buffer. The Cu and Pb batch sorption tests were not

re-run because the adsorption data trend showed a significant linear relationship, and sorption capacity and removal percentage did not seem to be significantly affected at high pH values as previously stated.

Both the Langmuir and the Freundlich adsorption models, which are classified as isotherms type I and are associated with systems where adsorption occurs in the monomolecular layer, showed that either representation of the metals data obtained through the activated carbon batch sorption tests may be suitable with the exception of silver for which a coefficient of determination of 0.7633 was obtained with the Freundlich isotherm. The coefficient of determination was higher for the Freundlich isotherm models obtained for Cu and Pb, and for the Langmuir isotherm models obtained for Cr VI, Hg, and Ag. The Aroclor 1016 adsorption data was better fitted with the Freundlich isotherm. Similarly, both isotherms showed a good representation of the metals adsorption data obtained through the FilterMat™ adsorption tests. The coefficient of determination was higher for the Freundlich isotherm models obtained for Cr VI, and for the Langmuir isotherm models obtained for Cu, Pb, and Ag.

The activated carbon has more affinity for sorption of Aroclor 1016 as compared to the metals. This could be attributed to the hydrophobic nature of organic contaminants; therefore, the organic molecules will tend to sorb in the carbon rather than stay dissolved in the water. No data trend was discernible for the DOC batch sorption tests, however. Removal percentages of DOC were relatively low as compared to the other tested contaminants, which suggest that the carbon has low affinity for sorption of the form of DOC in the humic acid used for the batch sorption tests. Copper, lead and mercury had comparable sorption capacities which were higher than the ones obtained for the other metals. The isotherm constants seemed to be erroneous for silver because the shape of the

sorption capacity as a function of time plot was not characteristic of isotherm type I which is represented through the Langmuir and Freundlich models. The silver isotherm shape was better described by isotherm type III.

Small variability was observed for the analytical replicates obtained for the batch sorption tests as evidenced by the coefficient of variation which was generally smaller than 0.1, which suggests that the obtained data was consistent. The coefficient of variation was also evaluated on the replicates of different parameters including: equilibrium concentration, solution volume, amount of carbon, pH, sorption capacity, and removal percentage to assess the variability in the procedural replicates of activated carbon batch sorption test. The coefficient of variation was generally smaller than 0.3, from which it was therefore concluded that the sorption data was not highly variable.

The activated carbon and the FilterMat™ Langmuir isotherm constant  $X_m$  (monolayer capacity) was compared for the metals, as well as the Freundlich isotherm constant  $K$  (capacity at  $C_e=1$ ). This comparison could not be made for DOC because the data trend of the isotherms developed using the sorption data was not discernible. Based on the metals comparison, it was concluded that the FilterMat™ has a higher sorption capacity than the activated carbon. This information suggests that the FilterMat™ nonwoven fabric may be contributing to the sorption of metals, resulting in a higher affinity as compared to the activated carbon alone.

Column tests were conducted for copper and Aroclor 1016 to determine the efficiency of the curtains in the removal of metal and organic contaminants, and the expected life of the curtains. Predictions were made based on sorption capacities obtained through the batch sorption tests. However, these predictions were not expected to be representative because contact time between adsorbate and adsorbent in a flow through

regime is expected to be much smaller than that required to establish equilibrium, thus making performance difficult to predict on the basis of equilibrium batch testing.

The tests were design based on preliminary tests, from which it was concluded that a flow rate of 125 mL/min would result in sufficient removal of the contaminants of interest. The velocity resulting from this flow rate is smaller than then one estimated for the case study, but still results in a relatively high approach velocity. The detention time per double curtain layer that resulted from the tested flow rate was approximated to 3.80 seconds, which is relatively small as compared to the time required to establish equilibrium.

From the copper column test it was concluded that the pieces of fabric are not efficient in the removal of copper. The Cu treatment objective was only met for a short period of time (20 mins). Also, the curtains are exhausted at a relatively short period of time. The final copper column test configuration had three double curtain layers located in three separate ports. The exhaustion time resulting from this configuration ranged between 2.4 and 3.3 hrs, which is not practical and cost effective for CDF effluent and runoff treatment since it would not be possible to replace curtains that often during the life of a dredging project.

Also, the copper concentration in the effluent was reduced to the allowable concentration for only 20 minutes; therefore, copper concentrations would not be reduced sufficiently to meet WQC after dilution. The same sorption behavior is expected for other metals; therefore, it is concluded that another treatment alternative is needed for the removal of metals contaminants in CDF. An alternative that could be considered is to manufacture a FilterMat™ impregnated with zeolite, apatite, or a synthetic ion exchange resin which has been proven to have large affinity for sorption of metals, or a type of

activated carbon with larger sorption capacity for metals. The Cu effluent concentrations and cumulative mass sorbed in each layer showed very little variability as evidenced by the coefficient of variation, which means that the collected data was consistent.

The column system used for Aroclor 1016 was more efficient in the removal of Aroclor 1016. Breakthrough time did not occur for column 2, 3, and 4 over a period of 2.5, 6.0, and 2.5 days respectively. For column system 2, measurable effluent concentrations were obtained at 2.0 and 2.5 days, which resulted in an overall removal percentage of 90%, which was obtained by comparison of the influent and effluent concentrations. The total percentage of Aroclor 1016 mass sorbed by column 2 was approximated to 94%. Column test 3 is still ongoing to determine at which period of time the column system will reach breakthrough. Based on the sorption capacity obtained through the Aroclor 1016 batch sorption test, the breakthrough time is now projected to be 247 days in the future, which does not seem like a viable estimate based on the sorption behavior observed for the Aroclor 1016 column test 2 and the Cu column test. It is expected that the most favorable sorption sites are occupied in the flow-through regime and then no further sorption takes place. However, a higher percentage of the column system capacity is expected to be utilized for Aroclor 1016 as compared to Cu. Breakthrough time of the fabric pieces could be extrapolated through the extraction of Aroclor 1016 from the fabric pieces to determine if some of them have reached breakthrough. FilterMat™400 could be potentially used as a treatment alternative for removal of organic contaminants in CDF effluent and runoff, although the economics of this treatment alternative require further analysis and multiple treatments might be required in order to address other contaminants that may be present in the effluent and runoff.



## 5.2 Recommendations

The main recommendations for future work include the following:

- Conduct laboratory test to determine the sorption kinetics of the FilterMat™ and the activated carbon impregnated in the fabric.
- Conduct batch sorption tests using pieces of the PP non-woven geotextile alone (fabric with no activated carbon) to determine the sorption capacity of the material itself for each tested contaminant.
- Impregnate the FilterMat™ with a type of carbon that has a larger sorption capacity for metals or with another type of material that has been proven to have large affinity for sorption of metals, such as zeolite, apatite, or perhaps a synthetic ion exchange resin. Determine the sorption kinetics of the material, conduct batch sorption tests and conduct column tests to determine its effectiveness and expected life for treatment of metal contaminants.
- Test the FilterMat™ 400 with elutriate water generated with sediment samples from a site known to be contaminated with organic contaminants to determine how the sediment matrix affects the curtain sorption capacity, the effectiveness for removal of organic contaminants in a flow-through regime, and the expected life of the curtain with a more representative effluent.
- Generate elutriate water with sediment samples known to be contaminated with organic and metal contaminants in order to test the combination of curtain layers that have a good sorption capacity for organics (e.g. FilterMat™ 400) and for metals (FilterMat™ impregnated with a material

proven to have large affinity for sorption of metals; e.g. zeolite, apatite, or synthetic ion exchange resin). Conduct column tests to determine the effectiveness the combined materials for the removal of organic and metals contaminants, and expected life of the treatment alternative. Determine how the sediment matrix affects these parameters.

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APPENDIX A  
EQUILIBRIUM TESTS DATA AND PLOTS

## A.1 Metals

Table A.1 Metals equilibrium data

Time (hr)	Final Concentration (mg/L)
<b>Copper</b>	
0 (Initial)	28.56
24	26.14
36	25.95
48	26.50
60	26.11
72	25.63
<b>Chromium VI</b>	
0 (Initial)	4.73
24	4.44
36	4.38
48	4.45
60	4.44
72	4.44
<b>Lead</b>	
0 (Initial)	28.84
24	25.73
36	25.76
48	25.92
60	25.88
72	25.71
<b>Mercury</b>	
0 (Initial)	25.40
24	8.37
36	10.50
48	10.20
60	10.30
72	8.70
<b>Silver</b>	
0 (Initial)	5.12
24	4.89
36	4.54
48	4.79
60	4.81
72	4.75

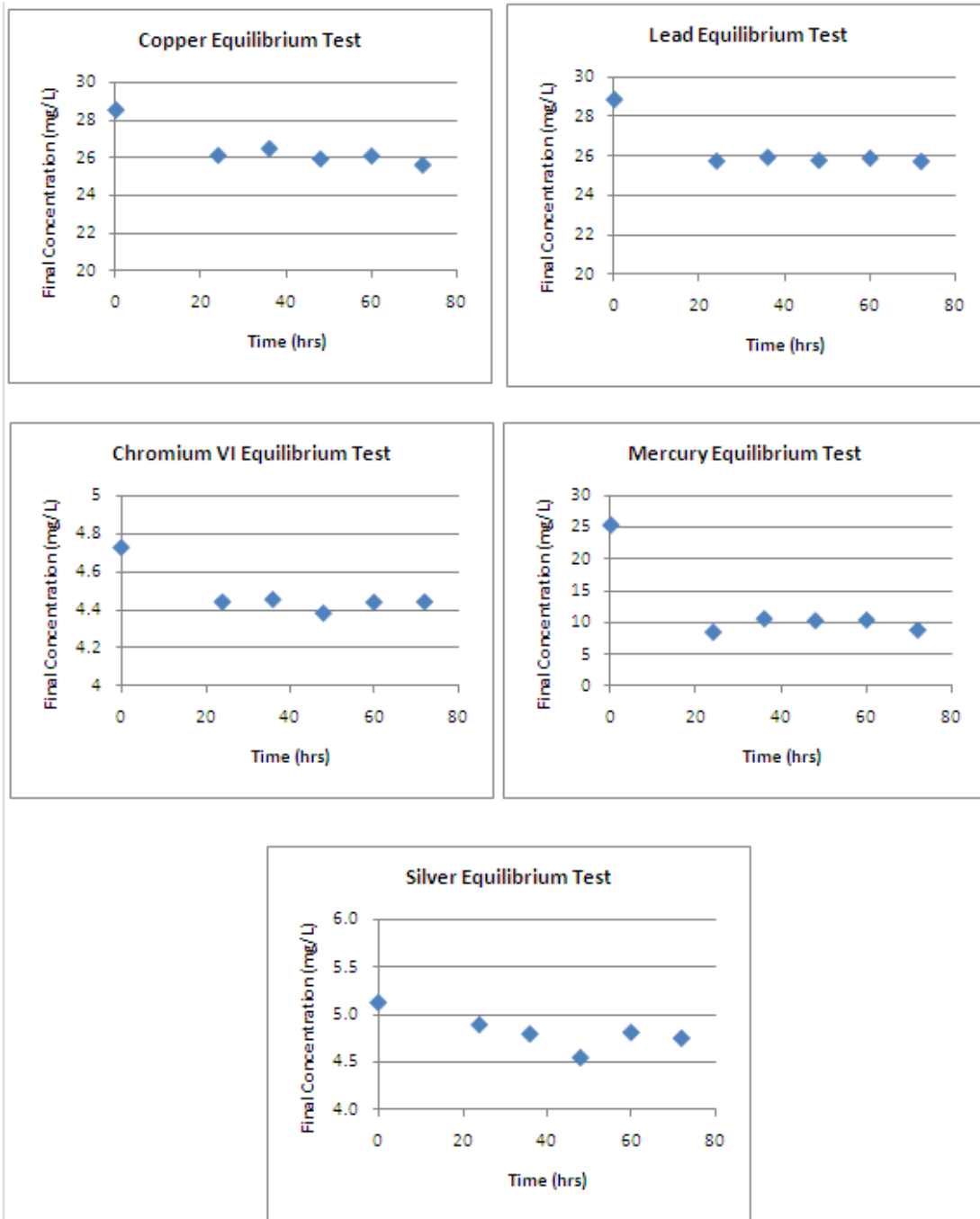


Figure A.1 Metals Equilibrium Test Plots

## A.2 Organics

Table A.2 Organics equilibrium data

Time (hr)	Final Concentration
<b>Aroclor 1016 (<math>\mu\text{g/L}</math>)</b>	
<b>0 (Initial)</b>	0.187
<b>24</b>	0.00443
<b>36</b>	0.00188
<b>48</b>	0.00038
<b>DOC (mg/L)</b>	
<b>0 (Initial)</b>	7.001
<b>24</b>	5.86
<b>36</b>	7.40
<b>48</b>	5.97
<b>60</b>	5.87
<b>72</b>	6.13

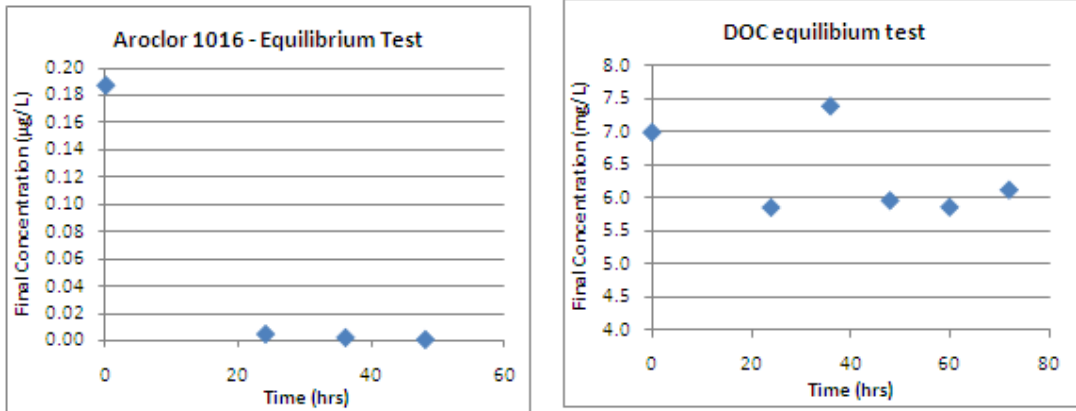


Figure A.2 Organics Equilibrium Test Plots

APPENDIX B  
ACTIVATED CARBON BATCH SORPTION TESTS

## B.1 Metals

### B.1.1 Copper

Table B.1 Copper activated carbon batch sorption test data

Sample ID	Ce (mg/L)	log(Ce)	Sln Mass (g)	Sln Vol (L)	AC Mass (g)	pH	X/M (mg/g)	log (X/M)	% Removal	1/Ce (L/mg)	M/X (g/mg)
IHNC_Cu_IC_1	32.30					4.00					
IHNC_Cu_0.1_1	29.78	1.47	104.0	0.1040	0.1008	4.15	2.600	0.4150	7.803	0.03358	0.3846
IHNC_Cu_0.1_2	29.20	1.47	101.5	0.1015	0.1008	4.16	3.115	0.4934	9.578	0.03424	0.3210
IHNC_Cu_0.1_3	29.39	1.47	106.5	0.1065	0.1001	4.16	3.096	0.4908	9.010	0.03403	0.3230
IHNC_Cu_0.5_1	19.19	1.28	107.5	0.1075	0.4990	4.64	2.823	0.4507	40.57	0.05210	0.3543
IHNC_Cu_0.5_2	17.74	1.25	100.5	0.1005	0.5006	4.69	2.922	0.4656	45.06	0.05636	0.3423
IHNC_Cu_0.5_3	18.28	1.26	101.0	0.1010	0.4997	4.68	2.834	0.4524	43.41	0.05471	0.3529
IHNC_Cu_1.0_1	7.74	0.89	118.0	0.1180	1.0009	5.09	2.895	0.4616	76.03	0.1291	0.3455
IHNC_Cu_1.0_2	5.64	0.75	105.0	0.1050	1.0012	5.22	2.795	0.4464	82.53	0.1773	0.3577
IHNC_Cu_1.0_3	7.68	0.89	116.5	0.1165	0.9990	5.08	2.870	0.4579	76.21	0.1302	0.3484
IHNC_Cu_2.0_1	0.18	-0.74	106.5	0.1065	2.0010	6.58	1.709	0.2328	99.43	5.450	0.5851
IHNC_Cu_2.0_2	0.12	-0.93	103.0	0.1030	2.0004	6.64	1.657	0.2193	99.64	8.602	0.6035
IHNC_Cu_2.0_3	0.18	-0.75	107.0	0.1070	2.0018	3.29	1.717	0.2347	99.44	5.563	0.5825
IHNC_Cu_3.0_1	0.02	-1.67	102.5	0.1025	2.9993	7.29	1.103	0.04257	99.93	46.25	0.9066
IHNC_Cu_3.0_2	0.02	-1.67	103.5	0.1035	3.0007	6.09	1.113	0.04659	99.93	47.03	0.8983
IHNC_Cu_3.0_3	0.03	-1.54	112.0	0.1120	3.0007	5.04	1.204	0.08077	99.91	34.90	0.8303

Table B.2 Statistical parameters copper activated carbon batch sorption test data

<i>Copper</i>		Mean				
ID	Ce (mg/L)	Sln Vol (mL)	AC Mass (g)	pH	X/M (mg/g)	% Removal
IHNC_0.1	29.455556	104	0.100567	4.156667	2.936956	8.796917
IHNC_0.5	18.404444	103	0.499767	4.67	2.859439	43.01441
IHNC_1.0	7.0224444	113.1667	1.000367	5.13	2.853516	78.25644
IHNC_2.0	0.15983	105.5	2.001067	5.503333	1.694281	99.50512
IHNC_3.0	0.0238467	106	3.000233	6.14	1.140207	99.92616

<i>Copper</i>		Standard Deviation				
ID	Ce (mg/L)	Sln Vol (mL)	AC Mass (g)	pH	X/M (mg/g)	% Removal
IHNC_0.1	0.2928089	2.5	0.000404	0.005774	0.291963	0.906623
IHNC_0.5	0.7333965	3.905125	0.000802	0.026458	0.054205	2.270812
IHNC_1.0	1.1961691	7.112196	0.001193	0.078102	0.051762	3.703692
IHNC_2.0	0.0377908	2.179449	0.000702	1.917038	0.03254	0.117012
IHNC_3.0	0.0041666	5.220153	0.000808	1.125833	0.055821	0.012901

<i>Copper</i>		Coefficient of Variation				
ID	Ce	Sln Vol	AC Mass	pH	X/M	% Removal
IHNC_0.1	0.0099407	0.024038	0.004019	0.001389	0.09941	0.103061
IHNC_0.5	0.0398489	0.037914	0.001605	0.005665	0.018957	0.052792
IHNC_1.0	0.1703351	0.062847	0.001193	0.015225	0.01814	0.047328
IHNC_2.0	0.2364438	0.020658	0.000351	0.348341	0.019206	0.001176
IHNC_3.0	0.174724	0.049247	0.000269	0.18336	0.048957	0.000129

## B.1.2 Chromium VI

Table B.3 Chromium VI activated carbon batch sorption test data

Sample ID	Ce (mg/L)	log(Ce)	Sln Mass (g)	Sln Vol (L)	AC Mass (g)	pH	X/M (mg/g)	log (X/M)	% Removal	1/Ce (L/mg)	M/X (g/mg)
IHNC_CrVI_IC_BT1	3.53				0	4.57					
IHNC_CrVI_0.1_BT1_1	2.28	0.36	100.5	0.1005	0.1008	4.57	1.245947421	0.095499715	35.42808543	0.439045807	0.802602087
IHNC_CrVI_0.1_BT1_2	2.77	0.44	101.0	0.101	0.1004	4.56	0.760853254	-0.118699098	21.44207144	0.360880549	1.314313891
IHNC_CrVI_0.1_BT1_3	2.79	0.45	100.0	0.1	0.1017	4.57	0.72402491	-0.140246492	20.87507088	0.358294518	1.381167949
IHNC_CrVI_0.5_BT1_1	1.49	0.17	100.5	0.1005	0.5017	4.58	0.408517042	-0.388789821	57.81515782	0.672043011	2.447878294
IHNC_CrVI_0.5_BT1_2	1.41	0.15	100.0	0.1	0.502	4.59	0.421049137	-0.375667219	59.92250992	0.707380335	2.375019713
IHNC_CrVI_0.5_BT1_3	1.35	0.13	101.0	0.101	0.5033	4.59	0.437071329	-0.359447681	61.74636175	0.741106719	2.287956068
IHNC_CrVI_1.0_BT1_1	0.79	-0.10	100.0	0.1	1.0014	4.62	0.273550363	-0.562962705	77.66017766	1.269035533	3.655633974
IHNC_CrVI_1.0_BT1_2	0.78	-0.11	100.5	0.1005	0.9993	4.61	0.276736215	-0.557934003	78.00982801	1.28921358	3.613549454
IHNC_CrVI_1.0_BT1_3	0.77	-0.12	100.5	0.1005	0.9974	4.61	0.278170243	-0.555689331	78.26497826	1.304347826	3.594920832
IHNC_CrVI_2.0_BT1_1	0.31	-0.51	100.5	0.1005	1.9999	4.66	0.161779589	-0.791076272	91.26819127	3.246753247	6.181249478
IHNC_CrVI_2.0_BT1_2	0.31	-0.50	100.0	0.1	1.999	4.67	0.16074704	-0.793857015	91.0980911	3.184713376	6.220954357
IHNC_CrVI_2.0_BT1_3	0.30	-0.53	101.0	0.101	1.9999	4.66	0.163106322	-0.787529205	91.56114156	3.359462486	6.130970203
IHNC_CrVI_3.0_BT1_1	0.18	-0.74	100.5	0.1005	3.0002	4.71	0.11210586	-0.950371687	94.87809488	5.535055351	8.920140334
IHNC_CrVI_3.0_BT1_2	0.17	-0.78	100.5	0.1005	3.0032	4.72	0.112451219	-0.949035833	95.26554527	5.988023952	8.892744886
IHNC_CrVI_3.0_BT1_3	0.17	-0.77	100.5	0.1005	2.998	4.71	0.112489827	-0.948886753	95.13324513	5.825242718	8.88969279



Table B.4 Statistical parameters chromium VI activated carbon batch sorption test data

<i>Chromium VI</i>		Mean				
ID	Ce (mg/L)	Sln Vol (mL)	AC Mass (g)	pH	X/M (mg/g)	% Removal
IHNC_0.1	2.613222222	100.5	0.100966667	4.566666667	0.910275195	25.9150759
IHNC_0.5	1.417	100.5	0.502333333	4.586666667	0.422212503	59.8280098
IHNC_1.0	0.514111111	100.3333333	0.999366667	4.613333333	0.302382218	85.4249354
IHNC_2.0	0.306555556	100.5	1.9996	4.663333333	0.16187765	91.3091413
IHNC_3.0	0.173111111	100.5	3.000466667	4.713333333	0.112348968	95.0922951

<i>Chromium VI</i>		Standard Deviation				
ID	Ce (mg/L)	Sln Vol (mL)	AC Mass (g)	pH	X/M (mg/g)	% Removal
IHNC_0.1	0.290771643	0.5	0.000665833	0.005773503	0.291283306	8.24338431
IHNC_0.5	0.069393403	0.5	0.00085049	0.005773503	0.014312648	1.96730496
IHNC_1.0	0.445256023	0.288675135	0.002000833	0.005773503	0.043184229	12.6230209
IHNC_2.0	0.008261916	0.5	0.000519615	0.005773503	0.001182694	0.23422556
IHNC_3.0	0.006946888	0	0.002610236	0.005773503	0.000211421	0.19694448

<i>Chromium VI</i>		Coefficient of Variation				
ID	Ce	Sln Vol	AC Mass	pH	X/M	% Removal
IHNC_0.1	0.11126939	0.004975124	0.006594581	0.001264271	0.319994775	0.31809223
IHNC_0.5	0.048972056	0.004975124	0.001693079	0.001258758	0.033899157	0.03288267
IHNC_1.0	0.866069636	0.002877161	0.002002101	0.001251482	0.142813388	0.14776740
IHNC_2.0	0.026950796	0.004975124	0.00025986	0.001238063	0.007306097	0.00256519
IHNC_3.0	0.040129651	0	0.000869943	0.00122493	0.001881828	0.00207109

### B.1.3 Lead

Table B.5 Lead activated carbon batch sorption test data

Sample ID	Ce (mg/L)	log(Ce)	Sln Mass (g)	Sln Vol (L)	AC Mass (g)	pH	X/M (mg/g)	log (X/M)	% Removal	I/Ce (L/mg)	M/X (g/mg)
IHNC_Pb_IC_1	32.88				0	3.83					
IHNC_Pb_0.1_1	28.21	1.45	101.0	0.101	0.1016	2.61	4.639107612	0.666434447	14.19446416	0.035448423	0.215558699
IHNC_Pb_0.1_2	28.79	1.46	105.5	0.1055	0.1016	3.94	4.246998031	0.62808206	12.44043395	0.034738305	0.235460434
IHNC_Pb_0.1_3	28.19	1.45	99.0	0.099	0.1007	3.97	4.604270109	0.663160794	14.24515867	0.035469378	0.21718969
IHNC_Pb_0.5_1	12.46	1.10	108.0	0.108	0.5016	4.55	4.396650718	0.643121965	62.1109196	0.080278298	0.227445859
IHNC_Pb_0.5_2	11.23	1.05	101.5	0.1015	0.5014	4.54	4.382003723	0.641672742	65.84203589	0.089047195	0.228206105
IHNC_Pb_0.5_3	16.48	1.22	105.5	0.1055	0.5008	4.49	3.454872204	0.538431987	49.88340262	0.060691888	0.289446307
IHNC_Pb_1.0_1	1.55	0.19	107.5	0.1075	0.9994	3.82	3.370176272	0.527652617	95.30061847	0.647249191	0.296720385
IHNC_Pb_1.0_2	1.74	0.24	109.5	0.1095	0.9987	5.09	3.413720336	0.533227939	94.7024232	0.574162679	0.292935537
IHNC_Pb_1.0_3	1.30	0.11	103.5	0.1035	0.9996	5.12	3.269527311	0.514484969	96.04684173	0.769428058	0.30585461
IHNC_Pb_2.0_1	0.0077	-2.11	100.0	0.1	2.0018	5.35	1.641971059	0.215365498	99.97660955	130.0390117	0.609024132
IHNC_Pb_2.0_2	0.0086	-2.07	100.5	0.1005	1.9997	6.52	1.651869521	0.21797574	99.97392578	116.6543532	0.605374691
IHNC_Pb_2.0_3	0.0063	-2.20	100.5	0.1005	1.9999	6.6	1.651818097	0.21796222	99.98081213	158.5204756	0.605393537
IHNC_Pb_3.0_1	0.0039	-2.41	101.0	0.101	3.0003	7.37	1.106605739	0.043992918	99.98813039	256.2569403	0.903664209
IHNC_Pb_3.0_2	0.0028	-2.56	100.0	0.1	2.9993	6.27	1.096052968	0.039831542	99.99163541	363.6363636	0.912364666
IHNC_Pb_3.0_3	0.0038	-2.41	100.5	0.1005	2.9986	7.38	1.101753588	0.042084474	99.98829666	259.8977735	0.907643969

Table B.6 Statistical parameters lead activated carbon batch sorption test data

<i>Lead</i>	<b>Mean</b>					
<b>ID</b>	<b>Ce (mg/L)</b>	<b>Sln Vol (mL)</b>	<b>AC Mass (g)</b>	<b>pH</b>	<b>X/M (mg/g)</b>	<b>% Removal</b>
IHNC_0.1	28.396667	101.83333	0.1013	3.5066667	4.4967919	13.626686
IHNC_0.5	13.387778	105	0.5012667	4.5266667	4.0778422	59.278786
IHNC_1.0	1.5294444	106.83333	0.9992333	4.6766667	3.3510696	95.347933
IHNC_2.0	0.0075236	100.33333	2.0004667	6.1566667	1.6485529	99.977116
IHNC_3.0	0.0035	100.5	2.9994	7.0066667	1.1014708	99.989354

<i>Lead</i>	<b>Standard Deviation</b>					
<b>ID</b>	<b>Ce (mg/L)</b>	<b>Sln Vol (mL)</b>	<b>AC Mass (g)</b>	<b>pH</b>	<b>X/M (mg/g)</b>	<b>% Removal</b>
IHNC_0.1	0.3378527	3.3291641	0.0005196	0.776681	0.217028	1.0276367
IHNC_0.5	2.7444678	3.2787193	0.0004163	0.0321455	0.5395576	8.3477679
IHNC_1.0	0.2215223	3.0550505	0.0004726	0.7420467	0.0739295	0.6737981
IHNC_2.0	0.0011411	0.2886751	0.001159	0.699738	0.0057001	0.003471
IHNC_3.0	0.0006501	0.5	0.0008544	0.6379916	0.0052821	0.0019774

<i>Lead</i>	<b>Coefficient of Variation</b>					
<b>ID</b>	<b>Ce</b>	<b>Sln Vol</b>	<b>AC Mass</b>	<b>pH</b>	<b>X/M</b>	<b>% Removal</b>
IHNC_0.1	0.0118976	0.0326923	0.0051295	0.221487	0.0482629	0.0754135
IHNC_0.5	0.204998	0.0312259	0.0008306	0.0071014	0.1323145	0.1408222
IHNC_1.0	0.1448384	0.0285964	0.0004729	0.15867	0.0220615	0.0070667
IHNC_2.0	0.1516757	0.0028772	0.0005794	0.1136553	0.0034576	3.472E-05
IHNC_3.0	0.1857411	0.0049751	0.0002849	0.0910549	0.0047955	1.978E-05

## B.1.4 Mercury

Table B.7 Mercury activated carbon batch sorption test data

Sample ID	Ce (mg/L)	log(Ce)	Sln Mass (g)	Sln Vol (L)	AC Mass (g)	pH	X/M (mg/g)	log (X/M)	% Removal	I/Ce (L/mg)	M/X (g/mg)
IHNC_Hg_IC_BT1	12.63				0	4.52					
IHNC_Hg_0.1_BT1_1	5.56	0.74	95.0	0.095	0.1004	4.49	6.696049137	0.825818632	56.01583113	0.179964007	0.149341795
IHNC_Hg_0.1_BT1_2	5.48	0.74	95.5	0.0955	0.1032	4.5	6.622690568	0.821034464	56.64907652	0.182592818	0.150996032
IHNC_Hg_0.5_BT1_1	2.72	0.44	95.0	0.095	0.4973	4.52	1.893122863	0.277178801	78.44327177	0.367197062	0.528227734
IHNC_Hg_0.5_BT1_2	3.01	0.48	95.0	0.095	0.4972	4.51	1.838093323	0.264367557	76.14775726	0.331858407	0.544042018
IHNC_Hg_1.0_BT1_1	1.70	0.23	95.0	0.095	0.9984	4.53	1.040014022	0.017039195	86.5171504	0.587084149	0.961525497
IHNC_Hg_1.0_BT1_2	1.88	0.27	95.0	0.095	1.0027	4.54	1.018815864	0.008095699	85.11873351	0.531914894	0.981531634
IHNC_Hg_2.0_BT1_1	0.83	-0.08	95.0	0.095	1.9976	4.61	0.561506308	-0.250645361	93.4591029	1.210165389	1.780923894
IHNC_Hg_2.0_BT1_2	0.86	-0.06	95.0	0.095	2.0051	4.6	0.557652985	-0.253635969	93.16622691	1.158301158	1.793229889
IHNC_Hg_3.0_BT1_1	0.40	-0.40	95.0	0.095	3.0023	4.66	0.387144856	-0.412126507	96.8469657	2.510460251	2.583012497
IHNC_Hg_3.0_BT1_2	0.40	-0.40	95.0	0.095	3.0026	4.66	0.387106175	-0.412169901	96.8469657	2.510460251	2.5832706

Table B.8 Statistical parameters mercury activated carbon batch sorption test data

<i>Mercury</i>	<b>Mean</b>					
<b>ID</b>	<b>Ce (mg/L)</b>	<b>Sln Vol (mL)</b>	<b>AC Mass (g)</b>	<b>pH</b>	<b>X/M (mg/g)</b>	<b>% Removal</b>
IHNC_0.1	5.5166667	95.25	0.1018	4.495	6.6593699	56.332454
IHNC_0.5	2.8683333	95	0.49725	4.515	1.8656081	77.295515
IHNC_1.0	1.7916667	95	1.00055	4.535	1.0294149	85.817942
IHNC_2.0	0.8448333	95	2.00135	4.605	0.5595796	93.312665
IHNC_3.0	0.3983333	95	3.00245	4.66	0.3871255	96.846966

<i>Mercury</i>	<b>Standard Deviation</b>					
<b>ID</b>	<b>Ce (mg/L)</b>	<b>Sln Vol (mL)</b>	<b>AC Mass (g)</b>	<b>pH</b>	<b>X/M (mg/g)</b>	<b>% Removal</b>
IHNC_0.1	0.0565685	0.3535534	0.0019799	0.0070711	0.0518723	0.4477721
IHNC_0.5	0.205061	0	7.071E-05	0.0070711	0.0389118	1.6231739
IHNC_1.0	0.1249222	0	0.0030406	0.0070711	0.0149894	0.9888301
IHNC_2.0	0.026163	0	0.0053033	0.0070711	0.0027247	0.2070946
IHNC_3.0	0	0	0.0002121	0	2.735E-05	0

<i>Mercury</i>	<b>Coefficient of Variation</b>					
<b>ID</b>	<b>Ce</b>	<b>Sln Vol</b>	<b>AC Mass</b>	<b>pH</b>	<b>X/M</b>	<b>% Removal</b>
IHNC_0.1	0.0102541	0.0037118	0.0194489	0.0015731	0.0077894	0.0079487
IHNC_0.5	0.0714913	0	0.0001422	0.0015661	0.0208574	0.0209996
IHNC_1.0	0.069724	0	0.0030389	0.0015592	0.014561	0.0115224
IHNC_2.0	0.0309682	0	0.0026499	0.0015355	0.0048692	0.0022194
IHNC_3.0	0	0	7.065E-05	0	7.065E-05	0

## B.1.5 Silver

Table B.9 Silver activated carbon batch sorption test data

Sample ID	Ce (mg/L)	log(Ce)	Sln Mass (g)	Sln Vol (L)	AC Mass (g)	pH	X/M (mg/g)	log (X/M)	% Removal	1/Ce (L/mg)	M/X (g/mg)
IHNC_Ag_5mg/L_0.2M	1.05				0	4.54					
IHNC_Ag_5mg/L_0.1g_0.2M_1	0.50	-0.30	100.5	0.1005	0.1007	4.54	0.553232373	-0.257092414	52.60993357	2.002670227	1.807558719
IHNC_Ag_5mg/L_0.1g_0.2M_2	0.51	-0.29	100.0	0.1	0.0999	4.53	0.545211879	-0.2634344691	51.69250237	1.964636542	1.834149327
IHNC_Ag_5mg/L_0.1g_0.2M_3	0.52	-0.29	100.5	0.1005	0.1011	4.53	0.531824926	-0.274231312	50.77507118	1.928020566	1.880318036
IHNC_Ag_5mg/L_0.5g_0.2M_1	0.48	-0.32	100.5	0.1005	0.5009	4.55	0.1155542	-0.937214264	54.57133818	2.08913649	8.653947653
IHNC_Ag_5mg/L_0.5g_0.2M_2	0.48	-0.32	100.5	0.1005	0.502	4.55	0.115047809	-0.939121649	54.53970263	2.087682672	8.692038647
IHNC_Ag_5mg/L_0.5g_0.2M_3	0.46	-0.34	100.0	0.1	0.4994	4.55	0.118742491	-0.925393845	56.27965834	2.170767004	8.42158516
IHNC_Ag_5mg/L_1.0g_0.2M_1	0.45	-0.35	100.5	0.1005	1.0001	4.58	0.061131387	-1.213735751	57.73489402	2.245508982	16.35820896
IHNC_Ag_5mg/L_1.0g_0.2M_2	0.45	-0.35	100.5	0.1005	1.0006	4.59	0.0610004	-1.214667319	57.63998735	2.240477969	16.39333519
IHNC_Ag_5mg/L_1.0g_0.2M_3	0.44	-0.35	101.0	0.101	1	4.59	0.061576333	-1.210586175	57.86143625	2.252252252	16.24000563
IHNC_Ag_5mg/L_2.0g_0.2M_1	0.40	-0.40	101.0	0.101	2.001	4.63	0.033128269	-1.479801253	62.29041443	2.516778523	30.18570013
IHNC_Ag_5mg/L_2.0g_0.2M_2	0.41	-0.39	100.0	0.1	2.001	4.64	0.032333833	-1.490342808	61.40461879	2.459016393	30.92735703
IHNC_Ag_5mg/L_2.0g_0.2M_3	0.39	-0.41	101.0	0.101	1.9988	4.64	0.033720566	-1.472105149	63.33438785	2.588438309	29.65549302
IHNC_Ag_5mg/L_3.0g_0.2M_1	0.32	-0.49	101.0	0.101	2.9992	4.71	0.0247067	-1.607185266	69.62986397	3.125	40.47485167
IHNC_Ag_5mg/L_3.0g_0.2M_2	0.36	-0.45	101.0	0.101	3.0004	4.7	0.023518642	-1.628587759	66.30813034	2.816901408	42.51946187
IHNC_Ag_5mg/L_3.0g_0.2M_3	0.33	-0.48	100.5	0.1005	2.9998	4.7	0.024300287	-1.614388603	68.83897501	3.045685279	41.15177788

Table B.10 Statistical parameters silver activated carbon batch sorption test data

<i>Silver</i>	Mean					
ID	Ce (mg/L)	Sln Vol (mL)	AC Mass (g)	pH	X/M (mg/g)	% Removal
IHNC 0.1	0.509	100.333333	0.100566667	4.533333333	0.54342306	51.69250237
IHNC 0.5	0.472777778	100.333333	0.500496667	4.55	0.11644817	55.13023305
IHNC 1.0	0.445222222	100.666667	1.000233333	4.586666667	0.06123604	57.74543921
IHNC 2.0	0.396777778	100.666667	2.000266667	4.636666667	0.03306089	62.34314036
IHNC 3.0	0.334444444	100.833333	2.9998	4.703333333	0.02417521	68.25898977

<i>Silver</i>	Standard Deviation					
ID	Ce (mg/L)	Sln Vol (mL)	AC Mass (g)	pH	X/M (mg/g)	% Removal
IHNC 0.1	0.009666667	0.28867513	0.00061101	0.005773503	0.01081525	0.91743119
IHNC 0.5	0.010489854	0.28867513	0.001346861	0	0.00200301	0.99555717
IHNC 1.0	0.001170628	0.28867513	0.000321455	0.005773503	0.00030189	0.11110043
IHNC 2.0	0.010178045	0.57735027	0.001270171	0.005773503	0.00069582	0.96596438
IHNC 3.0	0.018282759	0.28867513	0.0006	0.005773503	0.00060382	1.73515582

<i>Silver</i>	Coefficient of Variation					
ID	Ce	Sln Vol	AC Mass	pH	X/M	% Removal
IHNC 0.1	0.018991487	0.00287716	0.006075672	0.001273567	0.01990208	0.01774786
IHNC 0.5	0.022187705	0.00287716	0.002691048	0	0.01720088	0.01805828
IHNC 1.0	0.002629312	0.00286763	0.00032138	0.001258758	0.00492998	0.00192397
IHNC 2.0	0.025651751	0.00573527	0.000635001	0.001245184	0.02104654	0.01549432
IHNC 3.0	0.054666055	0.00286289	0.000200013	0.001227534	0.02497699	0.02542018

## B.2 Organics

### B.2.1 Aroclor 1016

Table B.11 Aroclor 1016 activated carbon batch sorption test data

Sample ID	Ce (µg/L)	log(Ce)	Sln Mass (g)	Sln Vol (L)	AC Mass (g)	pH	X/M (µg/g)	log (X/M)	% Removal	1/Ce (L/µg)	M/X (g/µg)
IHNC_Aroclor1016_IC	192.00				0	4.93					
IHNC_Aroclor1016_0.1_1	0.63	-0.20	1008.5	1.0085	0.1003	4.7	1924.1939	3.2842488	99.671875	1.5873016	0.0005197
IHNC_Aroclor1016_0.1_2	0.48	-0.32	1013.0	1.0130	0.1003	5.97	1934.2947	3.2865226	99.75	2.0833333	0.000517
IHNC_Aroclor1016_0.5_1	1.40	0.15	996.5	0.9965	0.4995	6.48	380.24605	2.5800647	99.270833	0.7142857	0.0026299
IHNC_Aroclor1016_0.5_2	1.11	0.05	1033.5	1.0335	0.5015	6.49	393.38946	2.5948227	99.421875	0.9009009	0.002542
IHNC_Aroclor1016_1.0_1	3.02	0.48	974.0	0.974	1.0013	6.8	183.82754	2.2644106	98.427083	0.3311258	0.0054399
IHNC_Aroclor1016_1.0_2	2.34	0.37	1013.5	1.0135	1.0002	7.01	192.18197	2.2837126	98.78125	0.4273504	0.0052034
IHNC_Aroclor1016_2.0_1	5.01	0.70	1029.5	1.0295	1.9996	7.33	96.272357	1.9835016	97.390625	0.1996008	0.0103872
IHNC_Aroclor1016_2.0_2	5.51	0.74	973.0	0.973	1.9976	7.24	90.836389	1.9582599	97.130208	0.1814882	0.0110088
IHNC_Aroclor1016_3.0_1	7.46	0.87	1031.0	1.031	2.9988	7.4	63.445625	1.8024017	96.114583	0.1340483	0.0157615
IHNC_Aroclor1016_3.0_2	6.96	0.84	980.0	0.98	2.9999	7.81	60.448415	1.7813849	96.375	0.1436782	0.016543



Table B.12 Statistical parameters Aroclor 1016 activated carbon batch sorption test data

<i>Aroclor 1016</i>		Mean				
ID	Ce (mg/L)	Sln Vol (mL)	AC Mass (g)	pH	X/M (mg/g)	% Removal
IHNC_0.1	0.555	1010.75	0.1003	5.335	1929.24429212	99.7109375
IHNC_0.5	1.255	1015	0.5005	6.485	386.81775383	99.3463542
IHNC_1.0	2.68	993.75	1.00075	6.905	188.00475890	98.6041667
IHNC_2.0	5.26	1001.25	1.9986	7.285	93.55437282	97.2604167
IHNC_3.0	7.21	1005.5	2.99935	7.605	61.94701993	96.2447917

<i>Aroclor 1016</i>		Standard Deviation				
ID	Ce (mg/L)	Sln Vol (mL)	AC Mass (g)	pH	X/M (mg/g)	% Removal
IHNC_0.1	0.10606602	3.1819805	0	0.898025612	7.14237773	0.0552427
IHNC_0.5	0.20506097	26.1629509	0.00141421	0.007071068	9.29379828	0.1068026
IHNC_1.0	0.48083261	27.9307179	0.00077782	0.148492424	5.90747369	0.2504337
IHNC_2.0	0.35355339	39.9515331	0.00141421	0.06363961	3.84381005	0.1841424
IHNC_3.0	0.35355339	36.0624458	0.00077782	0.28991378	2.11934749	0.1841424

<i>Aroclor 1016</i>		Coefficient of Variation				
ID	Ce	Sln Vol	AC Mass	pH	X/M	% Removal
IHNC_0.1	0.19110994	0.00314814	0	0.1683272	0.00370216	0.0005540
IHNC_0.5	0.16339519	0.02577631	0.00282560	0.001090373	0.02402630	0.0010751
IHNC_1.0	0.17941515	0.02810638	0.00077723	0.021505058	0.03142194	0.0025398
IHNC_2.0	0.06721547	0.03990166	0.00070760	0.008735705	0.04108638	0.0018933
IHNC_3.0	0.04903653	0.03586519	0.00025933	0.03812147	0.03421226	0.0019133

## B.2.2 DOC

Table B.13 DOC activated carbon batch sorption test data

Sample ID	Ce (mg/L)	log(Ce)	Sln Mass (g)	Sln Vol (L)	AC Mass (g)	pH	X/M (mg/g)	log (X/M)	% Removal	1/Ce (L/mg)	M/X (g/mg)
IHNC_DOC_IC	8.95				0	6.84					
IHNC_DOC_0.1_1	7.70	0.89	98.0	0.098	0.1016	7.7	1.202385443	0.08004371	13.92911813	0.129824311	0.831680062
IHNC_DOC_0.1_2	7.95	0.90	97.0	0.097	0.1003	8.3	0.968043943	-0.014104928	11.18501447	0.125813148	1.033010957
IHNC_DOC_0.1_3	7.77	0.89	100.5	0.1005	0.1018	8.16	1.161698184	0.06509331	13.14883593	0.128657953	0.860808783
IHNC_DOC_0.5_1	7.76	0.89	97.0	0.097	0.5013	8.81	0.229364621	-0.639473571	13.24538784	0.12880114	4.359870308
IHNC_DOC_0.5_2	7.08	0.85	103.0	0.103	0.5031	8.77	0.383431787	-0.416311886	20.92750654	0.141314539	2.608025817
IHNC_DOC_0.5_3	7.12	0.85	102.5	0.1025	0.5029	8.71	0.371946565	-0.429519448	20.39156706	0.140363182	2.688558236
IHNC_DOC_1.0_1	7.31	0.86	100.0	0.1	1.0011	9.06	0.163625124	-0.786150012	18.30373541	0.136776057	6.1115309
IHNC_DOC_1.0_2	7.36	0.87	110.5	0.1105	0.9978	9.06	0.176550237	-0.753131696	17.81401466	0.135961051	5.664110221
IHNC_DOC_1.0_3	7.22	0.86	105.5	0.1055	0.9999	9.07	0.182566974	-0.738577784	19.33475195	0.13852425	5.477441951
IHNC_DOC_2.0_1	8.62	0.94	101.5	0.1015	2.0007	8.97	0.016718358	-1.776806378	3.682322584	0.116012899	59.81448643
IHNC_DOC_2.0_2	7.33	0.87	101.0	0.101	1.9999	8.98	0.081582555	-1.088402698	18.05080142	0.136353902	12.25752246
IHNC_DOC_2.0_3	8.10	0.91	102.0	0.102	2.0003	8.86	0.043310622	-1.363405577	9.490774752	0.123458055	23.08902408
IHNC_DOC_3.0_1	9.20	0.96	103.0	0.103	2.999	9.08	-0.008694872	----	-2.828881287	0.108666873	-115.0103163
IHNC_DOC_3.0_2	9.05	0.96	106.0	0.106	3.0018	9.05	-0.0037278	----	-1.179616387	0.110438183	-268.2547192
IHNC_DOC_3.0_3	6.11	0.79	103.5	0.1035	2.9998	9.3	0.097905691	-1.009192061	31.70824239	0.163622864	10.21391081

Table B.14 Statistical parameters DOC activated carbon batch sorption test data

<i>DOC</i>	Mean					
ID	Ce (mg/L)	Sln Vol (mL)	AC Mass (g)	pH	X/M (mg/g)	% Removal
IHNC_0.1	7.807853176	98.5	0.101233333	8.053333333	1.11070919	12.75432284
IHNC_0.5	7.32156485	100.8333333	0.502433333	8.763333333	0.328247658	18.18815381
IHNC_1.0	7.295073793	105.3333333	0.9996	9.063333333	0.174247445	18.48416734
IHNC_2.0	8.017835016	101.5	2.0003	8.936666667	0.047203845	10.40796625
IHNC_3.0	8.122963729	104.1666667	3.0002	9.143333333	0.02849434	9.233248237

<i>DOC</i>	Standard Deviation					
ID	Ce (mg/L)	Sln Vol (mL)	AC Mass (g)	pH	X/M (mg/g)	% Removal
IHNC_0.1	0.1265383	1.802775638	0.000814453	0.313900196	0.125215385	1.413950724
IHNC_0.5	0.383828949	3.329164059	0.000986577	0.05033223	0.085827553	4.288940355
IHNC_1.0	0.069469485	5.251983752	0.001670329	0.005773503	0.009678613	0.776258487
IHNC_2.0	0.646854898	0.5	0.0004	0.066583281	0.032606884	7.228016755
IHNC_3.0	1.743441444	1.607275127	0.001442221	0.136503968	0.060163276	19.48137675

<i>DOC</i>	Coefficient of Variation					
ID	Ce	Sln Vol	AC Mass	pH	X/M	% Removal
IHNC_0.1	0.016206542	0.018302291	0.008045302	0.038977673	0.112734626	0.110860509
IHNC_0.5	0.052424442	0.033016503	0.001963597	0.005743503	0.261471943	0.235809549
IHNC_1.0	0.009522794	0.049860605	0.001670998	0.000637018	0.055545224	0.041995859
IHNC_2.0	0.080677003	0.004926108	0.00019997	0.007450572	0.690767546	0.694469657
IHNC_3.0	0.214631199	0.015429841	0.000480708	0.014929344	2.111411479	2.109915845

### B.3 Adsorption Isotherms (activated carbon)

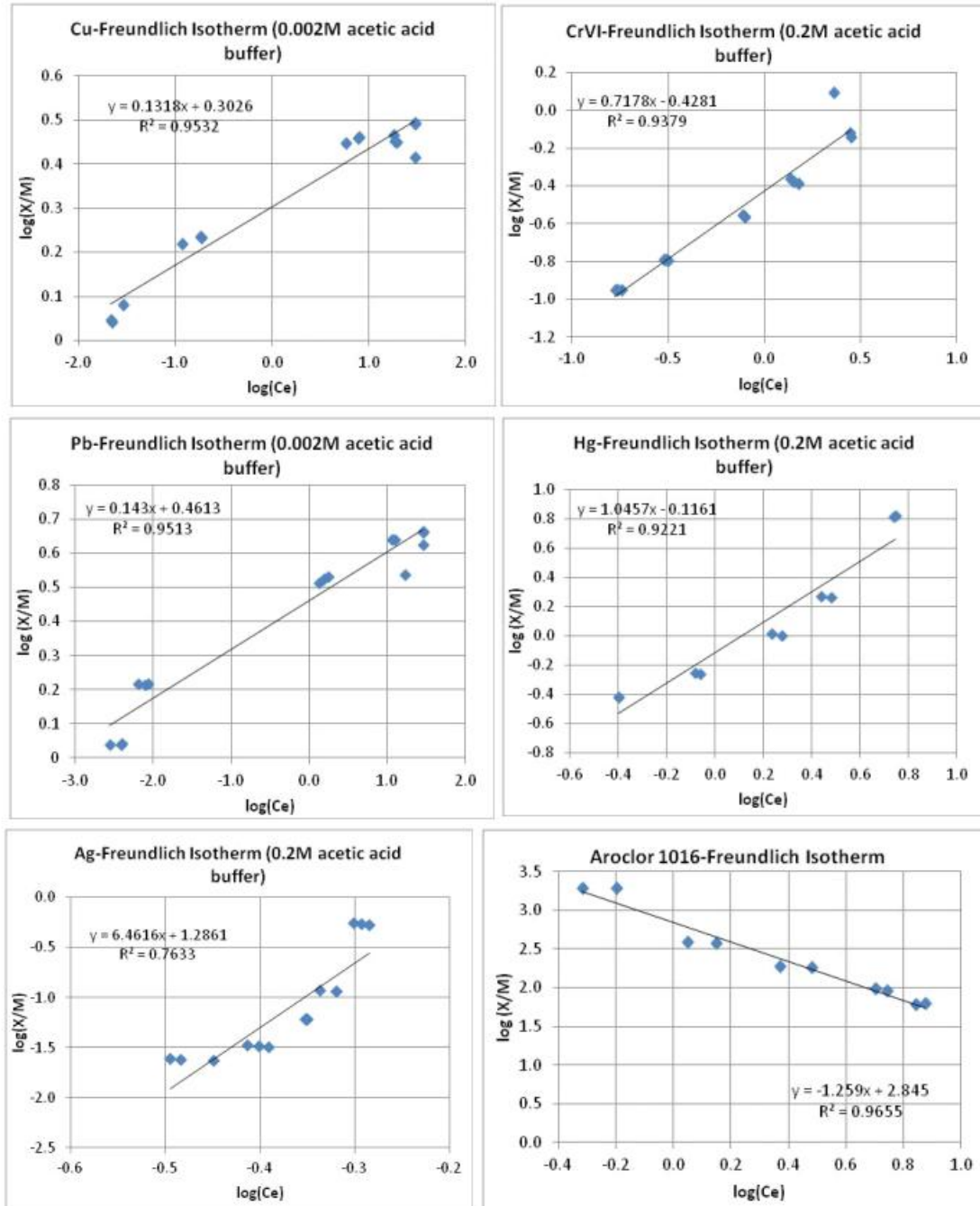


Figure B.1 Freundlich Adsorption Isotherms (activated carbon)

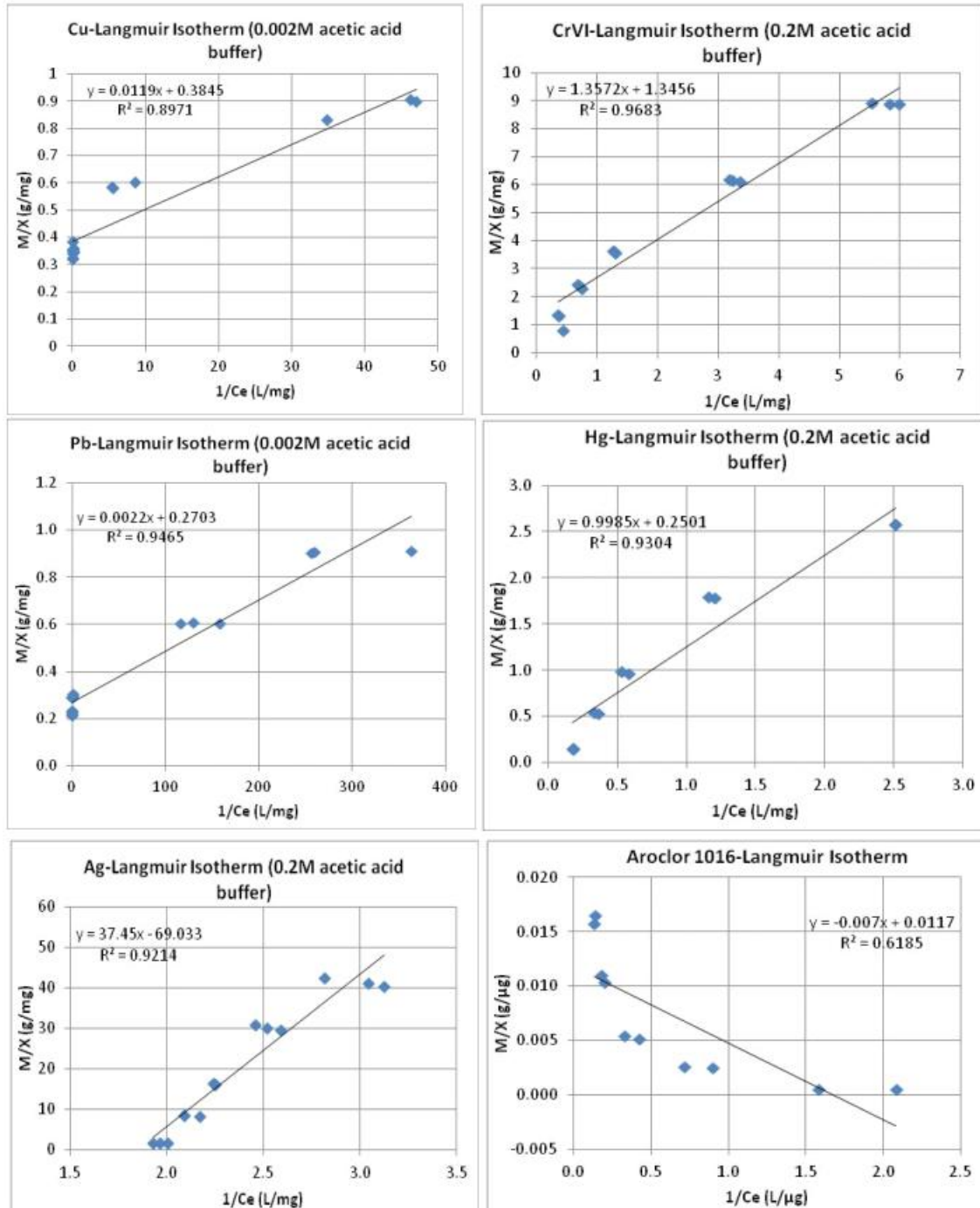


Figure B.2 Langmuir Adsorption Isotherms (activated carbon)

APPENDIX C  
FILTERMAT™ BATCH SORPTION TESTS

## C.1 Metals

### C.1.1 Copper

Table C.1 Copper FilterMat™ batch sorption test data

Sample ID	Ce (mg/L)	log(Ce)	Sln Mass (g)	Sln Vol (L)	AC Mass (g)	Area (in <sup>2</sup> )	pH	X/M (mg/g)	log (X/M)	% Removal	1/Ce (L/mg)	M/X (g/mg)
Cu_IC	30.84						4.58					
Cu_1	26.28	1.42	94.5	0.0945	0.05067198	0.196349541	4.58	8.493540176	0.929088745	14.76841593	0.03804596	0.117736536
Cu_2	21.31	1.33	95.0	0.095	0.10134396	0.392699082	4.59	8.936250326	0.951155326	30.91282495	0.046936604	0.111903759
Cu_3	13.45	1.13	95.5	0.0955	0.202687921	0.785398163	4.59	8.195176729	0.913558324	56.40166459	0.074377092	0.122022994
Cu_4	9.31	0.97	94.5	0.0945	0.304031881	1.178097245	4.62	6.690665105	0.825469292	69.80165379	0.107380629	0.149461972
Cu_5	6.38	0.80	95.0	0.095	0.405375842	1.570796327	4.64	5.73182076	0.758292601	79.31146301	0.156739812	0.174464632

## C.1.2 Chromium VI

Table C.2 Chromium VI FilterMat™ batch sorption test data

Sample ID	Ce (mg/L)	log(Ce)	SIn Mass (g)	SIn Vol (L)	AC Mass (g)	Area (in <sup>2</sup> )	pH	X/M (mg/g)	log (X/M)	% Removal	1/Ce (L/mg)	M/X (g/mg)
CrVI_IC	3.97						4.50					
CrVI_1	3.01	0.48	94.5	0.0945	0.05067198	0.196349541	4.5	1.785365395	0.251727113	24.11418976	0.331931843	0.560109434
CrVI_2	2.29	0.36	95.0	0.095	0.10134396	0.392699082	4.51	1.571397702	0.196286114	42.22502099	0.435983142	0.636376137
CrVI_3	1.45	0.16	95.0	0.095	0.202687921	0.785398163	4.53	1.18018873	0.071951463	63.4256927	0.688705234	0.847322106
CrVI_4	1.02	0.01	94.5	0.0945	0.304031881	1.178097245	4.54	0.918066548	-0.037125837	74.39966415	0.983929157	1.089245656
CrVI_5	0.93	-0.03	94.5	0.0945	0.405375842	1.570796327	4.47	0.708364856	-0.149742993	76.54072208	1.07372942	1.411701881



### C.1.3 Lead

Table C.3 Lead FilterMat™ batch sorption test data

Sample ID	Ce (mg/L)	log(Ce)	Sln Mass (g)	Sln Vol (L)	AC Mass (g)	Area (in <sup>2</sup> )	pH	X/M (mg/g)	log (X/M)	% Removal	I/Ce (L/mg)	M/X (g/mg)
Pb_IC	24.95						4.59					
Pb_1	21.88	1.34	95.0	0.095	0.05067198	0.196349541	4.59	5.758771059	0.760329813	12.31063136	0.045704535	0.17364816
Pb_2	18.62	1.27	96.0	0.096	0.10134396	0.392699082	4.6	5.996844776	0.777922808	25.37205761	0.05370377	0.166754358
Pb_3	14.38	1.16	94.5	0.0945	0.202687921	0.785398163	4.61	4.927316316	0.692610443	42.35578593	0.069526524	0.202950234
Pb_4	11.42	1.06	95.0	0.095	0.304031881	1.178097245	4.6	4.228931498	0.62623065	54.2415903	0.087586126	0.236466351
Pb_5	8.95	0.95	95.0	0.095	0.405375842	1.570796327	4.6	3.749763	0.574003819	64.12750154	0.111723522	0.266683521

## C.1.4 Silver

Table C.4 Silver FilterMa<sup>TM</sup> batch sorption test data

Sample ID	Ce (mg/L)	log(Ce)	Sln Mass (g)	Sln Vol (L)	AC Mass (g)	Area (in <sup>2</sup> )	pH	X/M (mg/g)	log (X/M)	% Removal	1/Ce (L/mg)	M/X (g/mg)
Ag_IC	4.11						4.60					
Ag_1	0.64	-0.19	94.5	0.0945	0.05067198	0.196349541	4.6	6.460759939	0.810283604	84.34507385	1.555209953	0.154780554
Ag_2	0.58	-0.24	96.0	0.096	0.10134396	0.392699082	4.6	3.340702281	0.523837774	85.86268463	1.722158439	0.299338258
Ag_3	0.47	-0.33	95.0	0.095	0.202687921	0.785398163	4.6	1.70700848	0.232235679	88.67067035	2.148997135	0.585820171
Ag_4	0.37	-0.44	94.5	0.0945	0.304031881	1.178097245	4.58	1.162580379	0.065422989	91.06476221	2.72479564	0.86015558
Ag_5	0.35	-0.45	95.0	0.095	0.405375842	1.570796327	4.57	0.879907721	-0.055562871	91.411373154	2.835538752	1.136482811

## C.2 Organics

### C.2.1 DOC

Table C.5 DOC FilterMat™ batch sorption test data

Sample ID	Ce (mg/L)	log(Ce)	Sln Mass (g)	Sln Vol (L)	AC Mass (g)	Area (in <sup>2</sup> )	pH	X/M (mg/g)	log (X/M)	% Removal	I/Ce (L/mg)	M/X (g/mg)
DOC_IC	9.25						6.10					
DOC_1	29.20	1.47	101.5	0.1015	0.05067198	0.196349541	3.23	-39.95431129	---	-215.6237628	0.034250068	-0.025028588
DOC_2	8.28	0.92	99.0	0.099	0.10134396	0.392699082	4.12	0.945936173	-0.024138166	10.4678056	0.120740205	1.057153779
DOC_3	7.70	0.89	101.0	0.101	0.202687921	0.785398163	7.34	0.772468355	-0.112119303	16.75785115	0.129863725	1.294551412
DOC_4	6.82	0.83	102.0	0.102	0.304031881	1.178097245	9.23	0.814214447	-0.089261196	26.23547287	0.146549241	1.228177668
DOC_5	7.36	0.87	101.0	0.101	0.405375842	1.570796327	8.83	0.472103236	-0.325963022	20.48352068	0.135948367	2.118180778

### C.3 Adsorption Isotherms (FilterMat™)

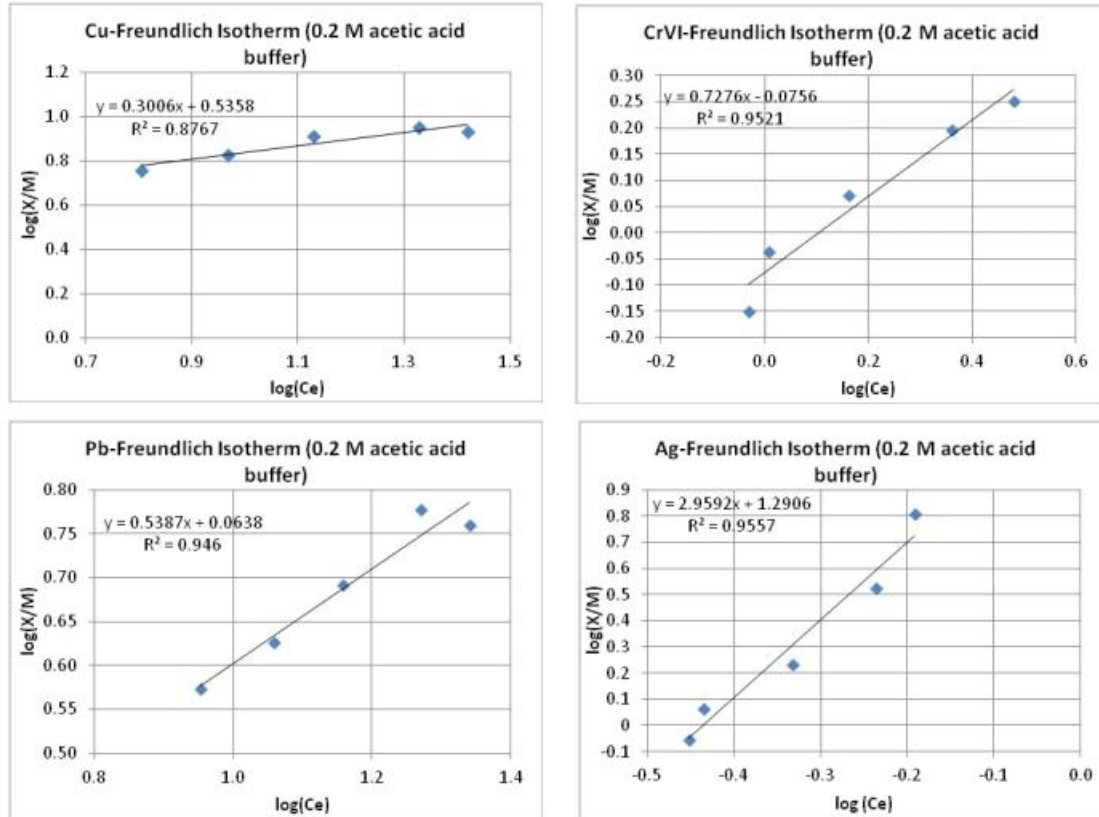


Figure C.1 Freundlich Adsorption Isotherms (FilterMat™)

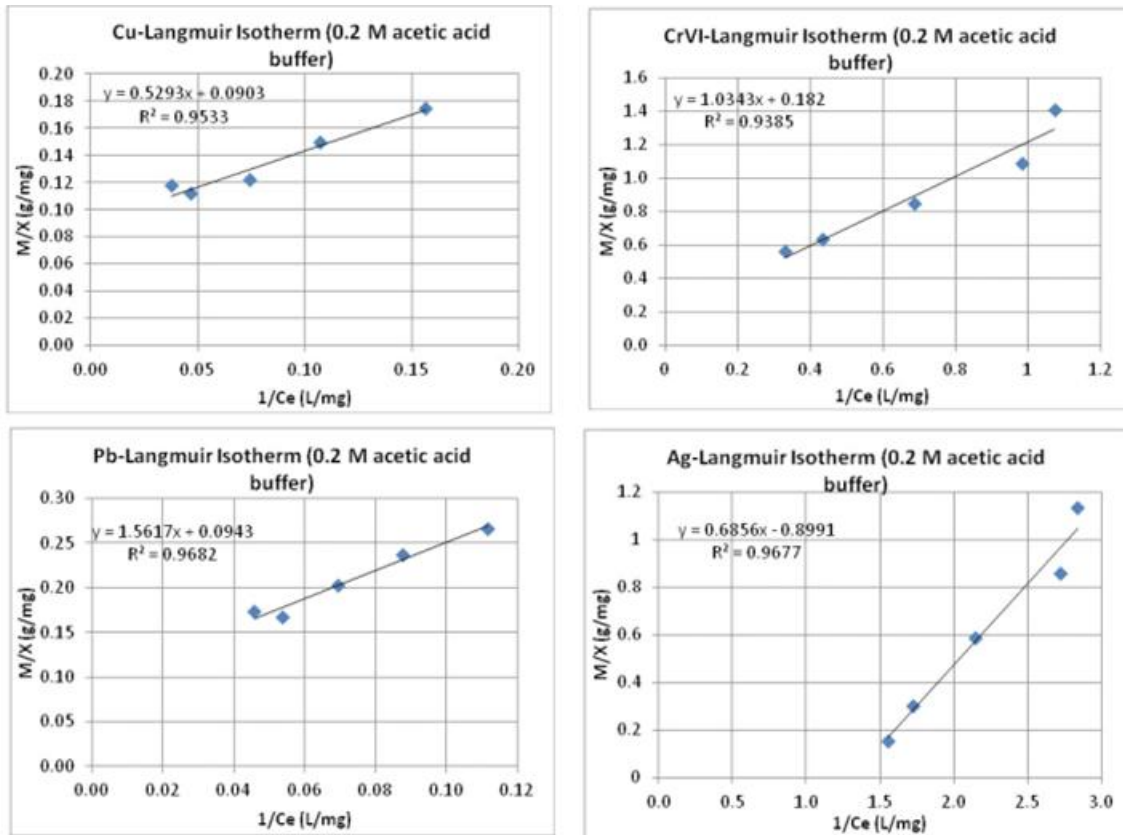


Figure C.2 Langmuir Adsorption Isotherms (FilterMat™)

APPENDIX D  
COLUMN TESTS DATA

## D.1 Copper

Table D.1 Copper column test 4 data

Column 4 (Cu initial concentration = 273.75 µg/L) (Note that the data presented in this table was interpolated from the original data set for comparison purposes)						
Time (mins)	Effluent Cu concentration (µg/L)	Overall removal percentage	Relative removal percentage as % of layer influent	Effluent concentration (as % of column influent)	Cu Mass sorbed by interval (µg)	Cumulative Cu mass sorbed by layer (µg)
<i>Double Curtain layer 1</i>						
7.666667	148.1833333	45.86910198	45.86910198	54.13089802	167.6555096	167.6555096
27.666667	176.9083333	35.37595129	35.37595129	64.62404871	225.6759228	393.3314324
47.666667	238.2416667	12.97108067	12.97108067	87.02891933	129.7361974	523.0676298
67.666667	258.0666667	5.729071537	5.729071537	94.27092846	78.1231238	601.1907536
87.666667	267.2083333	2.389649924	2.389649924	97.61035008	42.34781469	643.5385683
107.66667	285.8833333	-4.432267884	-4.432267884	104.4322679	14.9037485	658.4423168
127.66667	288.3583333	-5.336377473	-5.336377473	105.3363775	-7.375272737	651.0670441
147.66667	288.8166667	-5.503805175	-5.503805175	105.5038052	-26.13233449	624.9347096
167.66667	280.5416667	-2.480974125	-2.480974125	102.4809741	-42.33196323	582.6027464
187.66667	288.5117216	-5.392409721	-5.392409721	105.3924097	-56.58934625	526.0134001
<i>Double Curtain Layer 2</i>						
7.666667	80.0975	70.74063927	45.94702508	29.25936073	35.58057233	35.58057233
27.666667	54.35958333	80.14261796	69.27245749	19.85738204	251.8762439	287.4568162
47.666667	105.7583333	61.36681887	55.60880059	38.63318113	271.7259692	559.1827855
67.666667	216.175	21.03196347	16.23288556	78.96803653	247.2490429	806.4318283
87.666667	244.025	10.85844749	8.676126618	89.14155251	206.934352	1013.36618
107.66667	220.5791667	19.42313546	22.84294293	80.57686454	158.2884182	1171.654598
127.66667	226.3083333	17.33028919	21.51836546	82.66971081	104.4774394	1276.132038
147.66667	279.4	-2.063926941	3.260430492	102.0639269	47.14450115	1323.276539
167.66667	288.275	-5.305936073	-2.756572108	105.3059361	-12.74587011	1310.530669
187.66667	290.2441417	-6.025257238	-0.600467831	106.0252572	-74.57848709	1235.952182
<i>Double Curtain Layer 3</i>						
7.666667	50.95777778	81.38528666	36.38031427	18.61471334	62.03390694	62.03390694
27.666667	22.19	91.89406393	59.17923089	8.105936073	147.4201667	209.4540736
47.666667	56.46666667	79.37290715	46.60783232	20.62709285	126.5901667	336.0442403
67.666667	95.98666667	64.93637747	55.59770248	35.06362253	105.7601667	441.8044069
87.666667	178.0333333	34.96499239	27.04299423	65.03500761	84.93016667	526.7345736
107.66667	245.4666667	10.33181126	-11.28279718	89.66818874	64.10016667	590.8347403
127.66667	265.3666667	3.062404871	-17.25890194	96.93759513	43.27016667	634.1049069
147.66667	270.4666667	1.199391172	3.197327607	98.80060883	22.44016667	656.5450736
167.66667	301.6	-10.17351598	-4.622322435	110.173516	1.610166667	658.1552403
187.66667	300.570991	-9.79762228	-3.557987163	109.7976223	-19.21983333	638.9354069

Table D.2 Copper column test 5 data

Column 5 (Cu initial concentration = 299.7 µg/L)						
(Note that the data presented in this table was interpolated from the original data set for comparison purposes)						
Time (mins)	Effluent Cu concentration (µg/L)	Overall removal percentage	Relative removal percentage as % of layer influent	Effluent concentration (as % of column influent)	Cu Mass sorbed by interval (µg)	Cumulative Cu mass sorbed by layer (µg)
<i>Double Curtain Layer 1</i>						
7.666667	143.24	52.20553887	52.20553887	47.79446113	138.9179141	138.9179141
27.666667	250.96	16.2629296	16.2629296	83.7370704	214.8408447	353.7587588
47.666667	255.095	14.88321655	14.88321655	85.11678345	147.9670584	501.7258173
67.666667	252.5	15.74908242	15.74908242	84.25091758	111.9907031	613.7165204
87.666667	276.175	7.849516183	7.849516183	92.15048382	87.0538965	700.7704168
107.66667	262.32	12.47247247	12.47247247	87.52752753	67.92429601	768.6947129
127.66667	294.495	1.736736737	1.736736737	98.26326326	52.39493632	821.0896492
147.66667	281.875	5.947614281	5.947614281	94.05238572	39.3205218	860.410171
167.66667	290.35	3.119786453	3.119786453	96.88021355	28.02873932	888.4389103
187.66667	292.4754513	2.410593506	2.410593506	97.58940649	18.09077899	906.5296893
<i>Double Curtain Layer 2</i>						
7.666667	76.73775	74.39514515	46.42715024	25.60485485	95.90044211	95.90044211
27.666667	65.659	78.09175843	73.83686643	21.90824157	352.2759053	448.1763474
47.666667	66.95	77.66099433	73.75487563	22.33900567	353.4346916	801.611039
67.666667	137.52	54.11411411	45.53663366	45.88588589	323.6960469	1125.307086
87.666667	205.6925	31.36720053	25.52095592	68.63279947	282.9178535	1408.224939
107.66667	165.4525	44.79396063	36.92722629	55.20603937	236.332454	1644.557393
127.66667	222.715	25.68735402	24.37392825	74.31264598	186.1468137	1830.704207
147.66667	282.0325	5.895061728	-0.055875831	94.10493827	133.5062282	1964.210435
167.66667	278.9725	6.916082749	3.918546582	93.08391725	79.08301068	2043.293446
187.66667	253.52641	15.40660326	13.3170292	84.59339674	23.30597101	2066.599417
<i>Double Curtain Layer 3</i>						
7.666667	58.57	80.45712379	23.67511427	19.54287621	50.09106111	50.09106111
27.666667	38.27	87.2305639	41.71400722	12.7694361	118.8379167	168.9289778
47.666667	11.36	96.20954288	83.03211352	3.790457124	101.7279167	270.6568944
67.666667	51.88	82.68935602	62.27457824	17.31064398	84.61791667	355.2748111
87.666667	101.2	66.23289957	50.80034518	33.76710043	67.50791667	422.7827278
107.66667	192.8	35.66900234	-16.52891313	64.33099766	50.39791667	473.1806444
127.66667	232.7	22.35568902	-4.483308264	77.64431098	33.28791667	506.4685611
147.66667	234.6	21.72172172	16.81809721	78.27827828	16.17791667	522.6464778
167.66667	247.1	17.55088422	11.42496124	82.44911578	-0.932083333	521.7143944
187.66667	270.5	9.74307641	-6.694998746	90.25692359	-18.04208333	503.6723111



Table D.3 Copper column test 6 data

Column 6 (Cu initial concentration = 299.7 µg/L)						
(Note that the data presented in this table was interpolated from the original data set for comparison purposes)						
Time (mins)	Effluent Cu concentration (µg/L)	Overall removal percentage	Relative removal percentage as % of layer influent	Effluent concentration (as % of column influent)	Cu Mass sorbed by interval (µg)	Cumulative Cu mass sorbed by layer (µg)
<i>Double Curtain Layer 1</i>						
7.666667	185.9070833	37.96894116	37.96894116	62.03105884	166.40911	166.4091106
27.666667	200.95575	32.9476977	32.9476977	67.0523023	249.91047	416.3195757
47.666667	242.1054167	19.21741186	19.21741186	80.78258814	166.42786	582.7474339
67.666667	271.1263333	9.534089645	9.534089645	90.46591035	121.51639	704.2638237
87.666667	269.0706667	10.21999778	10.21999778	89.78000222	90.38626	794.650084
107.66667	274.4769167	8.416110555	8.416110555	91.58388945	66.505619	861.1557028
127.66667	295.0751667	1.543154265	1.543154265	98.45684573	47.119376	908.2750792
147.66667	298.0184167	0.561088867	0.561088867	99.43891113	30.797791	939.0728702
167.66667	294.79375	1.63705372	1.63705372	98.36294628	16.701574	955.7744437
187.66667	281.1690332	6.183172108	6.183172108	93.81682789	4.2954143	960.0698581
<i>Double Curtain Layer 2</i>						
7.666667	92.523075	69.1281031	50.23154936	30.8718969	71.58858	71.58858032
27.666667	49.49453333	83.48530753	75.37043188	16.51469247	325.00912	396.5976986
47.666667	113.0690833	62.27257813	53.29758215	37.72742187	342.06673	738.6644238
67.666667	115.0041667	61.62690468	57.58281195	38.37309532	320.55319	1059.217617
87.666667	188.497	37.10477144	29.9451693	62.89522856	285.25832	1344.47594
107.66667	163.275	45.52052052	40.51412338	54.47947948	242.71396	1587.189905
127.66667	243.9430833	18.60424313	17.32849427	81.39575687	195.67521	1782.865112
147.66667	240.36125	19.79938272	19.34684685	80.20061728	145.57179	1928.436904
167.66667	284.8515833	4.954426649	3.372583939	95.04557335	93.24301	2021.679914
187.66667	284.3536378	5.120574658	-1.132629907	94.87942534	39.224169	2060.904083
<i>Double Curtain Layer 3</i>						
7.666667	67.29	77.54754755	24.64382564	22.45245245	49.79526	49.79525955
27.666667	21.11	92.95628962	61.09661086	7.043710377	119.03904	168.8343012
47.666667	26.21	91.25458792	76.84919681	8.745412079	107.89904	276.7333429
67.666667	92.53	69.12579246	23.22189516	30.87420754	96.759042	373.4923845
87.666667	120.2	59.89322656	35.585984	40.10677344	85.619042	459.1114262
107.66667	202.7	32.36569903	-19.71054056	67.63430097	74.479042	533.5904679
127.66667	210.4	29.79646313	13.65528737	70.20353687	63.339042	596.9295095
147.66667	250.4	16.44978312	-2.750114614	83.55021688	52.199042	649.1285512
167.66667	284	5.238571905	0.285883677	94.76142809	41.059042	690.1875929
187.66667	297.2	0.834167501	-3.68896644	99.1658325	29.919042	720.1066345

Table D.4 Statistical parameter copper column test data (effluent concentration and cumulative mass sorbed)

Time (mins)	Mean		Standard Deviation		Coefficient of variation	
	Effluent Cu concentration (µg/L)	Cumulative Cu mass sorbed by layer (µg)	Effluent Cu concentration (µg/L)	Cumulative Cu mass sorbed by layer (µg)	Effluent Cu concentration	Cumulative Cu mass sorbed by layer
<b>Double Curtain Layer 1</b>						
7.666667	159.11014	157.66084	23.338087	16.243813	0.1466788	0.1030301
27.666667	209.60803	387.80326	37.776431	31.64466	0.1802242	0.0815998
47.666667	245.14736	535.84696	8.8288607	41.995346	0.0360145	0.0783719
67.666667	260.56433	639.7237	9.5610579	56.243173	0.0366937	0.0879179
87.666667	270.818	712.98636	4.731824	76.29282	0.0174723	0.1070046
107.66667	274.22675	762.76424	11.783658	101.48673	0.0429705	0.1330512
127.66667	292.64283	793.47726	3.7218078	130.80836	0.0127179	0.1648546
147.66667	289.57003	808.13925	8.0980331	163.46218	0.0279657	0.2022698
167.66667	288.56181	808.9387	7.2923727	198.88311	0.0252714	0.2458568
187.66667	287.3854	797.53765	5.7367429	236.6658	0.0199618	0.2967456
<b>Double Curtain Layer 2</b>						
7.666667	83.119442	67.689865	8.3152402	30.348339	0.1000397	0.4483439
27.666667	56.504372	377.41029	8.2929238	82.059792	0.1467661	0.2174286
47.666667	95.259139	699.81942	24.787442	125.79573	0.2602106	0.1797546
67.666667	156.23306	996.98551	53.117965	168.30028	0.3399918	0.1688092
87.666667	212.73817	1255.3557	28.426585	211.97918	0.1336224	0.1688599
107.66667	183.10222	1467.8006	32.474242	258.06901	0.1773558	0.1758202
127.66667	230.98881	1629.9005	11.36169	307.30476	0.0491872	0.188542
147.66667	267.26458	1738.6413	23.336121	360.16086	0.0873147	0.2071508
167.66667	284.03303	1791.8347	4.7049603	416.96157	0.0165648	0.2327009
187.66667	276.0414	1787.8186	19.719736	477.93879	0.0714376	0.2673307
<b>Double Curtain Layer 3</b>						
7.666667	58.939259	53.973409	8.1723702	6.9821625	0.1386575	0.129363
27.666667	27.19	182.40578	9.610744	23.424554	0.3534661	0.12842
47.666667	31.345556	294.47816	22.987677	36.12527	0.7333632	0.1226755
67.666667	80.132222	390.19053	24.52811	45.617583	0.3060955	0.116911
87.666667	133.14444	469.54291	40.018861	52.755175	0.3005673	0.1123543
107.66667	213.65556	532.53528	27.990402	58.834145	0.1310071	0.1104793
127.66667	236.15556	579.16766	27.645782	65.645805	0.117066	0.1133451
147.66667	251.82222	609.44003	17.97558	75.256842	0.071382	0.1234852
167.66667	277.56667	623.35241	27.813726	89.466376	0.1002056	0.1435246
187.66667	289.42366	620.90478	16.47482	109.33792	0.0569228	0.1760945

Table D.5 Statistical parameter copper column test data (mass sorbed by the system, mass through the system, % mass sorbed)

<b>Parameter</b>	<b>Mean</b>	<b>Standard Deviation</b>	<b>Coefficient of variation</b>
Total Cu mass sorbed ( $\mu\text{g}$ )	3214.3098	719.0429	0.2237006
Total Cu mass through the system ( $\mu\text{g}$ )	6846.2792	368.75208	0.0538617
% Cu mass sorbed	46.657268	8.2360311	0.1765219

## D.2 Aroclor 1016

Table D.6 Aroclor 1016 column test data

Time (mins)	Influent Concentration (µg/L)	Effluent Concentration (µg/L)	Overall Removal %	Effluent concentration (as % of column influent)
Column Test 2				
10	0.093	0	100	0
720	0.081	0	100	0
1440	0.095	0	100	0
2160	0.095	0	100	0
2880	0.059	0.006	89.8	10.2
3600	0.044	0.0037	91.6	8.4
Column Test 3				
10	0.08	0	100	0
720	0.08	0	100	0
1440	0.07	0	100	0
2160	0.05	0	100	0
2880	0.05	0	100	0
3600	0.05	0	100	0
5040	0.06	0	100	0
6480	0.09	0	100	0
7920	0.07	0	100	0
8880	0.06	0	100	0
Column Test 4				
10	0.07	0	100	0
720	0.09	0	100	0
1440	0.03	0	100	0
2160	0.05	0	100	0
2880	0.06	0	100	0
3600	0.06	0	100	0