

ADSORPTION CURVE FITS FOR LANDFILL VOCS ON BITUMINOUS COAL  
BASED AND COCONUT SHELL BASED ACTIVATED CARBON

by

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## ABSTRACT

### ADSORPTION CURVE FITS FOR LANDFILL VOCS ON BITUMINOUS COAL BASED AND COCONUT SHELL BASED ACTIVATED CARBON

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This study explores adsorption as a method of controlling hazardous gas emissions from Municipal Solid Waste Landfills (MSWL). In particular, the hazardous air pollutants (HAPs) *para*, *meta*, and *ortho*-xylene, ethylbenzene and methyl ethyl ketone are selected for experimental study.

Activated carbon is a good adsorbent and well known for its high surface area. Among the many varieties of activated carbon, bituminous coal based activated carbon (BPL) and coconut shell based activated carbon (OVC) are compared in this study.

Each experiment was conducted in a vial with a known amount of carbon in it. The pollutant concentration remaining in the vial headspace at equilibrium was measured using gas chromatography (GC), model SRIGC8610. PeakSimple software associated with the GC was used for plotting chromatograms of concentration vs time.

Adsorption curve fits of Langmuir and Freundlich isotherms were determined for each compound and each type of activated carbon and compared with the measured adsorbed values to find the best isotherm curve fits for these compounds. Linear and non-linear approaches were used for finding isotherm constants.

This study found that bituminous coal based activated carbon is more effective than coconut shell based activated carbon for the compounds tested, which is likely due to its different physical structure and the properties of the compounds. The non-linear approach of finding the constants is found to be better than linear analysis.

For OVC, MEK, ethylbenzene and para xylene fit Freundlich isotherm (FI) better, whereas ortho- xylene fit Langmuir isotherm (LI) better. For BPL, MEK, and ethylbenzene follow FI and para and ortho-xylene isomers follow LI.. For BPL and OVC, meta-xylene fits for both LI and FI.

## TABLE OF CONTENTS

ACKNOWLEDGMENTS .....	ii
ABSTRACT .....	iv
LIST OF ILLUSTRATIONS.....	x
LIST OF TABLES.....	xii

### Chapter

1. INTRODUCTION.....	1
2. BACKGROUND AND LITERATURE REVIEW.....	8
2.1 Municipal Solid Waste Landfills .....	8
2.1.1 Landfill Gas Emissions.....	9
2.1.2 Gas Emission Control .....	11
2.2 Hazardous Air Pollutants (HAPs).....	12
2.2.1 Xylene.....	12
2.2.2 Ethylbenzene.....	14
2.2.3 Methyl Ethyl Ketone.....	14
2.3 Adsorption.....	15
2.3.1 Adsorption Mechanism.....	15
2.3.2 Types of Adsorption .....	16
2.3.3 Adsorption Isotherms.....	17
2.3.3.1 Langmuir Isotherm Equation .....	18

2.3.3.2 Freundlich Isotherm Equation .....	18
2.4 Activated Carbon.....	18
2.4.1 Adsorption Properties of Activated Carbon .....	19
2.4.2 Comparison of Activated Carbon .....	20
2.4.3 Reactivation of Carbon .....	21
2.5 Gas Chromatography .....	22
2.5.1 History.....	22
2.5.2 Components .....	23
2.5.2.1 Carrier Gas .....	24
2.5.2.2 Support Gas .....	24
2.5.2.3 Inject Port .....	24
2.5.2.4 Column .....	24
2.5.2.5 Oven .....	25
2.5.2.6 Flame Ionization Detector .....	25
2.5.2.7 Regulator .....	27
2.6 Summary of Literature Review .....	27
2.7 Conclusion.....	33
3. METHODOLOGY.....	34
3.1 Equipment Used.....	34
3.1.1 Gas Chromatograph .....	34
3.1.2 Peaksimple Software .....	36
3.1.3 Other apparatus .....	37

3.2 Adsorbents.....	38
3.3 Volatile Organic Compounds .....	38
3.4 Experimental Procedure.....	39
4. RESULTS AND DISCUSSION.....	42
4.1 Results.....	42
4.1.1 Replicates.....	42
4.1.2 Adsorption Isotherms.....	43
4.2 Discussion.....	56
4.2.1 Adsorption Capacity....	56
4.2.1.1 Micropores and Macropores .....	57
4.2.1.2 Shape .....	58
4.2.1.3 Molecular weight .....	58
4.2.1.3 Volatility .....	58
4.2.2 Comparison of Maximum Adsorption Capacities With Langmuir $Q_0$ .....	59
4.2.3 Isotherm Studies .....	60
4.2.4 Similarities and Differences Compared to Manufacturer Isotherms .....	61
5. CONCLUSIONS AND RECOMMENDATIONS.....	62
5.1 Conclusion.....	62
5.2 Recommendations.....	63



## Appendix

A. SUMMARY OF LANDFILL GAS PRODUCTION AND EMISSION.....	65
B. HAZARDOUS AIR POLLUTANTS LIST.....	73
C. FORMULAS AND CALCULATIONS.....	81
D. EXPERIMENTAL DATA AND PLOT.....	84
REFERENCES.....	105
BIOGRAPHICAL INFORMATION.....	114

## LIST OF ILLUSTRATIONS

Figure	Page
2.1 Chemical structure of xylene isomers .....	13
2.2 Chemical structure of ethylbenzene .....	14
2.3 Chemical structure of methyl ethyl ketone .....	15
2.4 Adsorption mechanis .....	16
2.5 Typical adsorption isotherm.....	17
2.6 Schematic diagram of GC .....	23
2.7 Schematic diagram of FID .....	25
2.8 Regulator .....	27
3.1 GC setup in the lab .....	35
3.2 Capillary column and fid detector .....	35
3.3 Peaks for injected compounds in the GC .....	36
3.4 Miscellaneous apparatus used .....	37
3.5 Cylinder contains BTEX standard.....	39
4.1 Comparison of runs for ortho-xylene tested with BPL .....	42
4.2 Adsorption isotherm for ethylbenzene tested with BPL .....	44
4.3 Adsorption isotherm for ethylbenzene tested with OVC .....	45
4.4 Adsorption isotherm for methyl ethyl ketone tested with BPL.....	46
4.5 Adsorption isotherm for methyl ethyl ketone tested with OVC .....	47
4.6 Adsorption isotherm for meta-xylene tested with BPL.....	48

4.7	Adsorption isotherm for meta-xylene tested with OVC.....	49
4.8	Adsorption isotherm for para-xylene tested with BPL.....	50
4.9	Adsorption isotherm for <i>para</i> -xylene tested with OVC.....	51
4.10	Adsorption isotherm for ortho-xylene tested with BPL.....	52
4.11	Adsorption isotherm for ortho-xylene tested with OVC.....	53

## LIST OF TABLES

Table	Page
2.1 Hazardous Air Pollutants and their CAS Numbers .....	12
2.2 Comparison of Coconut Shell Based and Bituminous Coal Based Activated Carbon .....	20
2.3 Detectors And Their Purpose .....	26
2.4 Articles Related To Activated Carbon Adsorption .....	27
2.5 Articles Related To Regeneration .....	30
2.6 Article Related to Gas Chromatography .....	31
2.7 Article Related to Landfill.....	32
4.1 Articles Related To Activated Carbon Adsorption .....	54
4.2 Empirical Constants Comparison for Replicates .....	55
4.3 Experimental Maximum Adsorption Capacities (g VOC adsorbed/g carbon)	56
4.4 Comparison of Experimentally Determined Maximum Adsorption Capacities with Langmuir Isotherm Maximum Adsorption Capacities .....	56

## CHAPTER 1

### INTRODUCTION

Air and water are essential for living organisms. Nowadays, they are highly polluted by natural and human activities. Nitrogen and oxygen are the main constituents of air with concentrations of 78% and 21% by volume, respectively. Gases other than  $N_2$ ,  $O_2$ , Ar, and  $H_2O$  are known as trace gases and they constitute less than one percent of Earth's atmosphere.

Contamination of air, called air pollution, changes the natural characteristics and composition of air. It can be defined as any atmospheric condition where the constituents of air are present at concentrations higher or lower than their normal ambient levels, which produce measurable effects on human beings, animals, vegetation and materials (Cooper and Alley, 1986). Significant air pollutants include ground level ozone ( $O_3$ ), carbon monoxide (CO), carbon dioxide ( $CO_2$ ), chlorofluorocarbons (CFCs), hazardous air pollutants (HAPs), lead (Pb), nitrogen dioxide ( $NO_2$ ), particulate matter (PM), sulfur dioxide ( $SO_2$ ) and volatile organic compounds (VOCs). This paper deals with the hazardous air pollutants that accumulate in the air and cause concern to living organisms.

HAPs are chemicals that cause severe health impacts such as cancer or nervous system impacts. The sources of HAPs are classified into mobile and stationary sources. Landfills are one of the stationary sources of HAPs; they are the places where unwanted

solid wastes are dumped. In earlier times, solid wastes were disposed on open land. The Resource Conservation and Recovery Act (RCRA) of 1976 prohibited the open dumping method. Even now, developing countries and some places in developed countries still use the open dumping method.

Landfills are classified according to the type of wastes they receive, such as hazardous waste, designated waste and municipal solid waste landfills (MSWL). This paper concentrates on MSWL, which is defined as a unit that receives waste from residential, commercial and institutional sources. In the United States in 1995, 2500 active MSWL were estimated and the average capacity of each landfill was 208 million tons of waste per annum.

Solid wastes produce landfill gases (LFG) by three processes: bacterial decomposition, volatilization, and chemical reactions. Bacterial decomposition takes place in four different phases. In phase one, aerobic bacteria consume available oxygen and break down protein, lipids and complex carbohydrates into simpler forms and produce carbon dioxide. Phases other than phase one are anaerobic processes. In phase two, bacteria consume phase one byproducts and produce organic acids. In phase three, methane production begins. In phase four, decomposition and production rates are roughly equal and this introduces a steady state. The nitrogen level is high in initial stages of decomposition and declines through the various phases until it reaches a steady state. The summary of the gas production phases is given in Appendix, Table A.1. The constituents of LFG are methane, carbon dioxide and non-methane organic

compounds (NMOC). The NMOC include different HAPs, greenhouse gases (GHG), and some volatile organic compounds (VOC). This study focuses on HAPs/VOCs.

There are twenty-four compounds found in LFG which are hazardous air pollutants. The list of NMOC compounds, concentrations level in parts per million (ppm), environmental effects and related previous studies are given in the Appendix, Table A.2. It is taken from the Environmental Protection Agency (EPA) website.

This experimental study is conducted for xylenes, methyl ethyl ketone and ethylbenzene, which are found in concentrations of 12.1, 6.57, and 4.61 ppm, in LFG, respectively, according to Table A.2. Xylenes ( $C_8H_{10}$ ) actually involve all the three isomers: *ortho*-xylene, *para*-xylene and *meta*-xylene. Isomers specify the places where two methyl groups are attached to the benzene ring. Xylenes are colorless and flammable liquid, which is having less density than air. Exposure to xylene affects the brain and can cause dizziness, headache, stomach discomfort, loss of memory, liver and kidney problems, breathing difficulties, lung troubles, and skin, eye and throat irritation. Unconfirmed reports shows that the unborn fetus is affected when exposed to low levels of xylene during pregnancy, (EPA, 2008) the affect on the fetus is confirmed in animals but still not proved in human beings. Methyl ethyl ketone (MEK) ( $C_4H_{10}O$ ) is a colorless, flammable and high volatile liquid. Exposure to MEK causes throat, eye and nose irritationc (EPA, 2008). Ethylbenzene ( $C_8H_{10}$ ) is a colorless liquid. It smells like a gasoline. Exposure to ethylbenzene causes throat irritation, dizziness, chest constriction and eye irritation in humans (EPA, 2008).

According to New Source Performance Standard emission guidelines, if the landfill design capacity is greater than or equal to 2.75 million tons of solid waste, then a well-established control system to reduce the NMOCs in the collected gas by 98 weight-percent has to be installed to control the environmental effects. This was applicable for landfills, which started operating on or after November 8, 1987. The movement of gases in the landfill is one of the main criteria to be understood before designing gas collection systems. Diffusion, pressure and permeability are the various factors that affect landfill gas movement. Methane, which is less dense than air tends to move upward; conversely carbon dioxide, which is denser than air, moves downward and is collected under the surface of the landfill. Some landfill air collection methods separate methane and carbon dioxide based on their movement.

Collection of landfill gas can be either a passive or active process. In passive collection, a vertical pipe is located in the landfill to collect the emissions. The vertical pipe is connected to a horizontal perforated pipe, which is located under the landfill liners. The number of collection pipes, thus, depends on the landfill waste density. In active collection, a vertical perforated pipe is used to collect the gas. The system is more complicated, including a pump, vacuum, sampling port and control valves. The pump and vacuum move gases out of the landfill faster. The sampling port is useful to know the concentration coming out of landfill, and the valve controls the flow. The number of pipes used varies with the waste depth. The active collection system is more efficient than the passive one because of its various options and maximum collection volumes.



Controlling the collected gas is the next step in the process. The two basic types of technologies normally used are combustion and non-combustion. In combustion, collected landfill gas compounds are destroyed thermally by using methods such as boilers, incinerators, flares, turbines and other internal combustion engines (ATSDR, 2008). Combustion methods convert a large amount of methane into carbon dioxide. Even though CO<sub>2</sub> is also a greenhouse gas, it is 23 times less reactive than methane on a pound by pound basis. The opportunity to use methane as a fuel source, however, is lost. Over 98 percent removal of organic compounds is typically achieved through combustion techniques (ATSDR, 2008). However, emissions of other pollutants from combustion-control systems are still a problem. The byproducts from the combustion systems are carbon monoxide (CO), oxides of nitrogen (NO<sub>x</sub>), particulate matter (PM), hydrochloric acid (HCl), sulfur dioxide (SO<sub>2</sub>) and others. In addition, recent studies demonstrate that flare VOC control efficiencies drop below 70% under various conditions (for example, meteorological conditions like high winds which reduce flare performance). (HARC, 2007) New studies are being conducted to better understand and model flare efficiencies.

Non-combustion techniques can convert gas to products and recover energy from the pretreated collected landfill gas. A phosphoric Acid Fuel Cell (PAFC) is a common non-combustion energy recovery technique.

Due to the disadvantages associated with flares (loss of methane as an energy source, removal of VOCs/HAPs perhaps significantly lower than 98%, and generation of other pollutants as combustion by-products), adsorption can be considered as an

alternative control option for landfill HAPs. Adsorption captures the gas or liquid known as adsorbate on the surface of the solid adsorbent such as activated carbon. The capacity of an adsorbent is described through isotherms, the amount of adsorbate captured on the adsorbent at equilibrium at a given temperature as a function of pollutant partial pressure for gas and concentration for liquid. The adsorption process can either be a physical or a chemical process. The physical process is influenced by Van der Waal's forces that imply weak electrostatic adsorption between the adsorbate and adsorbent. Unlike physical adsorption, chemical adsorption involves a strong chemical bond between adsorbent and adsorbate.

Activated carbon is used as an adsorbent because of its significant properties such as pore size, pore volume, surface area and pore distribution. It is manufactured by using raw materials such as lignite, wood, coal, coconut shell, peanut shell, bones, petroleum coke, lignin and more. Depending on the raw material, different types of activated carbon have different physical and chemical characteristics. The typical surface area for gas phase adsorption for carbons is 800-1200 m<sup>2</sup>/g. Carbon can be reused by regenerating it, which means removing the attached adsorbate. The three different processes of regeneration are passing hot inert gas if the adsorbate is incombustible, pressure swing adsorption and contact with low-pressure steam. The advantages of adsorption are no byproducts, low space requirement, cost effectiveness and regenerative capacity.

In summary, emissions from landfills have to be controlled for several reasons, such as compliance with government regulations, to reduce health impacts and odor

problems, and to reduce environmental effects such as groundwater contamination and greenhouse gas emissions. This study deals with finding the best curve fits among Langmuir and Freundlich isotherms for hazardous air pollutants such as xylenes, methyl ethyl ketone and ethylbenzene on coconut shell based and bituminous coal based activated carbons as adsorbents. Experiments were designed to replicate typical field usage conditions, using ambient temperature and relative humidity values, and testing the carbon as is, without pretreatment to remove moisture.

The methodology chapter describes the experiment done in the lab and the gas chromatograph used. The results are discussed in the results and discussion chapter and recommendations are also mentioned. The experimental data tables and calculations are given in appendix.

## CHAPTER 2

### BACKGROUND AND LITERATURE REVIEW

#### 2.1 Municipal Solid Waste Landfills

A municipal solid waste landfill is a landfill which receives waste from households, commercial solid waste, and non-hazardous waste. It can also accept wastes from the following list.

- Household hazardous waste,
- Municipal sludge,
- Infectious waste,
- Waste tires,
- Municipal waste combustion ash,
- Industrial non-hazardous waste,
- Construction and demolition waste,
- Agricultural waste,
- Oil and gas wastes,
- Mining wastes, and
- Conditionally exempt small quantity hazardous waste.

Most of the landfills allow a few categories from the list given above. In the United States, the percentages for wastes landfilled, incinerated, and recycled/composted are 57 percent, 16 percent, and 27 percent, respectively. The emissions from

the landfill primarily include methane (CH<sub>4</sub>), carbon dioxide (CO<sub>2</sub>), non-methane organic compounds (NMOC), hazardous air pollutants (HAPs), and greenhouse gases (GHG). The concentration levels for various types of compounds after the gas generation reaches equilibrium are given in Appendix A.2.

### 2.1.1 Landfill Gas Emissions

Landfill gas is typically 60% methane and 40% carbon dioxide and a wide range of volatile organic compounds (VOCs) (Young *et al.*, 1982). According to a case study by Zou *et al.* (2003), trace VOCs concentrations are high in summer and low in winter. The rate of gas emission is controlled by gas production, which involves vaporization, biological decomposition or chemical reactions, and transport mechanisms involving diffusion, convection and displacement. A case study by Kim and Kim (2002) found that the VOCs distribution varies depending on the meteorology and source/sink relationships.

A landfill air emission estimation model is given below in equation 1, designed by Environmental Protection Agency (EPA) to estimate the landfill gas generation. It is available from the Office of Air Quality Planning and Standards Technology Transfer Network Website (OAQPS TTN Web). Equation 1 is also applicable for CO<sub>2</sub>. The NMOC emission estimation is calculated from equation 2.

#### Equation 1:

$$Q_{CH_4} = L_0 R (e^{-k_c} - e^{-k_t})$$

Where,

$Q_{CH_4}$  = Methane generation rate at time, m<sup>3</sup>/yr,

- $L_o$  = Methane generation potential,  $m^3 \text{ CH}_4/\text{Mg refuse}$ ,  
 $R$  = Average annual refuse acceptance rate during active life,  $\text{Mg/yr}$ ,  
 $e$  = Base log, unitless,  
 $k$  = Methane generation rate constant,  $\text{yr}^{-1}$ ,  
 $c$  = Time since landfill closure, yrs ( $c = 0$  for active landfills), and  
 $t$  = time since the initial refuse placement, yrs

**Equation 2:**

$$Q_p = 1.82 Q_{\text{CH}_4} * C_p / (1 * 10^6)$$

Where,

- $Q_p$  = Emission rate of pollutant P (ie NMOC),  $m^3/\text{yr}$ ,  
 $Q_{\text{CH}_4}$  =  $\text{CH}_4$  generation rate,  $m^3/\text{yr}$ ,  
 $C_p$  = Concentration of p in landfill gas, ppmv, and  
 1.82 = Multiplication factor (assumes that 55 percent of LFG is  $\text{CH}_4$   
 and 45 percent is  $\text{CO}_2$ ,  $\text{N}_2$  and other)

Once the gas emission rate is calculated, total uncontrolled mass emission per year is obtained using equation 3 given below for  $\text{CH}_4$ ,  $\text{CO}_2$ , NMOC and organic and inorganic compounds.

**Equation 3:**

$$\begin{aligned}
 \text{UM}_p &\equiv \frac{Q_p * (\text{MW}_p * 1 \text{ atm})}{(8.205 * 10^{-5} \text{ m}^3 \text{ -atm/gmol-}^\circ \text{K}) (1000 \text{ g/kg}) (273 + T^\circ \text{K})}
 \end{aligned}$$

Where,

- $\text{UM}_p$  = uncontrolled mass emission of pollutant P (i.e. NMOC),  $\text{kg/yr}$ ,

$MW_p$  = Molecular weight of P, g/gmol, (86.18 for NMOC as hexane)

$Q_p$  = NMOC emission rate of P, m<sup>3</sup>/yr, and

$T$  = Temperature of landfill gas, °C

Uncontrolled gas emissions of MSW for NMOC and their concentrations are listed on the EPA website. The list was identified by available literature. From the provided list, compounds with high concentrations and significant effects on humans and the environment were chosen for study. The compounds chosen were also those with few previous activated carbon studies. The concentrations of NMOC, effects, and previous related study articles are given in Appendix A Table A.2.

#### *2.1.2 Gas Emission Control*

Landfill gas (LFG) control is a two step process, collecting the gas and controlling the emissions. Gas movements have to be studied before designing the collecting system. In the Ward *et al.* (1996) case study, changes in subsurface migration of major and trace component LFG were studied. Control processes can be combustion or non-combustion based. In the Zamorano *et al.* (2007) case study, recovery of biogas at sealed landfills was shown to be a good alternative in urban waste management. Using the biogas as a fuel source decreases greenhouse gas emissions significantly. Combustion using incineration is the most common gas control. However, considering the pollution from incineration; non-combustion, adsorption process is considered in this experiment.

The advantages of adsorption over other methods are,

- no operating pollution from system,

- readily available,
- low cost,
- easily regenerative.

## 2.2 Hazardous Air Pollutants (HAPs)

Toxic air pollutants, which cause severe health problems such as cancer, neurological problems, immune system damage, birth defects or reproductive effects, are known as HAPs. There are 188 compounds listed as hazardous air pollutants in the Clean Air Act of 1990, given in Appendix B. Of the twenty-five HAPs from landfill gas, five compounds have been selected for this experimental study. The compounds and their HAP CAS numbers are listed in Table 2.1.

Table 2.1: Hazardous Air Pollutants and their CAS Numbers

<b>Serial no.</b>	<b>Pollutant</b>	<b>HAP CAS no.</b>
1	o-Xylene	95476
2	m-Xylene	108383
3	p-Xylene	106423
4	Ethylbenzene	118741
5	Methyl ethyl ketone	78933

### *2.2.1 Xylene*

According to the EPA default concentration for LFG constituents, the concentration of xylene in the LFG is 12.1 ppm and it has moderate incremental reactivity for ozone formation of 0.50 mol O<sub>3</sub> / mol C (Carter 1991). Xylene has a methyl group attached to a benzene ring. The International Union of Pure and Applied Chemistry (IUPAC)



nomenclature for *ortho*, *para* and *meta*-xylenes are 1,2-dimethylbenzene, 1,4-dimethylbenzene, and 1,3-dimethylbenzene, respectively. In *ortho*-xylene the methyl groups are placed next to each other in the benzene ring. In *meta*-xylene, they are separated by a carbon atom, and in *para*-xylene, they are placed on opposite sides of the benzene ring, as shown in Figure 2.1. The chemical properties of xylene are: melting point from  $-47.87^{\circ}\text{C}$  to  $13.26^{\circ}\text{C}$ , boiling point around  $140^{\circ}\text{C}$  and density  $0.87\text{ Kg/L}$  (Wikipedia, 2008). The other name for xylene is xylol. It is naturally present in coal tar and petroleum, and can easily form during forest fires. It is used as a solvent in many fields such as printing, painting, rubber industries, leather industries, and in varnishing. Exposure to xylene affects the brain.

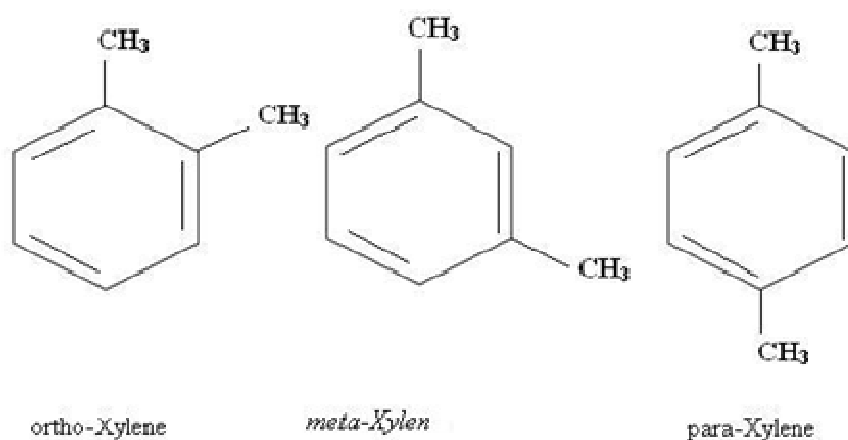


Figure 2.1: Chemical structure of xylene isomers

### 2.2.2 Ethylbenzene

According to the EPA default concentration for LFG constituents, the concentration of ethylbenzene in the landfill gas is 4.61ppm and the low incremental reactivity for ozone formation is 0.6 ppm O<sub>3</sub> / ppm C (Carter, 1991). The colorless hydrocarbon smells like gasoline. It is used as a solvent, bonding for plastic, and to make styrene. The chemical structure is shown below in Figure 2.2.

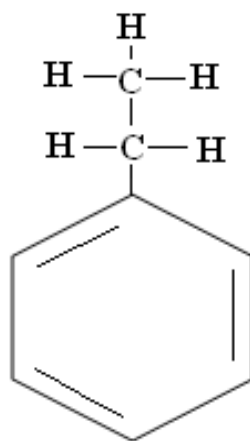


Figure 2.2: Chemical structure of ethylbenzene

The boiling point of ethylbenzene is 136 °C, melting point is -95 °C and density is 0.87 Kg/L (Wikipedia, 2008).

### 2.2.3 Methyl Ethyl Ketone

According to the EPA default concentration for LFG constituents, the concentration of methyl ethyl ketone (MEK) in landfill gas is 7.09 ppm and the low incremental reactivity for ozone formation is 0.3 ppm O<sub>3</sub> / ppm C (Carter, 1991). It is used as a solvent. Exposure to MEK causes irritation of throat, eyes and nose. The

boiling point of MEK is 80 °C, melting point is -86 °C and density is 0.805 Kg/L (Wikipedia, 2008). The chemical structure is given below in Figure 2.3.



Figure 2.3: Chemical structure of methyl ethyl ketone

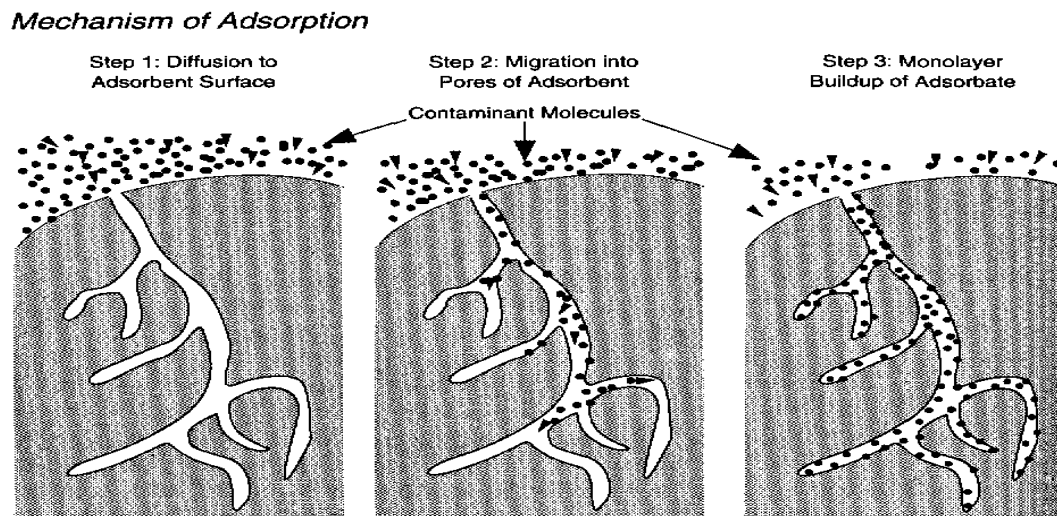
### 2.3 Adsorption

Attachment of a gas or liquid phase molecule to a solid is called adsorption. The process of adsorption occurs when the gas or liquid substance accumulates on the surface of the solid. The solid is known as the adsorbent and the attached molecule is known as the adsorbate. Giradet *et al.* (2006) found that adsorbate–adsorbent interactions depend highly on polarisability, ionization potential and average microporous radius. Granular activated carbon is used as an adsorbent in this study and landfill HAPs, xylene, ethylbenzene and methyl ethyl ketone, are the studied adsorbates. The previous studies related to adsorption of these compounds are mentioned in Appendix A Table A.2.

#### *2.3.1 Adsorption Mechanism*

The mechanism of adsorption is a three step process, which is shown in Figure 2.4. In step 1, the pollutant moves to the external surface of the adsorbent by advection and diffusion. In step 2, the pollutant molecules start migrating from the external surface to the pores of the adsorbent by diffusion. The internal surface area is large

compared to the external surface area. In step 3, pollutants adhere to the surface in the pores. Step 3 is very fast compared to step 2. The rate of adsorption depends on the temperature, humidity, residence time, adsorbate characteristics, partial pressure, adsorbate chemical composition, molecular size, and adsorbent surface area, pore size and polarity.



Source: Noll, 1999

Figure 2.4: Adsorption mechanism

### 2.3.2 Types of Adsorption

Adsorption can be physical or chemical. In air pollution control applications, physical adsorption is more common than chemical adsorption. In physical adsorption the bonding between the adsorbent and adsorbate is weak, occurring via van der Waals forces. The bond can be easily broken by heating the adsorbent or reducing the pressure, in a process called regeneration. On the other hand, in chemical adsorption, bonding is very strong and the adsorbent cannot be recovered.

### 2.3.3 Adsorption Isotherms

Adsorption isotherms show the equilibrium adsorption capacity of carbon at given operating conditions, and thus provide critical information for designing adsorption systems. Isotherms can be used to find the maximum adsorbent capacity. A typical adsorption isotherm is given in Figure 2.5. The mass of pollutant adsorbed per unit mass of adsorbent for a given adsorbate partial pressure is adsorbent capacity. Three common types of adsorption isotherm are Langmuir, which assumes monolayer coverage; Freundlich, which also considers monolayer coverage; and (Brunauer-Emmett-Teller) BET, which allows multilayer coverage. According to Benkhedda *et al.* (2000), the Langmuir model is best to describe the adsorption isotherm for m-xylene.

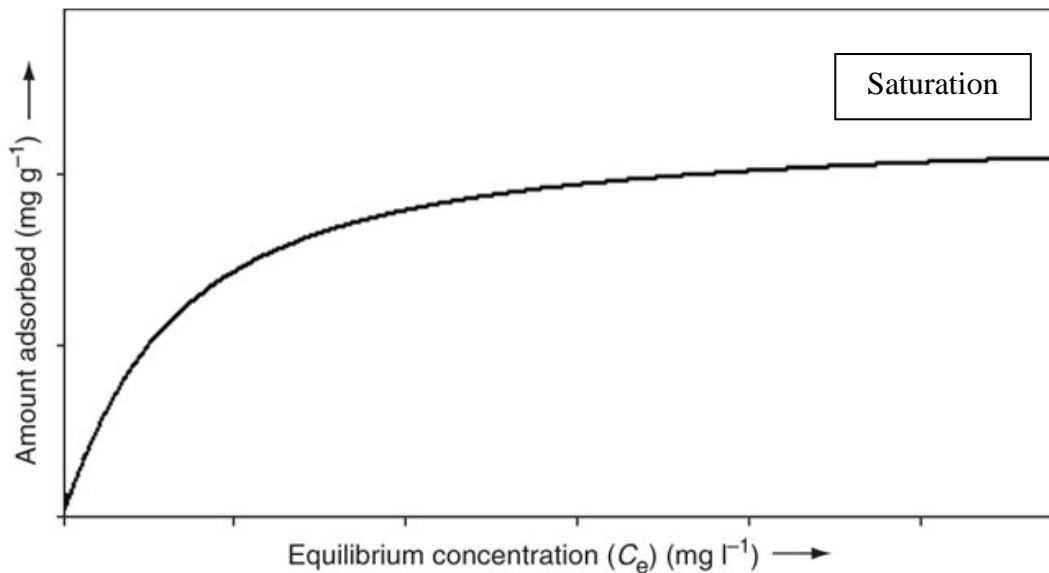


Figure 2.5: Typical adsorption isotherm

Equations of the Langmuir and the Freundlich isotherms are given below.

#### 2.3.3.1 Langmuir Isotherm Equation

$$q_e = \frac{Q_0 K C_e}{K C_e + 1} \quad \text{equation 2.4}$$

Linearized forms

$$C_e/q_e = 1/(Q_0 K) + (C_e/Q_0) \quad \text{equation 2.5}$$

$$1/q_e = 1/Q_0 + (1/KQ_0) \times (1/C_e) \quad \text{equation 2.6}$$

where,

$q_e$  = amount of pollutant adsorbed per unit mass of adsorbent, (g/g)

$C_e$  = equilibrium pollutant concentration after adsorption, (mg/L)

$Q_0$ ,  $K$ ,  $K_f$ ,  $n$  = empirical constants.

$Q_0$  represent the maximum adsorption capacity.

#### 2.3.3.2 Freundlich Isotherm Equation

$$q_e = K_f C_e^{1/n} \quad \text{equation 2.7}$$

Linearized form

$$\text{Log } q_e = \text{Log } K_f + 1/n \text{ Log } C_e \quad \text{equation 2.8}$$

$K_f$  and  $n$  can be determined by plotting  $\log q_e$  vs  $\log C_e$ .

$K_f$ ,  $n$  = empirical constants.

### 2.4 Activated Carbon

Activated carbon (AC) is one of the most commonly used adsorbents. It has long been recognized as one of the most versatile adsorbents due to its high porosity and the resulting high surface area (Prakash *et al.*, 1994 and Yang, 2003). Carbon is nothing but

a charcoal, which is produced by heating the substance at high temperature in the absence of oxygen. Then to activate the charcoal, it is treated with oxygen to open up millions of tiny pores between the carbon atoms. AC can be made from variety of commonly used raw materials such as bituminous coal, wood, lignite coal and coconut shell. The type of AC is named according to the raw materials used. It is available in powdered form, granular and pellet form. Granular activated carbon is used in this study (GAC). The internal surface area of activated carbon ranges from 800 to 1200 m<sup>2</sup>/g (Cooper and Alley, 2002). AC was first used for decolorizing sugar and has been used to treat water since 1930. It was initially produced in powder form and then slowly granular activated carbon was introduced.

#### *2.4.1 Adsorption Properties of Activated Carbon*

Properties that affect the amount of pollutant adsorbed are listed below.

1. Surface area - Adsorption capacity is proportional to the surface area of the AC
2. Pore size - Proper pore size distribution is needed to transport the adsorbate.
3. Temperature - Lower temperature increases the adsorption capacity.
4.  $p^H$  - Lower  $p^H$  decreases the solubility of adsorbate thus increases adsorption capacity, in liquids.
5. Contact time - Sufficient contact time is needed to adsorb the chemical.
6. Concentration of adsorbate - Increased concentration increases the adsorption capacity, until maximum adsorption capacity is reached.
7. Humidity – An increase in humidity allows water molecules to enter pores and it decreases adsorption capacity.

There are studies related to the effect of adsorption capacity based on its physical characteristics. According to Shin *et al.* (2002), increased humidity decreases the adsorption capacity and breakthrough time. The time it takes to attain an equilibrium concentration is called breakthrough time. According to the Pires *et al.* (2003) study, high surface area and high micropore volumes are considered important in the adsorption process.

#### 2.4.2 Comparison of Activated Carbon

Of the many varieties of granular activated carbon, two types were selected for comparison in this study: coconut shell based activated carbon and bituminous coal based activated carbon from Calgon Corporation. Comparison of these two types of activated carbon is given in Table 2.2. These two types were selected because the reactivation is good for both, compared to other types of carbon (Carbochem, 2008).

Table 2.2: Comparison of Coconut Shell Based and Bituminous Coal Based Activated Carbon

<b>Properties</b>	<b>Coconut shell based activated carbon</b>	<b>Bituminous coal based activated carbon</b>
Micropores	High	High
Macropores	Low	Medium
Ash	5%	10%
Hardness	High	High
Density	0.48 g/cc	0.48 g/cc
Reactivation	Good	Good
Iodine no.	1100	1000
Dust	Low	Medium
Water soluble ash	High	Low



### 2.4.3 Reactivation of Carbon

Reactivation is done when carbon reaches its saturation level. The adsorbate is removed from the carbon, which can often be reused 8 to 10 times. There are different types of reactivation available such as steam regeneration, thermal regeneration, chemical regeneration, biological regeneration and regeneration using ultrasound. Thermal regeneration is the most common reactivation process. It is achieved by heating the carbon at more than 800° C in the absence of oxygen to avoid burning of carbon. Once the carbon is heated two to three times, it is washed with acid to remove ash.

According to Lim and Okada (2005), ultrasound regeneration can alternate with a thermal or chemical regeneration process. They found that desorption using ultrasound is effective in reactivating the surface layer of granular activated carbon. In the Luo *et al.* (2006) case study, electrothermal regeneration shows a wide range of controllable concentration factors. According to Abumaizar *et al.* (1998), carbon can be biologically regenerated by microorganisms in biofilter media. Biological regeneration is a comparatively cheaper and effective way of regenerating carbon. It will improve the removal efficiency of biofilter and also at the same time carbon can be regenerated by the microorganism presented in the media. Hong and Tseng (2008) demonstrated the advantages of water-based regeneration of granular activated carbon.

## 2.5 Gas Chromatography

Gas chromatography is used in this experimental study to detect the concentration level for each experimental run. It is defined as separation of compounds while travelling through a stationary phase column. It is used for a wide range of chemicals. Komenda *et al.* (2001) measured 27 different VOCs using gas chromatography (GC) with a flame ionization detector (FID). Das *et al.* (2004) used a GC with FID to identify adsorption of VOCs onto activated carbon fiber. Tanner *et al.* (2006) continuously monitored C<sub>2</sub> to C<sub>6</sub> hydrocarbons using an unattended, automated, on-line, cryogen-free, remotely controlled gas chromatography system.

### *2.5.1 History*

The history of chromatography is based on biotechnology. In 1903, the Russian botanist Mikhail Semenovich Tswett first reported the process of column adsorption chromatography. He was considered the founder of chromatography. In 1915, analyzing chlorophyll and other plant pigments was presented by R. M. Willstätter, considered to be the pope of German chemistry. In 1922, L. S. Palmer, an American scientist, used Tswett's technique on various natural products. In 1931, Richard Kuhn and others used chromatography to separate isomers of polyene pigments.

In 1938, drop chromatography in horizontal thin layers was introduced by Russian scientists N.A. Izmailor and M.S. Shraiber. In 1940, foundations of liquid-liquid partition chromatography were developed by Archer John Porter Martin and Richard Laurence Millington Synge using a liquid phase column. In 1944, Martin R. Consden and A. H. Gordon created paper chromatography, which involves a solid phase

column. In 1945, Fritz Prior, a student of Erika Cremer in Institute of Physical Chemistry at Innsbruck University, first used gas solid adsorption chromatography.

In 1952, Martin and Synge went on to win the Nobel prize for liquid-liquid partition chromatography, which was developed in 1940. In 1958, Fredrick Sangers won the Nobel prize for determining the first amino acid sequence of a protein insulin. In 1966, Csaba Horvath at Yale University introduced High-Pressure Liquid Chromatography (HPLC), which became popular in 1970's. In 1970, Hemishsmall and co-workers at Dow Chemical Company developed ion chromatography, which is more useful for environmental and water quality research. A 1990 survey reveals that Gas liquid Chromatography (GLC) is the most frequently used analytical instrument in environmental and water quality research (Today's Chemist at Work, 1998)

### 2.5.2 Components

The components of a typical GC are shown in Figure 2.6, and a explanation for each component is given.

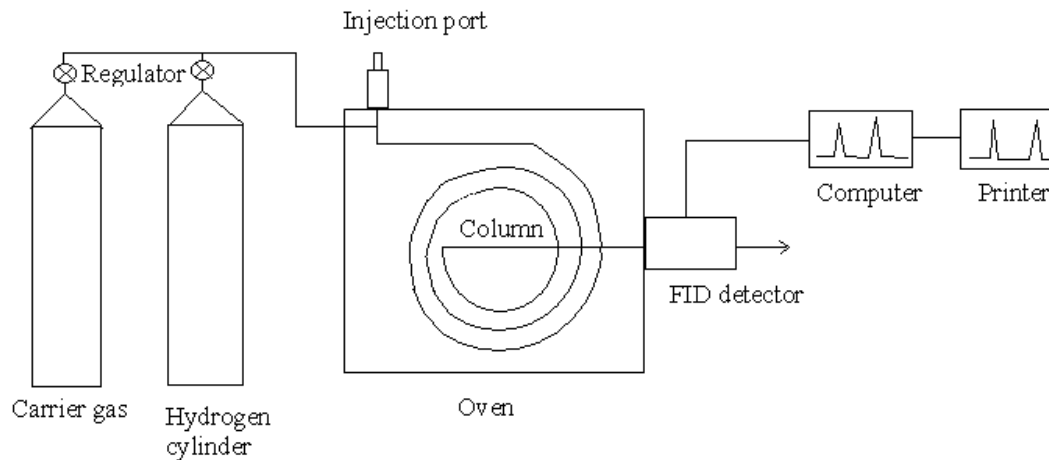


Figure 2.6: Schematic diagram of GC

#### 2.5.2.1 Carrier Gas

The carrier gas carries the injected sample through the column. It should be an inert gas to avoid any reaction while carrying the gas through the column. Different types of carrier gases are available, such as argon, nitrogen, helium and carbon dioxide. The selection of a carrier gas depends on the type of detector in the GC. The gas is connected to the GC using a copper tube.

#### 2.5.2.2 Support Gas

Air and hydrogen are the support gases for the flame combination at the jet's tip of the Flame Ionization Detector (FID). An air compressor is inbuilt in some systems.

#### 2.5.2.3 Injection Port

Injection can be manual or automated using available flow controllers. Wang *et al.* (2007) installed a splitter for dual column gas chromatography. The flow can be divided or adjusted using the flow meter connected to the GC. The SRI GC 8610 model used in this experiment is a direct manual injection through the injection port. To avoid leaking, a 1/8 inch Swagelok stainless steel nut and septa are used. A quick injection results in good sharp peak and slow injection results in a broad ugly peak.

#### 2.5.2.4 Column

There are two types of columns available, capillary and packed. Packed column is filled with solid material inside the column but a capillary column is an open tube. Packed column diameter ranges from 2-4 mm and length ranges from 1.5 to 10 m. Depending on the compounds to be tested the type of column varies. In this experiment, a 60M capillary column is used. The diameter of the capillary column is a few tenths of

a millimeter. The advantages of a capillary column over other columns are its flexibility, low reactivity to chemicals, higher retention time and durability.

#### 2.5.2.5 Oven

It is the GC component, in which column is placed. It is a closed surface and bakes the column while running the process. The oven temperature can be adjustable according to the boiling point of the compound to be tested and in principle the temperature of the oven should be higher than the boiling point of the compounds to be analyzed.

#### 2.5.2.6 Flame Ionization Detector

A detector has the capacity to detect the compound and report it to the computer. There are different types of detectors available. The FID (Flame Ionization Detector) is commonly used for detecting organic hydrocarbons. It is shown in Figure 2.7 below.

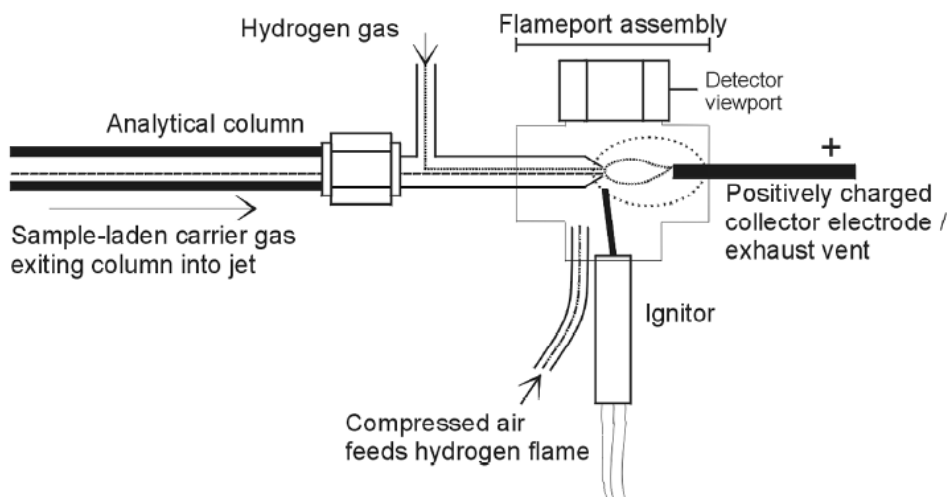


Figure 2.7: Schematic diagram of FID

The effluent from the column is mixed first with hydrogen and then it is mixed with compressed air. The hydrogen supports the jet tip. Effluent gas from the column is ionized by the flame and positive and negative ions are produced. The positive ions exhaust and negative ions are attracted by the collector electrode to the amplifier. The amplifier sends an analog signal to the system to produce a peak. The difference between the positive ions and FID produces an electromagnetic field. The different types of detector and their purpose are given in Table 2.3.

Table 2.3: Detectors and Their Purposes

<b>Detectors</b>	<b>Carrier gas</b>	<b>Support gas</b>	<b>Responds to</b>	<b>Sensitive</b>
Catalytic Combustion Detector (CCD)	Air	No support gas needed	All hydro carbons	Concentration
Flame Ionization Detector (FID)	Helium	Hydrogen and air	All hydrocarbons	Mass flow
Nitrogen-Phosphorus Detector (NPD)	Helium	Hydrogen	Organic compounds containing nitrogen and phosphorus	Mass flow
Flame Photometric Detector (FPD)	Helium	Hydrogen and air	Specific for sulphur and phosphorus compounds	Mass flow
Photo Ionization Detector(PID)	Helium or nitrogen		Aromatics and molecules with double bonds	Concentration
Electron Capture Detector (ECD)	Nitrogen		Chlorinated, fluorinated or brominated molecules.	Concentration
Dry Electrolytic Conductivity Detector (DELCD)	Helium or nitrogen	Air	Chlorinated and brominated molecules	

#### 2.5.2.7 Regulator

A regulator, as shown in Figure 2.8, regulates the flow of the carrier gas, support gas and air. The right side measurement circle in the figure shows the pressure inside the cylinder and left side measurement circle in the figure shows the outflow pressure from the cylinder.



Figure 2.8: Regulator

### 2.6 Summary of Literature Review

Articles related to activated carbon, regeneration, landfills and gas chromatography are summarized below.

Table 2.4 Articles Related To Activated Carbon Adsorption

<b>Article:</b> Estimation of adsorption energies using the physical characteristics of activated carbons and the molecular properties of volatile organic compounds( 2006 )				
<b>Author</b>	<b>Adsorbent</b>	<b>Adsorbate</b>	<b>Conclusion</b>	<b>Other</b>
Giraudet,S., Pré,P., Tezel,H, and Le Cloirec,P.	Granular activated carbon	Acetone, methylethylketone, 3- methylbta-2-one, benzene,florobenzene, hex- 1-ene, hexane, cyclohexane, propanal, ethanol, arcylnitrile, ethylformate, dichlomethane, diisopropylether, triethylamine.	Adsorbate– adsorbent interactions highly depend on polarisability, ionization potential and average micropore radius.	Increase in temperature decreases the adsorption capacity.

Table 2.4 – Continued

<b>Article:</b> Determination of gas phase adsorption isotherms-a simple constant volume method ( 2006 )				
<b>Author</b>	<b>Adsorbent</b>	<b>Adsorbate</b>	<b>Conclusion</b>	<b>Other</b>
Daekeum Kim, Zhangli Cai, and George A. Sorial	Bituminous coal based and coconut shell based activated carbon	Toluene, methylethylketone, methylisobutylketone	Adsorption capacity is highly dependant on the physical characteristics of the adsorbate and adsorbent.	
<b>Article:</b> Effects of pore structure and temperature on VOC adsorption on activated carbon(2001)				
<b>Author</b>	<b>Adsorbent</b>	<b>Adsorbate</b>	<b>Conclusion</b>	<b>Other</b>
Yu-Chung Chiang, Pen-Chi Chiang, Chin-Pao Huang	Peat derived carbon, bituminous coal based carbon and coconut shell based carbon.	Carbon tetrachloride, chloroform, benzene, and methylene chloride	Physical adsorption is the predominant process in adsorption.	Benzene adsorption is temperature dependent: it increases with temperature.
<b>Article:</b> Removal characteristic of trace compounds of landfill gas by activated carbon adsorption (2002)				
<b>Author</b>	<b>Adsorbent</b>	<b>Adsorbate</b>	<b>Conclusion</b>	<b>Other</b>
Ho-Chul Shin, Jin-Won Park, Kwinam Park, and Ho-cheol	Granular activated carbon	Xylene, ethylbenzene, toluene, tri or tetrachloroethylene, benzene, carbon tetrachloride and chloroform	Benzene, toluene, and ethylbenzene adsorption capacity and breakthrough curves decreased with increased humidity over 60%.	Test is conducted in fixed bed adsorption column.
<b>Article:</b> Adsorption of acetone, methyl ethyl ketone, 1,1,1-trichloroethane, and trichloroethylene in granular activated carbons (2003)				
<b>Author</b>	<b>Adsorbent</b>	<b>Adsorbate</b>	<b>Conclusion</b>	<b>Other</b>
Joao pires, Moises Pinto, Ana Carvalho, and M. Brotas de Carvalho	Granular activated carbon	acetone, methyl ethyl ketone, 1,1,1-trichloroethane, and trichloroethylene	High micropore volume and high surface area are most important in adsorption.	Physical adsorption is predominant.



Table 2.4 - Continued

<b>Article:</b> Biofiltration of BTEX contaminated air streams using compost-activated carbon filter media (1998)				
<b>Author</b>	<b>Adsorbent</b>	<b>Adsorbate</b>	<b>Conclusion</b>	<b>Other</b>
Riyad J. Abumaizar, Walter Kocher, and Edward H. Smith	Granular activated carbon(GAC) mixed with compost	Benzene, toluene, ethylbenzene, and o-xylene.	The result shows higher removal efficiency of compound when compost is mixed with GAC.	Greater than or equal to 90% removal efficiency was achieved for compound concentration greater than or equal to 200ppm.
<b>Article:</b> Adsorption isotherm of m-xylene on activated carbon: measurements and correlation with different models (2000)				
<b>Author</b>	<b>Adsorbent</b>	<b>Adsorbate</b>	<b>Conclusion</b>	<b>Other</b>
Jamal Benkhedda, Jean-Noel Jaubert, Danielle Barth, Laurent Perrin, and Michel Bailly	Granular Activated carbon.	m-xylene	m-xylene loading decreases with increasing temperature. Among the model, Langmuir model is best for m-xylene adsorption on activated carbon.	The test was conducted in temperature range 298.15 to 333.15 K.

Table 2.5 Articles Related To Regeneration

Article: Regeneration of granular activated carbon using ultrasound (2005)				
Author	Adsorbent	Type of regeneration	Conclusion	Other
Jae-Lim Lim and Mitsumasa Okada	Granular activated carbon	Ultrasound method	Ultrasound desorption can be used as an alternate process for regeneration.	Desorption occurs only at the surface layer of GAC.
Article: Adsorption and electrothermal desorption of organic vapors using activated carbon adsorbents with novel morphologies (2006)				
Author	Adsorbent	Type of regeneration	Conclusion	Other
Lingai Luo, David Ramirez, Mark J. Rood, Georges Grevillot, K. James Hay, Deborah L. Thurston	Activated carbon monolith (ACM), Activated carbon fiber cloth (ACFC), and Activated carbon beads (ACB)	Direct electro thermal regeneration	The result shows that electrothermal regeneration shows the wide range of controllable concentrations.	Physical, electrical, cost and adsorption properties are compared for all three type of carbon to capture organic vapor from gas streams.
Article: Biofiltration of BTEX contaminated air streams using compost-activated carbon filter media (1998)				
Author	Adsorbent	Type of regeneration	Conclusion	Other
Riyad J. Abumaizar, Walter Kocher, and Edward H. Smith	Granular activated carbon(GAC) mixed with compost	Biological regeneration	There is evidence that carbon can be regenerated in a biological way using microorganisms.	
Article: Regeneration of granular activated carbon saturated with acetone and isopropyl alcohol via a recirculation process under H <sub>2</sub> O <sub>2</sub> /UV oxidation (2008)				
Author	Adsorbent	Type of regeneration	Conclusion	Other
Richard S. Hong, I.-Chin Tseng	Granular activated carbon	Water based regeneration	This method has advantages over other methods such as low cost, controllable parameters, and water can be reused.	

Table 2.6 Article Related to Gas Chromatography

<b>Article:</b> Devising an adjustable splitter for dual-column gas chromatography (2007)				
<b>Author</b>	<b>Detector</b>	<b>Compound tested</b>	<b>Conclusion</b>	<b>Other</b>
Chieh-Heng Wang, Chih-Chung Chang, and Jia-Lin Wang	Flame ionization detector	Benzene, toluene, ethylbenzene, and xylenes	Split ratio of p,m- xylene concentration are sensitive to aux flow.	Adjustable splitter installed with the dual column GC.
<b>Article:</b> Measurement of biogenic VOC emissions: Sampling, analysis and calibration (2001)				
<b>Author</b>	<b>Detector</b>	<b>Compound tested</b>	<b>Conclusion</b>	<b>Other</b>
M. Komenda, E. Parusel, A.Wedel, and R. Koppmann	Flame ionization detector (FID)	28 different VOCs	The system described in the article measures biogenic VOCs successfully.	GC is calibrated with 37 different compounds.
<b>Article:</b> Removal of volatile organic compound by activated carbon fiber (2004)				
<b>Author</b>	<b>Detector</b>	<b>Compound tested</b>	<b>Conclusion</b>	<b>Other</b>
Debasish Das, Vivekanand Gaur, and Nishith Verma	FID	Benzene, toluene xylene, dichloromethane, and trichloroethylene	Activated carbon fiber shows greater adsorption of VOCs than other carbon forms.	
<b>Article:</b> Gas chromatography system for the automated, unattended, and cryogen-free monitoring of C2 to C6 non-methane hydrocarbons in the remote troposphere (2006)				
<b>Author</b>	<b>Detector</b>	<b>Compound tested</b>	<b>Conclusion</b>	<b>Other</b>
David Tanner, Detlev Helming, Jacques Hueber, and Paul Goldan	FID	C <sub>2</sub> to C <sub>6</sub> hydrocarbons (HC)	The continuous monitoring of (HC) using an unattended, automated, cryogen-free, remotely controlled GC system was used.	12 Non Methane Hydro Carbons (NMHCs) in northern hemisphere are quantified.

Table 2.7 Article Related to Landfill

<b>Article:</b> Changes in major and trace components of landfill gas during subsurface migration (1996)			
<b>Author</b>	<b>Site description</b>	<b>Conclusion</b>	<b>Other</b>
R .S. Ward, G. M. Williams, and C.C. Hills	FoXhall Landfill in Suffolf (U.K)	Association of halogenated compound with methane is diagnostic of a landfill gas was measured.	79 VOCs were found similar to other landfill gas emission.
<b>Article:</b> Study of the energy potential of the biogas produced by an urban waste landfill in southern Spain (2007)			
<b>Author</b>	<b>Site description</b>	<b>Conclusion</b>	<b>Other</b>
Montserrat Zamorano, Jorge Ignacio Perez, Ignacio Aguilar Paves, and Angel Ramos Riado	Urban waste landfill in Southern Spain, 2 Km northeast of Granada.	Recovery of biogas at sealed landfill is a good alternative in urban waste management.	Using the biogas as a fuel source highly decreases the greenhouse gas effect.
<b>Article:</b> Characterization of ambient volatile organic compounds at a landfill site in Guangzhou, south china (2003)			
<b>Author</b>	<b>Site description</b>	<b>Conclusion</b>	<b>Other</b>
S.C. Zou, S.C. Lee, C.Y. Chan, K.F. Ho, X. M. Wang, L.Y. Chan, and Z.X. Zhang	Datianshan landfill is a municipal solid waste landfill located at Guangzhou, in south China.	Trace VOCs concentrations are high in summer and low in winter.	A total of 60 VOCs were found in summer and 38 VOCs in winter.
<b>Article:</b> The distributions of BTEX compounds in the ambient atmosphere of Nan-Ji-Do abandoned landfill site in Seoul (2002)			
<b>Author</b>	<b>Site description</b>	<b>Conclusion</b>	<b>Other</b>
Ki-Hyun Kim, and Min-Young Kim	Nan-Ji-Do landfill, South Korea	The seasonal distribution of VOC is affected by meteorology and source/sink relationship.	

## 2.7 Conclusion

From Table 2.6, one notes that comparison of coconut shell and bituminous coal based activated carbon studies are few and the compounds tested with these types of activated are also few. This study, focuses on developing adsorption isotherms for landfill VOCs on bituminous coal based (BPL) and coconut shell based (OVC) activated carbon.

## CHAPTER 3

### METHODOLOGY

The objective of this research is to develop adsorption isotherms for xylene, methyl ethyl ketone and ethylbenzene onto coconut shell and bituminous coal based activated carbon. Experiments are conducted to replicate typical field usage conditions, using ambient temperature and relative humidity values, and testing the carbon as is without pre-treatment to remove moisture. Although lab studies may heat carbon to remove initial moisture, this practice is not done before installing carbon for use in a column in the field. This section describes the experimental methods used to determine the adsorption isotherms. Gas chromatography with FID detector is selected for its linearity and a capillary column is chosen for its ability to detect the wide range of compounds to be tested. A digital weighing scale is used for weighing carbon and other miscellaneous apparatus such as tedlar bags, vials, and syringes are also used in this method.

#### 3.1 Equipment Used

##### *3.1.1 Gas Chromatograph*

Gas chromatography measures VOCs, by separating a mixture based on compound retention time while traveling through the column using helium as a carrier gas. The compound with a lower boiling point, or more volatile compound, comes out first from the column. When the temperature of the column oven increases, the less

volatile compounds separate from the column, resulting in a sequence of their release out of the column. The gas chromatography setup is shown in Figure 3.1.



Figure 3.1: GC setup in the lab

A SRI model No. 8610C instrument is used in this research. The flame ionization detector (FID), which is more sensitive to hydrocarbons compared to other methods, with a 60m capillary column is used. Capillary columns detect very low quantities of sample compared to packed columns. The capillary column and FID detector employed in this study are shown in Figure 3.2.

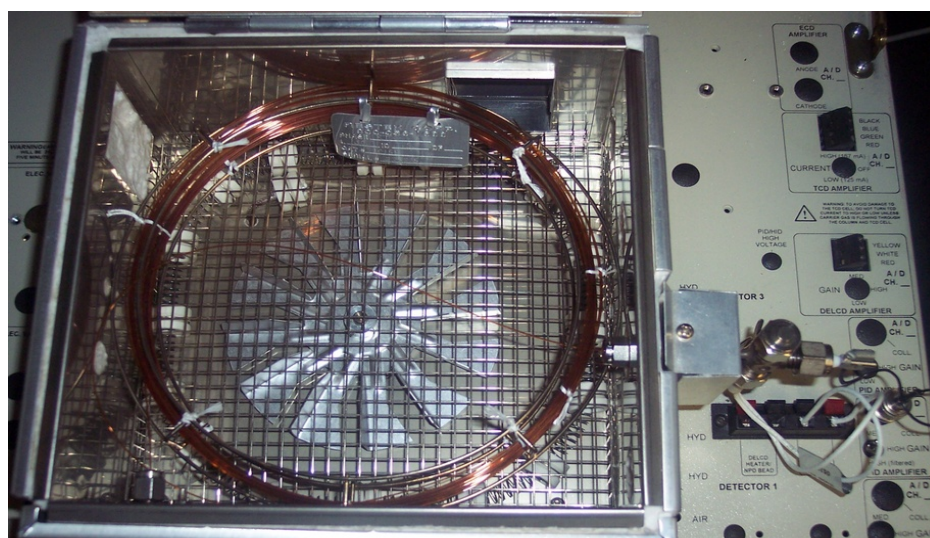
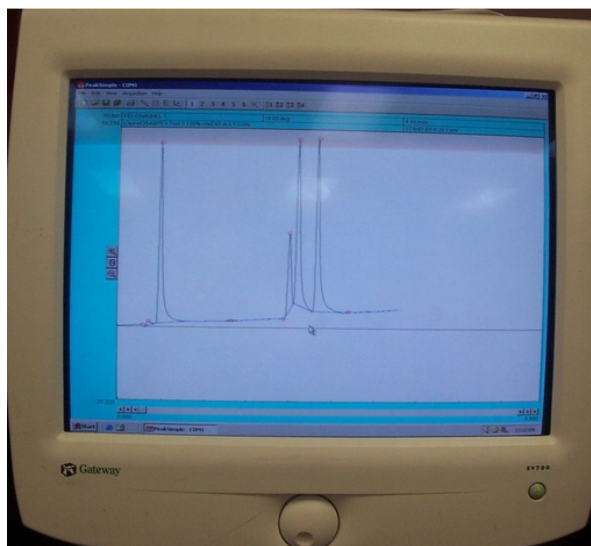


Figure 3.2: Capillary column and fid detector

### 3.1.2 PeakSimple Software

PeakSimple for windows software is manufactured and maintained by SRI Instruments, Inc. It has been under continuous development since 1994. It reads data from the detector and the results are listed in the results tab. Software is downloaded from the website and installed in the desktop. The computer is connected with the GC through a serial port. PeakSimple has to be calibrated before starting the experiments. Chromatographic data is highly variable in terms of peak shapes, interferences, co-eluting peaks, signal to noise ratio, selected integration parameters and data acquisition rate. According to the settings in the GC, the peak shapes and time vary and hence, before calibrating the GC, the settings have to be fixed. The settings are standardized after several trial runs. Peaks in the PeakSimple software are shown in Figure 3.3.





outflow from the cylinders. 1/8" copper tubing was used to connect the GC and regulator. The initial settings on the GC were helium as 7 psi, hydrogen 28 psi, detector temperature 200° C, and initial column oven temperature 40 ° C. According to the initial settings, peak retention time varies. The temperature settings in the PeakSimple software are linked with the GC. The temperature settings in the PeakSimple software are final temperature 150° C, hold time three seconds, and ramp 10 ° C / minute.

### 3.1.3 Other apparatus

A digital weighing scale was used as a measuring instrument. It was initially adjusted to zero in grams. Four decimal point displays were used to measure the activated carbon amount to be tested. Figure 3.4 shows the miscellaneous apparatus used in the Experiments (from left to right, humidity stick, 4 ml vial, syringe, septum, and digital weighing scale).

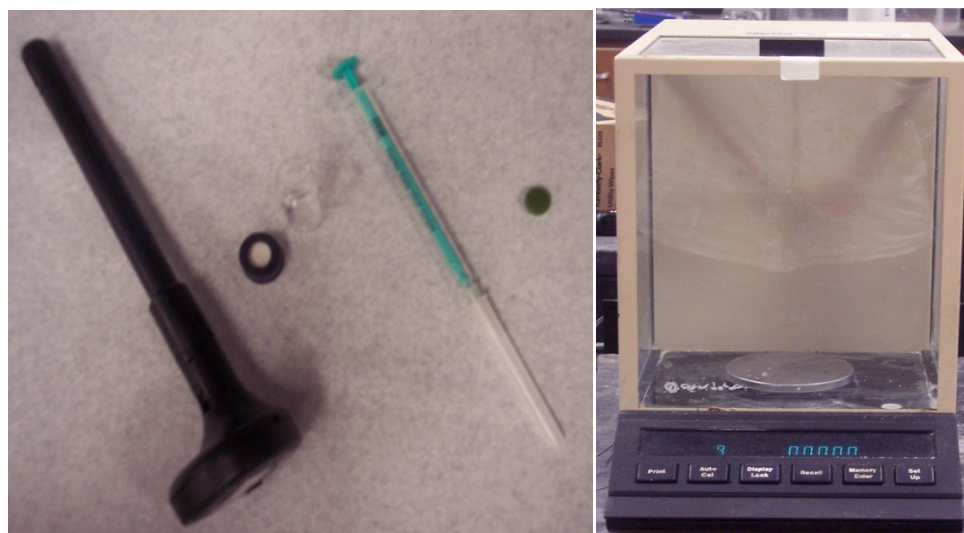


Figure 3.4: Miscellaneous apparatus used

Tedlar bags were used to transfer the polluted gases from cylinders and to allow liquid pollutants to volatilize to the gas phase. A 1 ml gas tight syringe with an increment of 0.05 ml and 27 gauge needles were used for injections. The syringe needle has to go through the column during injection into the GC. As the capillary column diameter is very small, a 27 gauge needle is used. Vials of 4ml volume with septa covers were used to do the experiments.

### 3.2 Adsorbents

Activated carbon was used as an adsorbent because of its high surface area and low cost. Bituminous coal based activated carbon and coconut shell based activated carbon with mesh size are 4\*6 were purchased from Calgon, Inc. The carbon is stored and handled at room temperature. Coconut shell based activated carbon is a little flatter than the bituminous coal based activated carbon. Properties of the activated carbon were given in Table 2.2.

### 3.3 Volatile Organic Compounds

The compounds selected, namely xylene, ethylbenzene and MEK, are hazardous air pollutants released from landfills. *Para*-xylene, *meta*-xylene and *ortho*-xylene were tested separately with both adsorbents and results compared. Xylene and ethylbenzene were purchased from Fisher Scientific in liquid form. To convert the liquid phase to gas phase, a known amount of liquid was injected into the air-filled tedlar bag. It was left aside for at least a week for complete evaporation to occur. The known concentration was then used for the experiments.

For calibration of the GC, gas standards were required. The standard contains xylene mixed isomer at 10 ppm, ethylbenzene 10 ppm and methyl ethyl ketone 10 ppm was purchased from Matheson Trigas. Figure 3.5 shows the standard cylinder.



Figure 3.5: Cylinder contains BTEX standard

### 3.4 Experimental Procedure

Calibrating the GC is the first step to start the experiment. The volume of gas for the injection into the GC has to be the same for calibration and experiment. For experiments, it is set as 0.5 ml. The GC is calibrated in the range from 5 ppm to 25,000 ppm for all compounds using a seven point calibration. In the lower concentration range, 10 ppm and 5 ppm are the direct and half dilution of mixture gas standards. The high range concentration gas (25,000 ppm) is made in the tedlar bag because high-level concentration for xylene, ethylbenzene and MEK are not available in market as gas phase. A 1 L tedlar bag is filled air tight, using air from the fume hood. The bag cannot be filled beyond its 1 L capacity. Visual inspection of the bag will ensure that it is filled to within 90 to 100%, of its 1 L capacity. Using the calculation given in Appendix C, a

specific amount of liquid phase compound is injected into the tedlar bag through septa to obtain the concentration needed in gas phase.

A carbon granule was measured using the digital weighing scale and dropped inside the 4 ml vials, which are well tightened with the septa cover. To find the adsorption equilibrium time, trials were conducted. The same volume of compound was injected at the same time in all the vials. Headspace concentrations were then measured using the GC at 10-minute intervals. Approximately after 60 minutes, the concentration in the headspace remained the same, indicating that adsorption had ceased and equilibrium had been reached. For all the compounds, for both bituminous coal based and coconut shell based activated carbon, trials showed that 1-hour was sufficient time to reach equilibrium. The data from these trials is included in Appendix D for high and low concentrations.

For actual experiments, a known amount of carbon was measured using a digital weighing scale and dropped inside the vials, which were well tightened with the septa cover. The carbon amounts in the vials were noted and the vials placed in a row under the hood. The volume of pollutant compound injected into the vials varied from 0.5 ml to 1.1 ml. The vial was allowed 1 hour to reach equilibrium, with intermediate shaking. The headspace concentration was then measured via GC injection after the equilibrium time had passed. Adsorption equilibrium concentrations were determined for enough points to enable an isotherm to be plotted for each pollutant and each adsorbent. Two replicates for one compound and one adsorbent combination were done to find the error percentage.

All runs were carried out under room temperature (70-80° F). Humidity of the fume hood air used to fill the tedlar bags is 45%. Relative humidity of the room air, used to fill the vials initially, varies from 45-70%. The resulting humidity for isotherm determination, which results from air from the tedlar bags being injected into vials already containing room air, is thus between 45-70%. Formulas and calculation methods are given in Appendix B.

The EPA default landfill concentrations for the selected VOCs MEK, ethylbenzene, and xylene are 7.09, 4.61, and 12.1 ppm, respectively. These low concentration values are tested with BPL and OVC but the equilibrium headspace concentration value was found to be zero. The GC was not sensitive to measure the very low concentrations remaining in the headspace. Hence, higher initial concentration values were used for finding the isotherm values.

## CHAPTER 4

### RESULTS AND DISCUSSION

#### 4.1 Results

This chapter presents and discusses results for experiments conducted according to the methodology described in Ch. 3.

##### *4.1.1 Replicates*

Two replicates were done for the ortho xylene on BPL; Figure 4.1 compares mass of pollutant adsorbed per mass of carbon versus equilibrium concentration for all three runs. As can be seen from the figure, replicates are consistent. The maximum variation in mass adsorbed per mass of carbon for a given equilibrium concentration is around 10%.

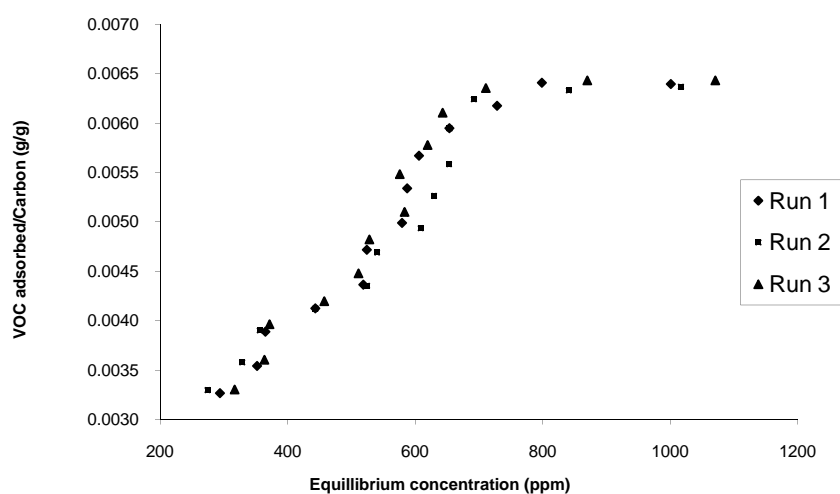


Figure 4.1 Comparison of runs for ortho-xylene tested with BPL

#### *4.1.2 Adsorption Isotherms*

Figures 4.2- 4.11 show the experimental data collected for mass of pollutant adsorbed per unit mass of carbon, versus equilibrium pollutant concentration, for each adsorbent/adsorbate combination.

The Langmuir and Freundlich equation constants were determined using the linearized forms of the equations (Eq. 2.5, 2.6, and 2.8) and using linear regression to fit a best-fit line through the experimental data. Langmuir and Freundlich equation constants were also determined using the non-linearized forms of the equation (Eq. 2.4 and 2.7) and non-linear regression (using Oakdale Engineering Data fit software version 9) to determine a best-fit curve through the data. The constants obtained from these methods and associated  $R^2$  values are compared in the Table 4.1

The constants obtained from non-linear regression are used to plot the Langmuir and Freundlich isotherms shown in Figures 4.2 - 4.11 along with the experimental data. The linearized plots used for the linear regression curve fits are shown in Appendix D. Maximum adsorption capacities from experimental data are given in Table 4.2. The experimental maximum adsorption capacities are compared with the Langmuir  $Q_0$  values obtained from non-linear regression in Table 4.3. The  $Q_0$  values represent maximum adsorption capacities.

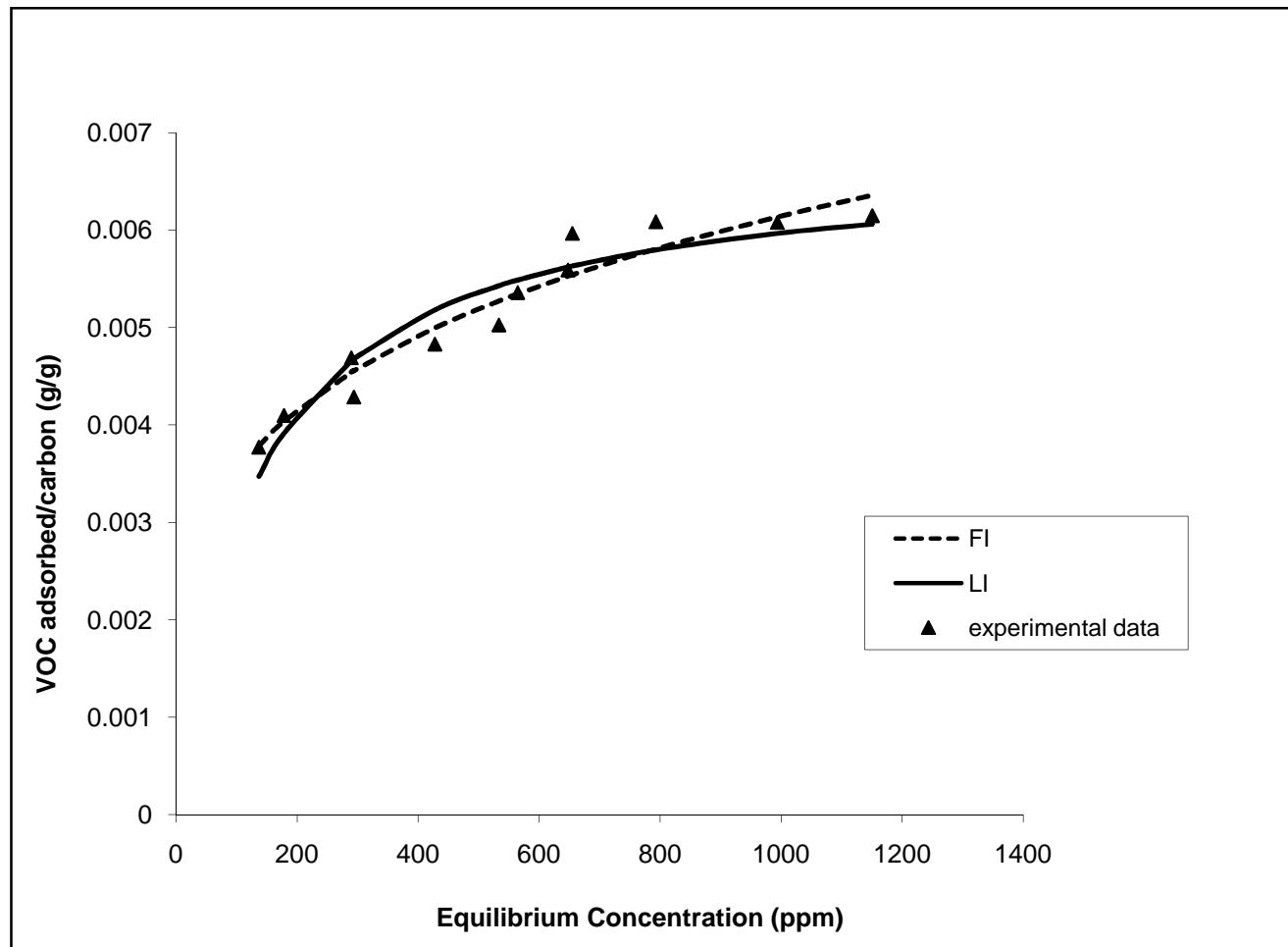


Figure 4.2 Adsorption isotherm for ethylbenzene tested with BPL



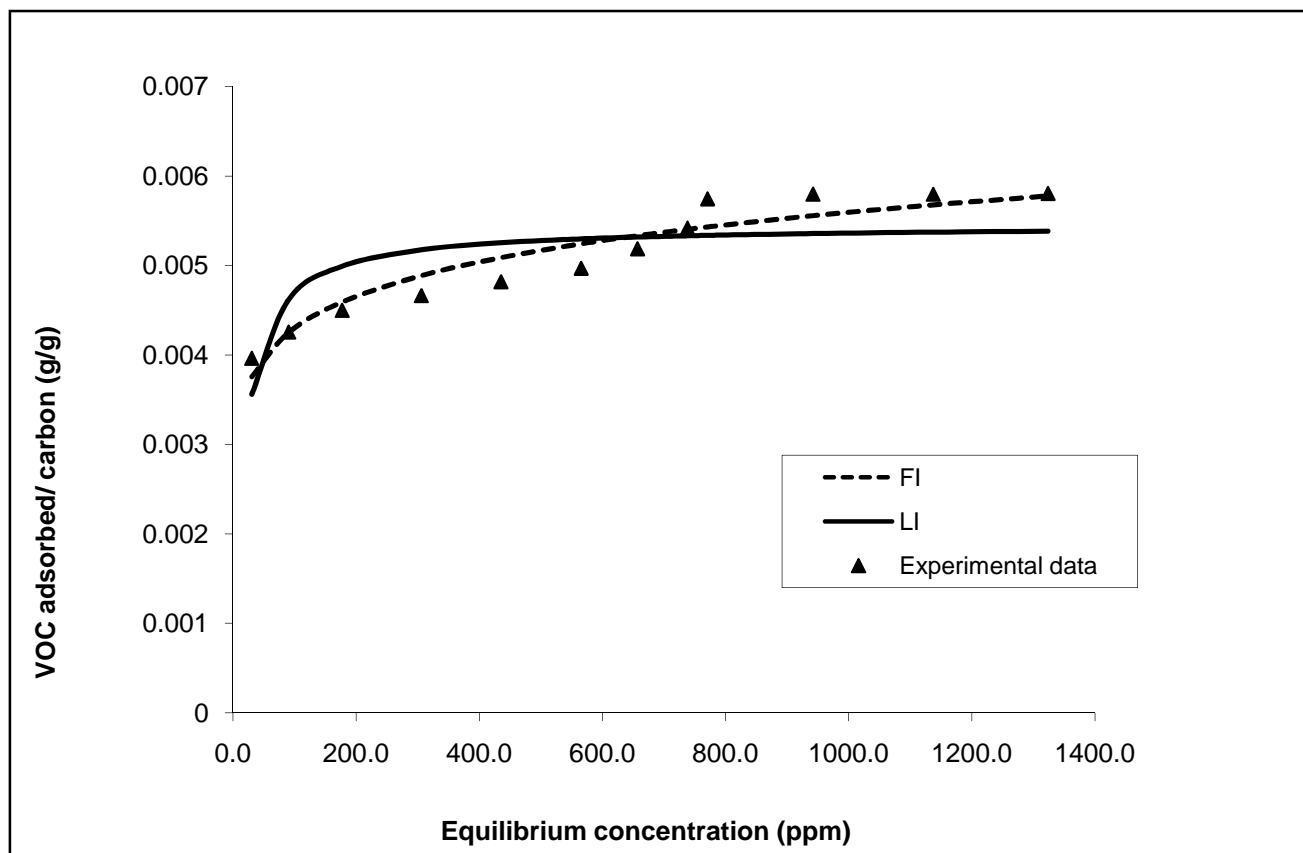


Figure 4.3: Adsorption isotherm for ethylbenzene tested with OVC

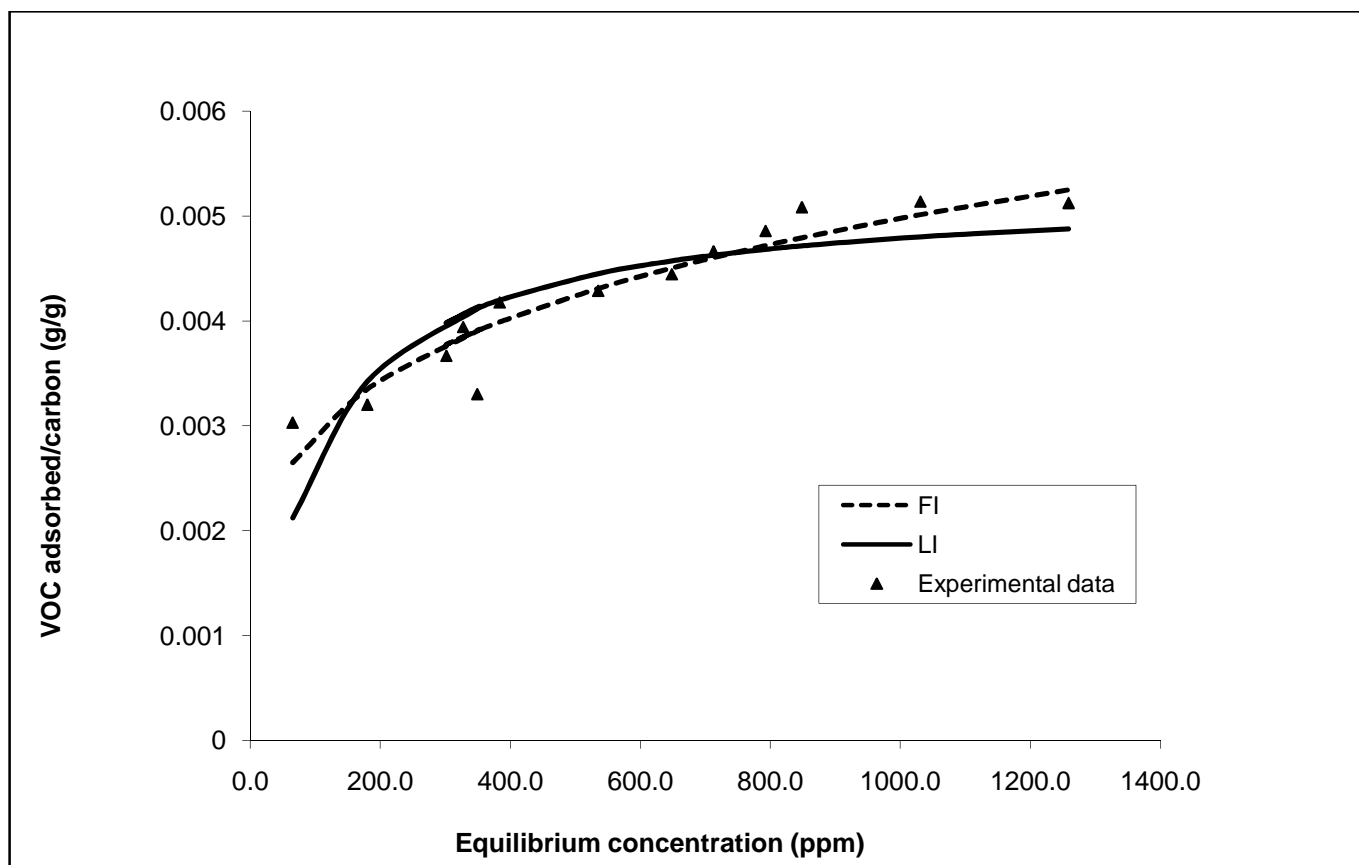


Figure 4.4: Adsorption isotherm for methyl ethyl ketone tested with BPL

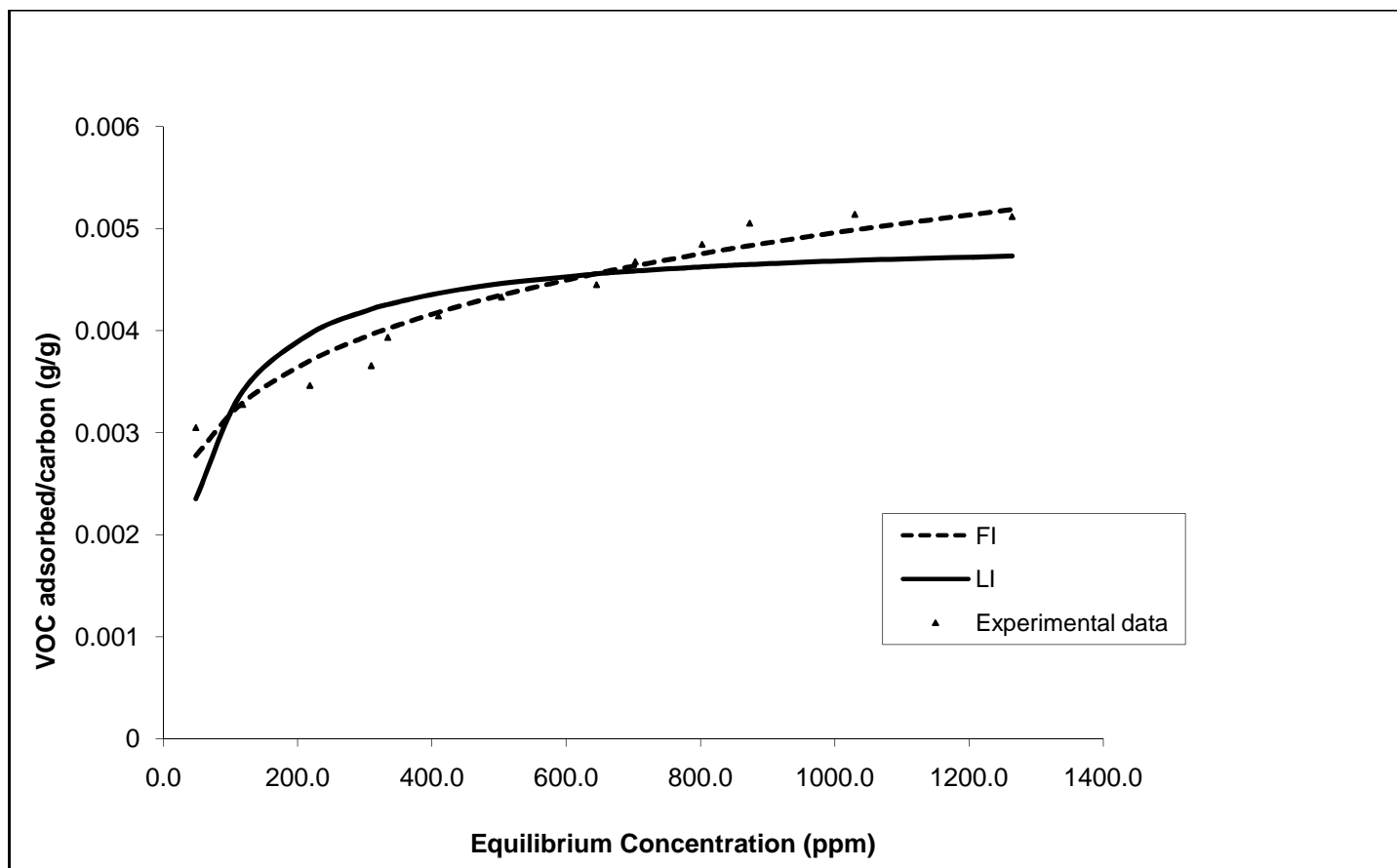


Figure 4.5: Adsorption isotherm for methyl ethyl ketone tested with OVC

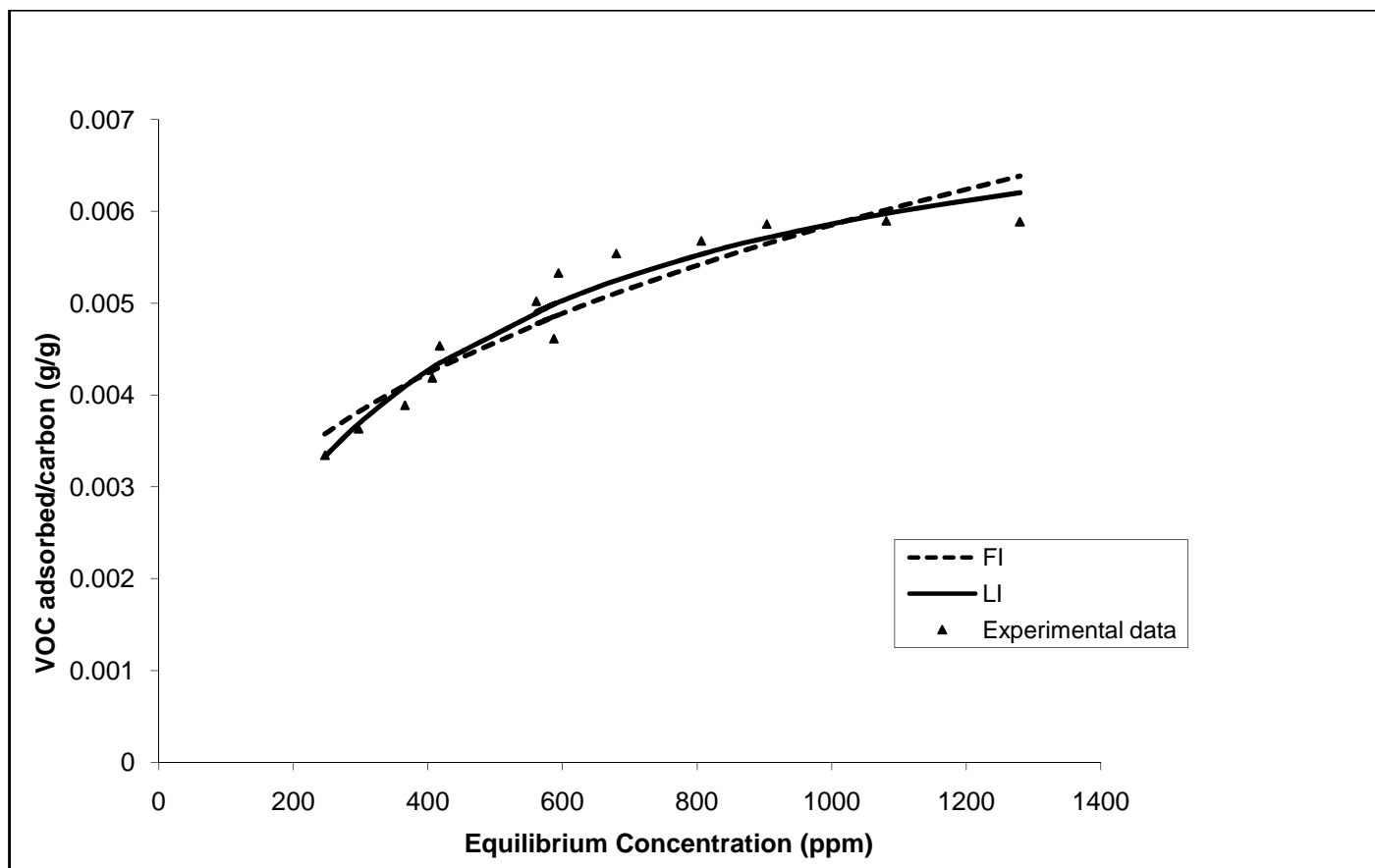


Figure 4.6: Adsorption isotherm for meta-xylene tested with BPL

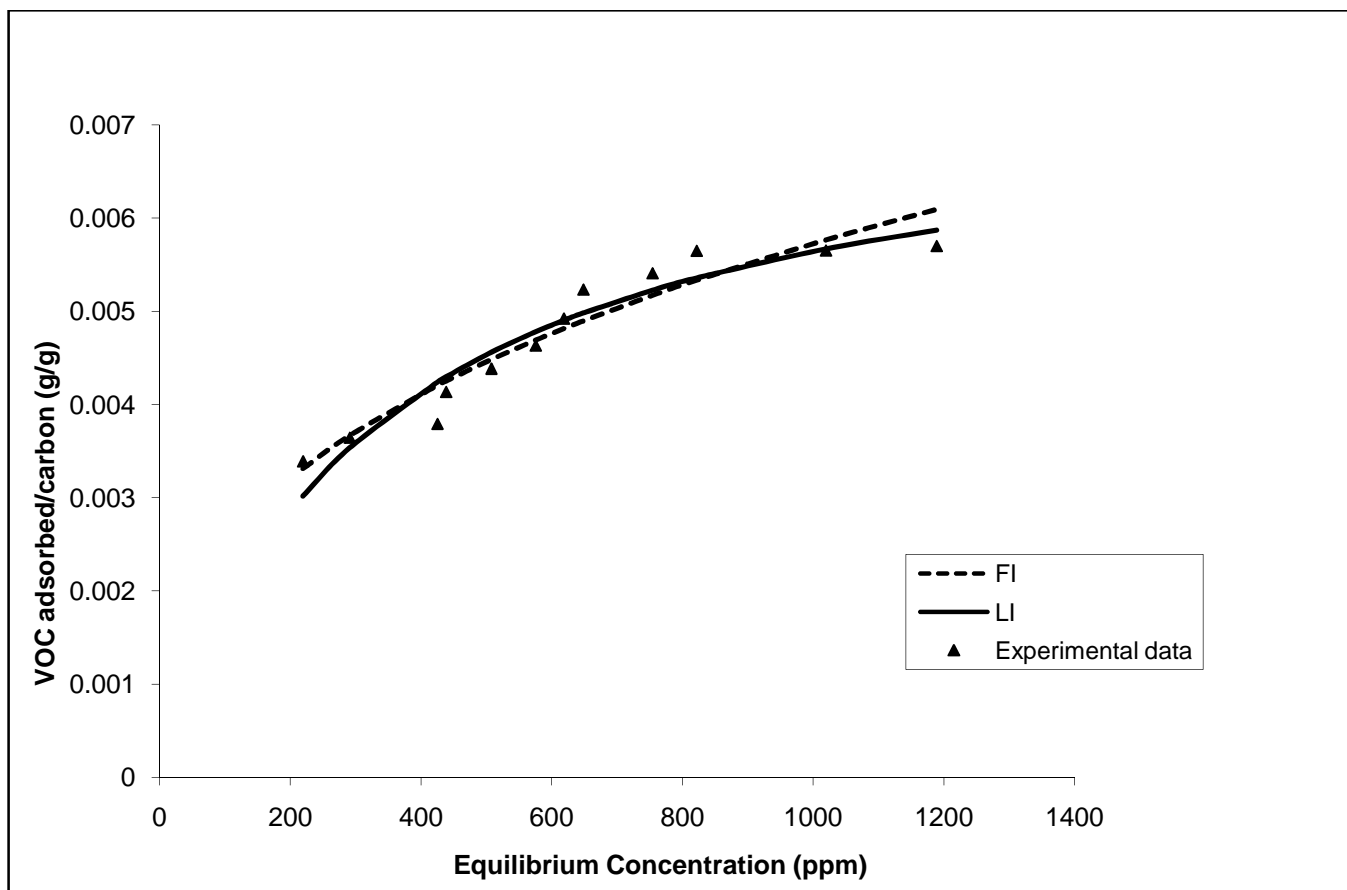


Figure 4.7: Adsorption isotherm for meta-xylene tested with OVC

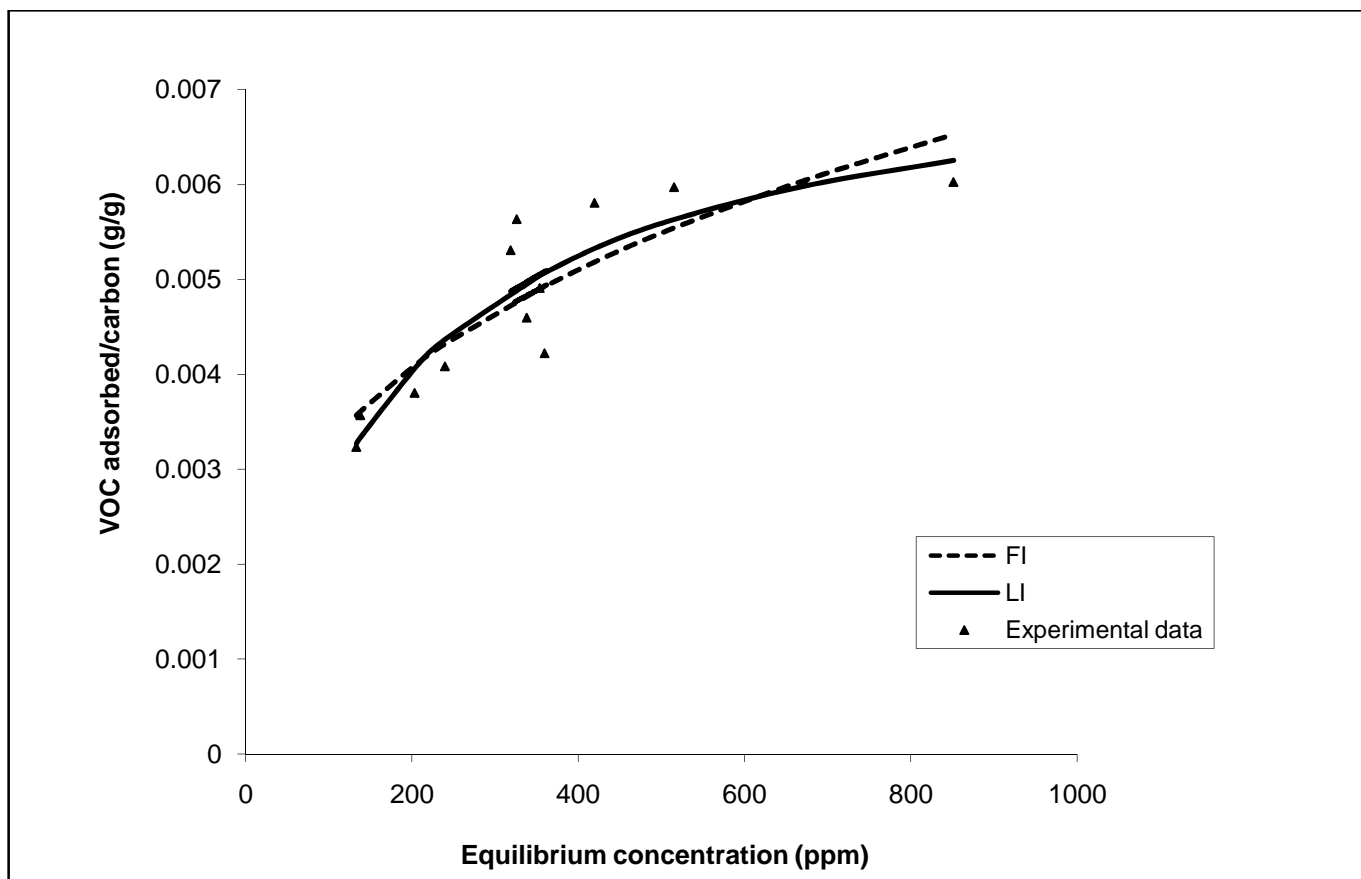


Figure 4.8: Adsorption isotherm for para-xylene tested with BPL

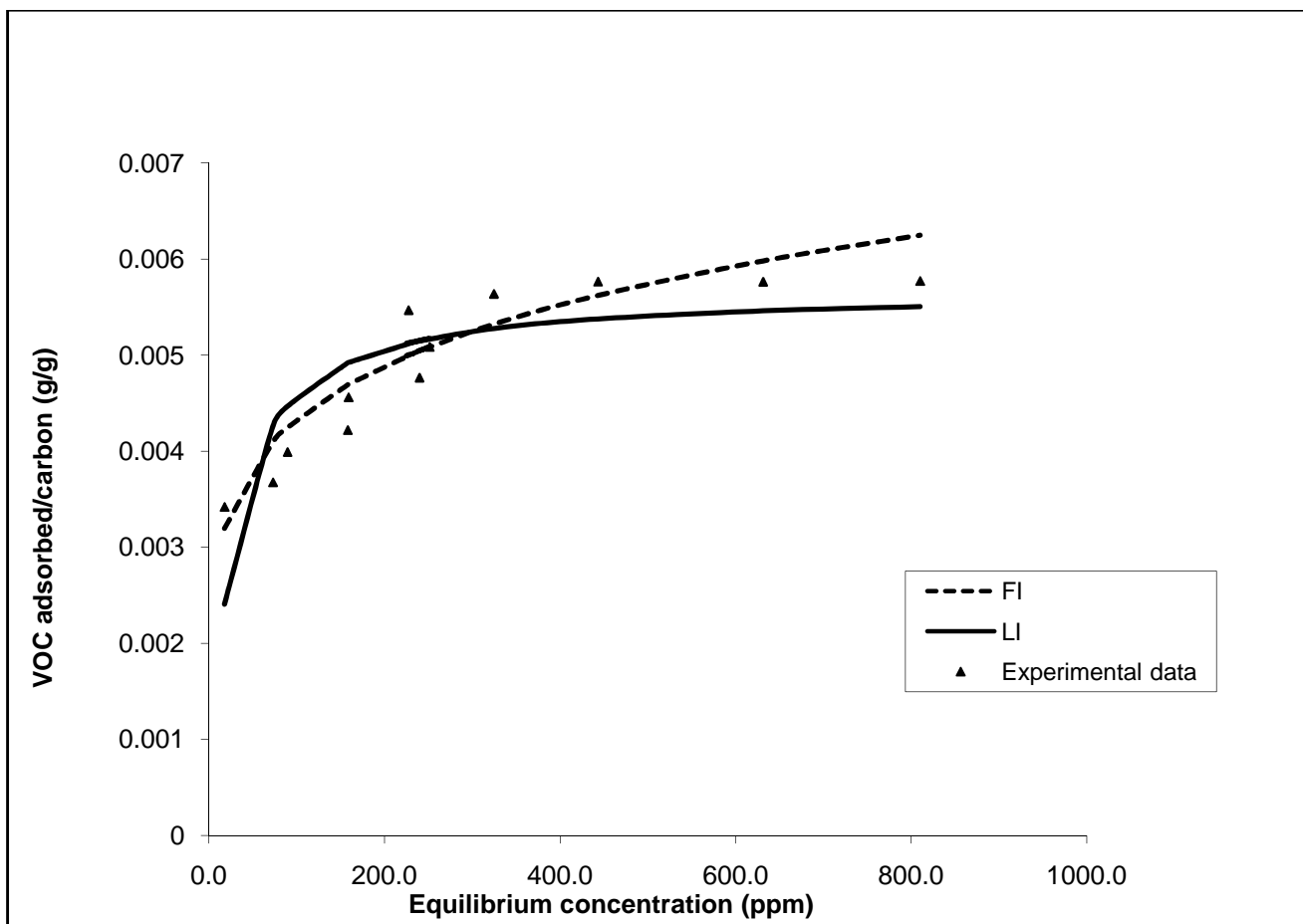


Figure 4.9: Adsorption isotherm for para-xylene tested with OVC

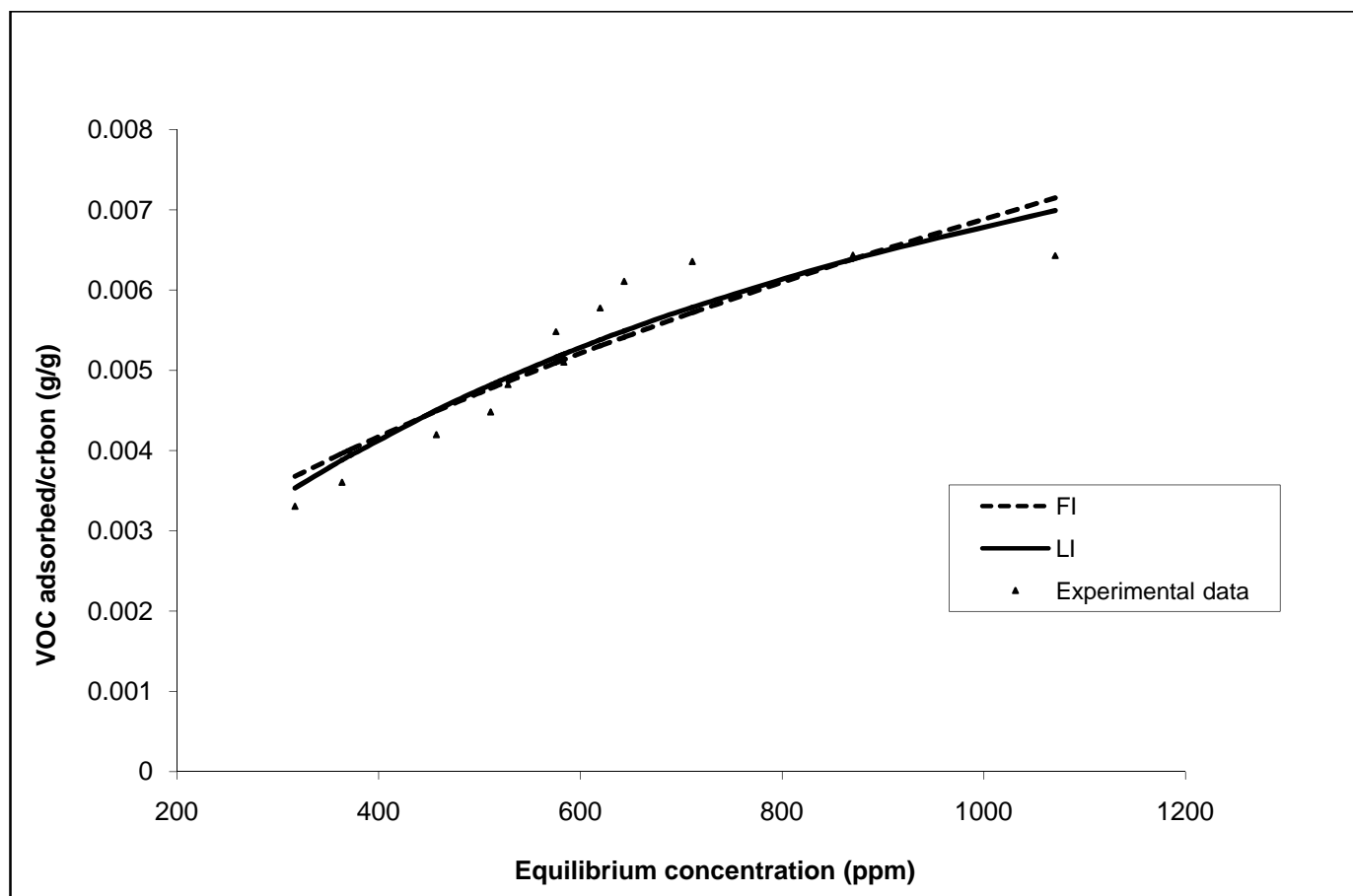


Figure 4.10: Adsorption isotherm for ortho-xylene tested with BPL



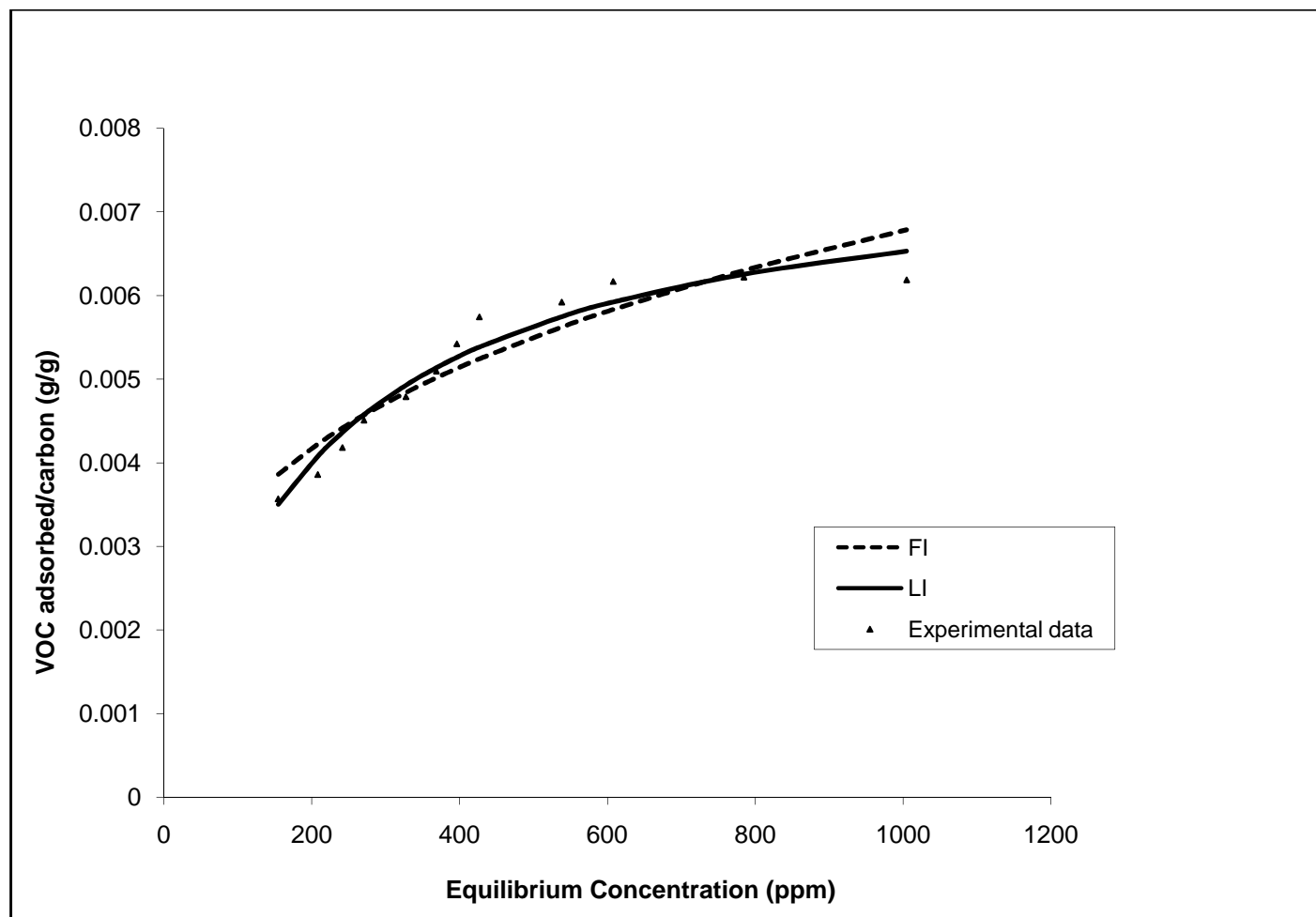


Figure 4.11: Adsorption isotherm for ortho-xylene tested with OVC

Table 4.1 Empirical Constants

Compound	Adsorbent	Isotherm	Constants	Linear (1/Q <sub>e</sub> )	Linear	Non linear
Ethylbenzene	BPL	FI	K <sub>f</sub>		1.12E-03	1.14E-03
			n		4.05E+00	4.10E+00
			R <sup>2</sup>		9.44E-01	9.20E-01
		LI	Q <sub>0</sub>	6.45E-03	6.97E-03	6.74E-03
			K	9.43E-03	6.62E-03	7.77E-03
			R <sup>2</sup>	9.00E-01	9.90E-01	8.90E-01
Ethylbenzene	OVC	FI	K <sub>f</sub>		2.58E-03	2.54E-03
			n		9.00E+00	8.75E+00
			R <sup>2</sup>		9.10E-01	9.10E-01
		LI	Q <sub>0</sub>	5.33E-03	6.04E-03	5.45E-03
			K	8.00E-02	1.49E-02	6.16E-02
			R <sup>2</sup>	6.30E-01	9.90E-01	6.00E-01
Methyl ethyl ketone	BPL	FI	K <sub>f</sub>		1.12E-03	1.01E-03
			n		4.66E+00	4.33E+00
			R <sup>2</sup>		8.70E-01	8.90E-01
		LI	Q <sub>0</sub>	4.67E-03	5.74E-03	5.25E-03
			K	2.28E-02	6.55E-03	1.04E-02
			R <sup>2</sup>	6.00E-01	9.80E-01	7.10E-01
Methyl ethyl ketone	OVC	FI	K <sub>f</sub>		1.38E-03	1.32E-03
			n		5.43E+00	5.22E+00
			R <sup>2</sup>		9.30E-01	9.40E-01
		LI	Q <sub>0</sub>	4.62E-03	5.50E-03	4.93E-03
			K	3.26E-02	8.73E-03	1.89E-02
			R <sup>2</sup>	6.68E-01	9.90E-01	6.90E-01
<i>ortho</i> -Xylene	BPL	FI	K <sub>f</sub>		9.53E-05	1.58E-04
			n		1.60E+00	1.83E+00
			R <sup>2</sup>		8.90E-01	8.40E-01
		LI	Q <sub>0</sub>	1.50E-02	1.21E-02	1.19E-02
			K	9.04E-04	1.28E-03	1.33E-03
			R <sup>2</sup>	9.41E-01	8.30E-01	8.80E-01
<i>ortho</i> -Xylene	OVC	FI	K <sub>f</sub>		6.82E-04	8.46E-04
			n		2.97E+00	3.32E+00
			R <sup>2</sup>		9.10E-01	8.90E-01
		LI	Q <sub>0</sub>	7.88E-03	7.51E-03	7.75E-03
			K	5.04E-03	5.89E-03	5.33E-03
			R <sup>2</sup>	9.65E-01	9.90E-01	9.60E-01

Table 4.1 - continued

Compound	Adsorbent	Isotherm	Constants	Linear (1/Qe)	Linear	Non linear
<i>para</i> -Xylene	BPL	FI	K <sub>f</sub>		6.01E-04	7.25E-04
			n		2.80E+00	3.07E+00
			R <sup>2</sup>		8.10E-01	7.70E-01
		LI	Q <sub>0</sub>	7.34E-03	7.43E-03	7.53E-03
			K	6.07E-03	5.89E-03	5.76E-03
			R <sup>2</sup>	8.52E-01	9.50E-01	8.20E-01
<i>para</i> -Xylene	OVC	FI	K <sub>f</sub>		1.96E-03	1.93E-03
			n		5.94E+00	5.70E+00
			R <sup>2</sup>		8.70E-01	8.70E-01
		LI	Q <sub>0</sub>	5.18E-03	6.13E-03	5.67E-03
			K	9.18E-02	2.25E-02	4.15E-02
			R <sup>2</sup>	5.93E-01	9.90E-01	6.60E-01
<i>meta</i> -Xylene	BPL	FI	K <sub>f</sub>		4.41E-04	5.14E-04
			n		2.65E+00	2.84E+00
			R <sup>2</sup>		9.10E-01	9.00E-01
		LI	Q <sub>0</sub>	7.92E-03	7.56E-03	7.82E-03
			K	2.90E-03	3.30E-03	3.00E-03
			R <sup>2</sup>	9.58E-01	9.80E-01	9.50E-01
<i>meta</i> -Xylene	OVC	FI	K <sub>f</sub>		4.65E-04	4.73E-04
			n		2.75E+00	2.77E+00
			R <sup>2</sup>		9.30E-01	9.20E-01
		LI	Q <sub>0</sub>	6.85E-03	7.38E-03	7.47E-03
			K	3.98E-03	3.19E-03	3.09E-03
			R <sup>2</sup>	8.92E-01	9.80E-01	9.20E-01

Table 4.2 Empirical constants comparison for replicates

Isotherm	Constants	R1	R2	R3	All
FI	Kf	0.00011	0.00015	0.00016	0.00014
	n	1.67	1.79	1.83	1.77
	R2	0.906	0.907	0.840	0.881
LI	Q0	0.0129	0.0151	0.0119	0.0121
	K	0.00114	0.00137	0.00133	0.00128
	R2	0.926	0.917	0.880	0.906

Table 4.3 Experimental Maximum Adsorption Capacities (g VOC adsorbed/g carbon)

<b>VOC</b>	<b>BPL</b>	<b>OVC</b>
Ethylbenzene	0.0061	0.0058
Methyl ethyl ketone	0.0051	0.0051
<i>para</i> -Xylene	0.0060	0.0058
<i>meta</i> -Xylene	0.0059	0.0057
<i>ortho</i> -Xylene	0.0064	0.0062

Table 4.4 Comparison of Experimentally Determined Maximum Adsorption Capacities with Langmuir Isotherm Maximum Adsorption Capacities

VOC	Maximum adsorption capacity g VOC adsorbed/g carbon					
	BPL			OVC		
	<b>Exp. Data</b>	<b>Langmuir Q<sub>0</sub></b>	<b>M</b>	<b>Exp. Data</b>	<b>Langmuir Q<sub>0</sub></b>	<b>M</b>
Ethylbenzene	0.0061	0.0067	0.41	0.0058	0.0055	0.39
Methyl ethyl ketone	0.0051	0.0053	0.38	0.0051	0.0049	0.38
<i>para</i> -Xylene	0.006	0.0075	0.44	0.0058	0.0057	0.44
<i>ortho</i> -Xylene	0.0064	0.0119	0.42	0.0062	0.0078	0.40
<i>meta</i> -Xylene	0.0059	0.0078	0.44	0.0057	0.0075	0.42

M- Manufacturer's maximum adsorption capacity

## 4.2 Discussion

### *4.2.1 Adsorption Capacity*

Table 4.3 shows that bituminous coal based activated carbon (BPL) maximum adsorption capacity is slightly higher than the coconut shell based activated carbon (OVC) for four of the five compound tested (and equal for the other one). For BPL, the adsorption capacity started lower and ended up higher than OVC as equilibrium concentration increased.

For xylene, the *para* and *meta* isomer adsorption capacities are almost equal and lower compared to *ortho*-xylene for both types of activated carbon (AC). According to Wang et al., (2004) *ortho*-xylene adsorption capacity is higher than *para* and *meta* xylene. In this study, methyl ethyl ketone (MEK) shows a similar adsorption capacity for the two different types of AC. Kim *et al.* (2005) found that MEK adsorption capacity is slightly lower for bituminous coal based carbon than coconut shell based activated carbon. In this study, BPL has a higher adsorption capacity for ethylbenzene than OVC. The properties of BPL and OVC that may have influenced pollutant adsorption capacity are compared below. Carbon physical properties were listed in Table 2.1.

#### 4.2.1.1 Micropores and Macropores

The number of micropores is high in both AC, but the number of macropores is medium in BPL and low in OVC. The pore size distribution impacts the adsorbate-adsorbent interaction. Micropores adsorb small molecules and macropores adsorb larger molecules. Large molecules tend to adsorb less, if the number of macropores is low. BPL's slightly higher adsorption capacity for the compounds tested, which are fairly large may have been due to its higher number of macropores. The fact that maximum adsorption capacity was the same for MEK for OVC and BPL may have been due to the fact that MEK is slightly smaller than the other molecules tested, and may thus not have taken advantage of the higher macropore space availability in OVC.

#### 4.2.1.2 Shape

The shape of the OVC is flatter than BPL, more easily accessible surface area is thus available on the outer surface for coconut shell based activated carbon. This may be the reason that OVC adsorption capacity is slightly higher than BPL for low concentrations. As concentrations increase, the inner BPL macropore space becomes more important, leading finally to greater overall maximum adsorption capacities for BPL.

#### 4.2.1.3 Molecular weight

The greater the MW, the greater the adsorption capacity. Xylene ( $C_8H_{10}$ ) MW is 106.17, ethylbenzene ( $C_8H_{10}$ ) MW is 106.17, and methyl ethyl ketone ( $C_4H_8O$ ) MW is 72.11. It can be noted from Table 4.3 that MEK with the lowest molecular weight, has a lower adsorption capacity than the other two VOCs.

#### 4.2.1.4 Volatility

An evaporation characteristic of chemicals is known as volatility. The higher the volatility, the higher the vapor pressure, and the greater tendency the compound has to exist in the gas phase, as opposed to the solid or liquid phase. Compounds with higher vapor pressures thus exhibit lower adsorption capacities. Compounds with higher vapor pressures also have lower boiling points, since less heat must be added to convert them to the gas phase. The boiling point of VOCs used in these experiments are *ortho*-xylene 144°C, *para*-Xylene 138°C, *meta*- xylene 139°C, ethylbenzene 136°C, and methyl ethyl ketone 80°C. Adsorption capacities would also be expected to follow this

order, with ortho-Xylene having the greatest capacity and MEK having the least. Comparing the results in Table 4.3, the adsorption capacity is higher for *ortho* xylene and lower for MEK.

#### 4.2.2 Comparison of Maximum Adsorption Capacities With Langmuir $Q_0$

From Table 4.4, it can be seen that the maximum adsorption capacity found from the Langmuir non-linear method is higher for ortho, meta- xylene tested with BPL and OVC and also higher for ethylbenzene, MEK, and para-xylene tested with BPL than the experimental maximum adsorption capacity. This may be due to the fact that the experiments did not test equilibrium concentrations high enough to reach the maximum adsorption capacity.

The Langmuir maximum adsorption capacities are lower compared to experimental maximum adsorption capacity for ethylbenzene, MEK and para-xylene tested with OVC. The experimental data has one or two low final concentrations in the set of experimental data for these compounds tested with OVC. When we remove those low concentration values from the data set and analyze through non-linear regression method, the Langmuir maximum adsorption capacity value is higher than experimental maximum adsorption capacity. R.D. Harter, (1984) found that Langmuir does not effectively identify the maximum adsorption capacity. He concludes that when lower concentrations are used, maximum adsorption capacities are on the order of 50% or more.

#### 4.2.3 Isotherm Studies

From Table 4.1, the Freundlich linear (equ. 2.8) and non-linear regression analysis R square values are not significantly different. However, for Langmuir, R square values have substantial differences when linear equations 2.5 and 2.6 are used. For the case of ethylbenzene adsorption onto OVC, forexample, the  $R^2$  value for equ. 2.5 was 0.99, whereas the  $R^2$  value for equ. 2.6 was 0.63. Because of how linear analysis works, equation 2.5 gives more importance to high pollutant concentration values, whereas equation 2.6 gives weight to low concentration values (Lawler, 1991). A low  $R^2$  value for eq. 2.6 indicates that low concentration values, which were weighted more heavily, did not fit the isotherm very well.

Considering the variations in linear Langmuir regression methods, non-linear regression analysis is used in this study Non-linear regression is supposed to fit isotherms more accurately than linear regression (Lawler, 1991).

From the summary of constants, Table 4.1, for the Freundlich isotherm (FI), it can be seen that R square value is higher for ethylbenzene tested with BPL and OVC, MEK tested with BPL and OVC, and para-xylene tested with OVC compared to Langmuir isotherm (LI). The pollutants ortho-xylene and meta-xylene tested with BPL and OVC have higher R square values for LI compared to FI. Para-xylene tested with BPL also has higher R square values for LI than FI.

From Table 4.2, it can be seen that the constant found from the replicates are all in the same range of values.



#### *4.2.4 Similarities and Differences Compared to Manufacturer Isotherms*

The isotherms obtained from the carbon manufacturer, Calgon Carbon, are given in Appendix E. The comparison of maximum adsorption capacity of experimental data and manufacturer's are given in Table 4.1.3. The similarities of experimental data with the manufacturer's isotherm are:

- In both, OVC starts with a slightly higher adsorption capacity but ends up with a slightly lower adsorption capacity compared with BPL.
- The compounds tested, have the same range of maximum adsorption capacity (Comparing among compounds for the Calgon isotherms, and comparing among compounds for the isotherms determined in this study).

However, the manufacturer's maximum adsorption capacities are substantially higher than the maximum adsorption capacity determined in this research. This is likely due to the fact that experiments in this research were conducted to reflect real-world conditions, using ambient humidity and without pre-treating the carbon via heating to remove moisture. Calgon carbon pre-treated the carbon by oven drying it and removed humidity from the gas stream.

## CHAPTER 5

### CONCLUSIONS AND RECOMMENDATIONS

#### 5.1 Conclusions

Adsorption isotherm studies were conducted for both BPL and OVC for the compounds MEK, ethylbenzene, ortho, para and meta xylene at ambient temperature and relative humidity. Non linear Langmuir isotherm (LI) and Freundlich isotherm (FI) were used to fit the adsorption data. For OVC, MEK, ethylbenzene and para xylene fit FI better, whereas ortho- xylene fit LI better. For BPL, MEK, and ethylbenzene follow FI and para and ortho-xylene isomers follow LI. For both BPL and OVC meta-xylene fits for both LI and FI.

Results show that BPL has a slightly higher maximum adsorption capacity than OVC, likely; because BPL has higher sphericity, macro pores and inner surface area than OVC. The rate of adsorption is initially higher for OVC than BPL due to its higher external surface area compared to BPL. The adsorption capacity is sensitive to physical characteristics of activated carbon such as pore size distribution and shape. It also depends on the VOC characteristics such as molecular weight, volatility, and size of the molecule. MEK, with the lowest molecular weight and highest volatility of the compounds studied, had the lowest adsorption capacity. Ortho-xylene, with the lowest volatility, had the highest adsorption capacity.

There is a difference between the isotherm constants determined using the two linearized forms of the LI; hence, the non-linear approach is best to find the isotherm constants. For FI also, the isotherm constants were determined using a non-linear curve-fit. Maximum adsorption capacities are lower than the manufacturer's maximum adsorption capacities, but the trends of OVC and BPL performance for the pollutants are the same. In this study, BPL has a slightly higher maximum adsorption capacity when compare to OVC, which is the same as the manufacturer's isotherm curve. The maximum adsorption capacities determined in this study are representative for real-world humidity values and carbon usage (which does not include thermal pre-treatment to remove moisture).

## 5.2 Recommendations

Carbon is readily available and it is a renewable source. It is one of the economical ways of treating a pollutant and cleaning the environment. It can be used in more effective ways by doing more research on the adsorption method using activated carbon.

Further research is needed to treat the landfill gas using a continuous flow method to determine breakthrough times and measure the change in adsorption capacity for different humidity levels and temperatures. Other HAPs emitted from landfills should be tested, and combinations of HAPs should be tested to evaluate potential competitive adsorption. Further research is recommended for testing adsorption of HAPs in the presence of carbon dioxide and methane, which are the principal

constituents of landfill gas, to determine whether competitive adsorption by methane or carbon dioxide poses a concern.

## APPENDIX A

### SUMMARY OF LANDFILL GAS PRODUCTION AND EMISSION

Table A.1: Summary of landfill gases production

<b>Content</b>	<b>Phase 1</b>	<b>Phase 2</b>	<b>Phase 3</b>	<b>Phase 4</b>
Process	Aerobic	Anaerobic	Anaerobic	Anaerobic
Objective	Breaking down Complex carbohydrates, proteins and lipids.	Landfill become acidic	Anaerobic bacteria consume acid from phase 2 and start producing methane	Achieve steady state
Duration	Days or months			More than 20 years.
Byproduct	Carbon dioxide	Carbon dioxide and hydrogen	Methane	Methane, Carbon dioxide, and other Non-methane organic compounds.
Nitrogen level	Declines	Declines	Declines	Achieve steady state

Table A.2: Emissions from landfills and related information

<b>Compound</b>	<b>*Default concentration (ppmv)</b>	<b>Effects</b>	<b>Previous studies in activated carbon</b>
1,1,1-Trichloroethane(methyl chloroform)	0.48	HAP	Pires et al.,2003, Fangmark et al.,2002, Yun ,2001, Rexwinkel et al.,1999, Yun et al.,1998, Born & Pichowski,1997, Born et al.,1996, Tanada et al.,1996, Tsai & Chang,1994.
1,1,2,2-tetrachloroethane	1.11	HAP	Fangmark et al.,2002, Zeid et al.,1995,

Table A.2 – Continued

<b>Compound</b>	<b>*Default concentration (ppmv)</b>	<b>Effects</b>	<b>Previous studies in activated carbon</b>
1,1-Dichloroethane(ethylidene dichloride)	2.35	HAP	Fangmark et al.,2002.
1,1-Dichloroethene (vinylidene chloride)	0.20		
1,2- Dichloroethane (ethylene chloride)	0.41	HAP	Fangmark et al.,2002, Pre et al.,2002.
1,2 – Dichloropropane (propylene dichloride)	0.18	HAP	Fangmark et al.,2002, Zhang et al.,2001.
2 – Propanol (isopropyl alcohol)	50.1		Nastaj et al.,2006 Downarowicz & Nastaj,2004 Tamon & Okazaki,1996
Acetone	7.01	0.055 mol O <sub>3</sub> / mol C	Pires et al.,2006, Joao et al.,2003, Pre et al.,2002, Gales et al.,2000, Wartelle et al.,2000, Huang et al.,1999, Lee & reucroft.,1999, Cal et al.,1996, Tamon & Okazaki,1996, Golden & Kumar,1993, Golden et al.,1991.
Acrylonitrile	6.33	HAP	Giraudet et al.,2006, Huang et al.,1999.
Bromodichloromethane	3.13		
Butane	5.03	0.124 mol O <sub>3</sub> / mol C	Marban et al.,2006, Walton et al.,2005, Zhu et al.,2005, Fuertes et al.,2003, Ahnert & Heschel, 2002, Walt Do et al.,2001, Do & Do,2000, Do et al.,2000 Fiani et al.,2000, Guezel,1999, Allen et al.,1999, Pan et al.,1998, Gadkaree,1998.

Table A.2 Continued

Compound	*Default concentration (ppmv)	Effects	Previous studies in activated carbon
			King & Do,1996, Hu et al.,1993, Golden & Kumar,1993, Golden et al.,1991, Do et al.,1991, Herden et al.,1991, Lu et al.,1991, Mayfield & Do,1991.
Carbon dioxide		GHG	Moon and Shim,2006, Cavenati et al.,2006, Przepiorski et al.,2004, Shin et al.,2002, Triebe & Tezel.,1995, Gray,1993.
Carbon disulfide	0.58	HAP	Masuda et al.,1999, Xun et al.,1991.
Carbon monoxide	141	0.019 mol O <sub>3</sub> / mol C	Al-khatib et al.,2002, Iyuke and Ahmadun,2002, Mohamad et al.,2000, Triebe & Tezel.,1995.
Carbon tetrachloride	0.004	HAP	Gauden et al.,2004, Shin et al.,2002, BanSode et al.,2003, Lee & reucroft.,1999, Bae and Do,2002, Cao et al.,2002.
Carbonyl sulfide	0.49	HAP	
Chlorobeneze	0.25	HAP	Fangmark et al.,2002.
Chlorodifluoromethane	1.30		
Chloroethane (ehtyl chloride)	1.25	HAP	Fangmark et al.,2002.
Chloroform	0.03	HAP	Shin et al.,2002, BanSode et al.,2003, Pre et al.,2002, Zeid et al.,1995.
Chloromethane	1.21		Fangmark et al.,2002, Ordonez et al.,2001.
dichlorobeneze	0.21		



Table A.2 –Continued

Compound	*Default concentration (ppmv)	Effects	Previous studies in activated carbon
Dichlorodifluoromethane	15.7		
Dichlorofluoromethane	2.62		Ordonez et al.,2001.
Dichloromethane (methylene chloride)	14.3	HAP	Giraudet et al.,2006, Pre et al.,2002, Burg et al.,2002, Fangmark et al.,2002, Carrott et al.,2001, Yun ,2001, Huang et al.,1999, Yun et al.,1998, Golden & Kumar,1993.
Dimethyl sulfide (methayl sulfide)	7.82		
Ethane	889	0.030 mol O <sub>3</sub> / mol C	Zhu et al.,2005, Walton et al.,2005, Walton et al.,2004, Ordonez et al.,2001, Do & Do,2000, Do et al.,2000 Do,1996, King & Do,1996, Hu et al.,1993, Do et al.,1991, Herden et al.,1991, Mayfield & Do,1991, Lu et al.,1991.
Ethanol	27.2	0.19 mol O <sub>3</sub> /mol C	El-Sharkawy et al., 2006, Giraudet et al.,2006, Pre et al.,2002, Gales et al.,2000, Masuda et al.,1999, Tamon & Okazaki,1996.
Ethyl mercaptan (ethanethiol)	2.28		
Ethylbeneze	4.61	HAP 0.6 ppm O <sub>3</sub> / ppmC	Shin et al.,2002.
Ethylene dibromide	0.001	HAP	

Table A.2 – Continued

<b>Compound</b>	<b>*Default concentration (ppmv)</b>	<b>Effects</b>	<b>Previous studies in activated carbon</b>
Fluorotrichloromethane	0.76		
Hexane	6.57	HAP	Giraudet et al.,2006, Walton et al.,2004, Pre et al.,2002, Huang et al.,1999, Golden & Kumar,1993, Golden et al.,1991.
Hydrogen sulfide	35.5		Ma et al.,2006, Bouzaza et al.,2004, Shin et al.,2002, Boudou et al.,2003, Cal et al.,2000, Masuda et al.,1999, Lee & reucroft.,1999, Mikhalovsky &.Zaitsev,1997.
Mercury (total)	$2.92 \times 10^{-4}$	HAP	Nabais et al.,2005, Li et al.,2003, Vidic and Siler 2001.
Methane		GHG 0.0025 mol O <sub>3</sub> / mol C	Delgado et al.,2006, Cavenati et al.,2006, Moon and Shim,2006, Walton et al.,2005, Walton et al.,2004, Almansa et al.,2004, Shin et al.,2002, Cao et al.,2002, Do et al.,2000, Brady et al.,1996, Herden et al.,1991, Lu et al.,1991.
Methyl ethyl ketone	7.09	HAP 0.3 ppm O <sub>3</sub> / ppmC	Pires et al.,2003, Huang et al.,2002, Pre et al.,2002, Burg et al.,2002, Chiang et al.,2002.
Methyl isobutyl ketone	1.87	HAP	Dusenbury & Cannon,1996.

Table A.2 – Continued

<b>Compound</b>	<b>*Default concentration (ppmv)</b>	<b>Effects</b>	<b>Previous studies in activated carbon</b>
Methyl mercaptan	2.49		Tamai et al.,2006, Bagreev et al.,2005, Bashkova et al.,2005, Shin et al.,2002, Bashkova et al.,2003.
Nitrogen			Cavenati et al.,2006, Gauden et al.,2004, Terzyk et al.,2002.
Pentane	3.29		Walton et al.,2004, Pre et al.,2002, Mayfield & Do,1991, Do et al.,1991.
Perchloroethylene (tetrachloroethylene)	3.73	HAP	Shin et al.,2002, Tanada et al.,1996.
Propane	11.1	0.069 mol O <sub>3</sub> / mol C	Grande et al.,2006, Zhu et al.,2005, Walton et al.,2004, Do et al.,2001, Ordonez et al.,2001, Do et al.,2000, Do & Do,2000, Pan et al.,1998, Do,1996, Olivier et al.,1996, King & Do,1996, Hu et al., 1993, Herden et al.,1991.
t-1,2-dicholorethene	2.84		
Tricholoroethylene (trichloroethene)	2.82	HAP	Pires et al.,2003, Pre et al.,2002, Fangmark et al.,2002, Yun ,2001, Shin et al.,2002, Yun et al.,1998, Born & Pichowski,1997, Born et al.,1996, Miyake & Suzuki,1993.

Table A.2 – Continued

<b>Compound</b>	<b>*Default concentration (ppmv)</b>	<b>Effects</b>	<b>Previous studies in activated carbon</b>
Vinyl chloride	7.34	HAP	
Xylenes	12.1	HAP 0.50 mol O <sub>3</sub> / mol C	Das et al.,2004, Shin et al.,2002.
Benzene		HAP 0.023 mol O <sub>3</sub> / mol C	Rodenas et al.,2006, Shin et al.,2002, BanSode et al.,2003, Bae and Do,2002, Chiang et al.,2002, Wartelle et al.,2000, Guezel,1999, Wang et al.,1999, Cal et al.,1996, Tamon & Okazaki,1996, Herden et al.,1991.
Toluene		HAP 0.106 mol O <sub>3</sub> / mol C	Kingsley and Davidson,2006, Rodenas et al.,2006, Yu et al.,2006, Ao and Lee 2005, Das et al.,2004, Cheng et al.,2004, Shin et al.,2002, Pre et al.,2002, Wartelle et al.,2000, Masuda et al.,1999, Wang et al.,1999, Gadkaree,1998, Golden & Kumar,1993.
Nitrogen dioxide			Ahnert & Heschel, 2002, Gray,1993.

GHG - Green House Gass

HAP - Hazardous Air Pollutant

mol O<sub>3</sub> / mol C – Incremental Reactivity\*Source for emissions: <http://www.epa.gov/ttn/chief/ap42/ch02/final/c02s04.pdf>

## APPENDIX B

### HAZARDOUS AIR POLLUTANTS LIST

Table B.1 The Original List of Hazardous Air Pollutants as Follows

<b>CAS Number</b>	<b>Chemical Name</b>
75070	Acetaldehyde
60355	Acetamide
75058	Acetonitrile
98862	Acetophenone
53963	2-Acetylaminofluorene
107028	Acrolein
79061	Acrylamide
79107	Acrylic acid
107131	Acrylonitrile
107051	Allyl chloride
92671	4-Aminobiphenyl
62533	Aniline
90040	o-Anisidine
1332214	Asbestos
71432	Benzene (including benzene from gasoline)
92875	Benzidine
98077	Benzotrichloride
100447	Benzyl chloride
92524	Biphenyl
117817	Bis(2-ethylhexyl)phthalate (DEHP)
542881	Bis(chloromethyl)ether
75252	Bromoform
106990	1,3-Butadiene
156627	Calcium cyanamide
105602	Caprolactam(See Modification)
133062	Captan
63252	Carbaryl
75150	Carbon disulfide
56235	Carbon tetrachloride
463581	Carbonyl sulfide
120809	Catechol

Table B.2 – Continued

<b>CAS Number</b>	<b>Chemical Name</b>
133904	Chloramben
57749	Chlordane
7782505	Chlorine
79118	Chloroacetic acid
532274	2-Chloroacetophenone
108907	Chlorobenzene
510156	Chlorobenzilate
67663	Chloroform
107302	Chloromethyl methyl ether
126998	Chloroprene
1319773	Cresols/Cresylic acid (isomers and mixture)
95487	o-Cresol
108394	m-Cresol
106445	p-Cresol
98828	Cumene
94757	2,4-D, salts and esters
3547044	DDE
334883	Diazomethane
132649	Dibenzofurans
96128	1,2-Dibromo-3-chloropropane
84742	Dibutylphthalate
106467	1,4-Dichlorobenzene(p)
91941	3,3-Dichlorobenzidene
111444	Dichloroethyl ether (Bis(2-chloroethyl)ether)
542756	1,3-Dichloropropene
62737	Dichlorvos
111422	Diethanolamine
121697	N,N-Dimethylaniline
64675	Diethyl sulfate
119904	3,3-Dimethoxybenzidine

Table B.1 – Continued

<b>CAS Number</b>	<b>Chemical Name</b>
60117	Dimethyl aminoazobenzene
119937	3,3'-Dimethyl benzidine
79447	Dimethyl carbamoyl chloride
68122	Dimethyl formamide
57147	1,1-Dimethyl hydrazine
131113	Dimethyl phthalate
77781	Dimethyl sulfate
534521	4,6-Dinitro-o-cresol, and salts
51285	2,4-Dinitrophenol
121142	2,4-Dinitrotoluene
123911	1,4-Dioxane (1,4-Diethyleneoxide)
122667	1,2-Diphenylhydrazine
106898	Epichlorohydrin (1-Chloro-2,3-epoxypropane)
106887	1,2-Epoxybutane
140885	Ethyl acrylate
100414	Ethyl benzene
51796	Ethyl carbamate (Urethane)
75003	Ethyl chloride (Chloroethane)
106934	Ethylene dibromide (Dibromoethane)
107062	Ethylene dichloride (1,2-Dichloroethane)
107211	Ethylene glycol
151564	Ethylene imine (Aziridine)
75218	Ethylene oxide
96457	Ethylene thiourea
75343	Ethylidene dichloride (1,1-Dichloroethane)
50000	Formaldehyde
76448	Heptachlor
118741	Hexachlorobenzene
87683	Hexachlorobutadiene
77474	Hexachlorocyclopentadiene



Table B.1 – Continued

<b>CAS Number</b>	<b>Chemical Name</b>
67721	Hexachloroethane
822060	Hexamethylene-1,6-diisocyanate
680319	Hexamethylphosphoramide
110543	Hexane
302012	Hydrazine
7647010	Hydrochloric acid
7664393	Hydrogen fluoride (Hydrofluoric acid)
7783064	Hydrogen sulfide
123319	Hydroquinone
78591	Isophorone
58899	Lindane (all isomers)
108316	Maleic anhydride
67561	Methanol
72435	Methoxychlor
74839	Methyl bromide (Bromomethane)
74873	Methyl chloride (Chloromethane)
71556	Methyl chloroform (1,1,1-Trichloroethane)
78933	Methyl ethyl ketone (2-Butanone)
60344	Methyl hydrazine
74884	Methyl iodide (Iodomethane)
108101	Methyl isobutyl ketone (Hexone)
624839	Methyl isocyanate
80626	Methyl methacrylate
1634044	Methyl tert butyl ether
101144	4,4-Methylene bis(2-chloroaniline)
75092	Methylene chloride (Dichloromethane)
101688	Methylene diphenyl diisocyanate (MDI)
101779	4,4'-Methylenedianiline
91203	Naphthalene
98953	Nitrobenzene

Table B.1 – Continued

<b>CAS Number</b>	<b>Chemical Name</b>
92933	4-Nitrobiphenyl
100027	4-Nitrophenol
79469	2-Nitropropane
684935	N-Nitroso-N-methylurea
62759	N-Nitrosodimethylamine
59892	N-Nitrosomorpholine
56382	Parathion
82688	Pentachloronitrobenzene (Quintobenzene)
87865	Pentachlorophenol
108952	Phenol
106503	p-Phenylenediamine
75445	Phosgene
7803512	Phosphine
7723140	Phosphorus
85449	Phthalic anhydride
1336363	Polychlorinated biphenyls (Aroclors)
1120714	1,3-Propane sultone
57578	beta-Propiolactone
123386	Propionaldehyde
114261	Propoxur (Baygon)
78875	Propylene dichloride (1,2-Dichloropropane)
75569	Propylene oxide
75558	1,2-Propylenimine (2-Methyl aziridine)
91225	Quinoline
106514	Quinone
100425	Styrene
96093	Styrene oxide
1746016	2,3,7,8-Tetrachlorodibenzo-p-dioxin
79345	1,1,2,2-Tetrachloroethane
127184	Tetrachloroethylene (Perchloroethylene)

Table B.1 – Continued

<b>CAS Number</b>	<b>Chemical Name</b>
7550450	Titanium tetrachloride
108883	Toluene
95807	2,4-Toluene diamine
584849	2,4-Toluene diisocyanate
95534	o-Toluidine
8001352	Toxaphene (chlorinated camphene)
120821	1,2,4-Trichlorobenzene
79005	1,1,2-Trichloroethane
79016	Trichloroethylene
95954	2,4,5-Trichlorophenol
88062	2,4,6-Trichlorophenol
121448	Triethylamine
1582098	Trifluralin
540841	2,2,4-Trimethylpentane
108054	Vinyl acetate
593602	Vinyl bromide
75014	Vinyl chloride
75354	Vinylidene chloride (1,1-Dichloroethylene)
1330207	Xylenes (isomers and mixture)
95476	o-Xylenes
108383	m-Xylenes
106423	p-Xylenes
0	Antimony Compounds
0	Arsenic Compounds (inorganic including arsine)
0	Beryllium Compounds
0	Cadmium Compounds
0	Chromium Compounds
0	Cobalt Compounds
0	Coke Oven Emissions
0	Cyanide Compounds <sup>1</sup>

Table B.1 – Continued

CAS Number	Chemical Name
0	Glycol ethers <sup>2</sup>
0	Lead Compounds
0	Manganese Compounds
0	Mercury Compounds
0	Fine mineral fibers <sup>3</sup>
0	Nickel Compounds
0	Polycyclic Organic Matter <sup>4</sup>
0	Radionuclides (including radon) <sup>5</sup>
0	Selenium Compounds

**NOTE:** For all listings above which contain the word "compounds" and for glycol ethers, the following applies: Unless otherwise specified, these listings are defined as including any unique chemical substance that contains the named chemical (i.e., antimony, arsenic, etc.) as part of that chemical's infrastructure.

1 X'CN where X = H' or any other group where a formal dissociation may occur. For example KCN or Ca(CN)<sub>2</sub>

2 Includes mono- and di- ethers of ethylene glycol, diethylene glycol, and triethylene glycol R-(OCH<sub>2</sub>CH<sub>2</sub>)<sub>n</sub> -OR' where  
n = 1, 2, or 3

R = alkyl or aryl groups

R' = R, H, or groups which, when removed, yield glycol ethers with the structure: R-(OCH<sub>2</sub>CH)<sub>n</sub>-OH. Polymers are excluded from the glycol category.

3 Includes mineral fiber emissions from facilities manufacturing or processing glass, rock, or slag fibers (or other mineral derived fibers) of average diameter 1 micrometer or less.

4 Includes organic compounds with more than one benzene ring, and which have a boiling point greater than or equal to 100 °C.

5 A type of atom which spontaneously undergoes radioactive decay.

Source: <http://www.epa.gov/ttn/atw/188polls.html>

Last updated on June 6th 2007

## APPENDIX C

### FORMULAS AND CALCULATIONS

## FORMULAS AND CALCULATIONS

Formula for converting gas phase to liquid phase

Moles of compound injected in the tedlar bag:

Mass of liquid compound injected in tedlar bag = Volume injected x density

Moles of compound = mass injected x 1/MW

Moles of air in the tedlar bag:

$$PV = nRT$$

Moles of air ( $n_{\text{air}}$ ) =  $PV/RT$  (V, volume of tedlar bag = 1L)

$$\text{ppm} = \frac{\text{moles of compound injected} \times 10^6}{\text{moles of air}}$$

Sample calculation:

Adsorption isotherm – ethylbenzene and bituminous coal based activated carbon

1) Weight of carbon measured using digital weighing scale = 0.011 g

2) Volume of carbon = mass/density =  $\frac{0.011\text{g}}{0.48 \text{ g/cm}^3} = 0.023\text{ml}$

3) Volume injected into the vial using syringe = 0.5 ml

4) Inlet concentration injected into the vial = 20341 ppm

5) Initial concentration in the vial

$$C_1V_1 = C_2V_2$$

$C_1$ ,  $V_1$  = Concentration and volume injected into the vial

$C_2$ ,  $V_2$  = Concentration and volume in the vial

(Volume of vial = total volume of vial – volume of carbon occupied)

$$C_2 = \frac{C_1 V_1}{V_2} \times \text{correction factor}$$

$$C_2 = \frac{20341 \text{ ppm} \times 0.5 \text{ ml}}{(4-0.023 \text{ ml})} \times \frac{(4-0.023)}{(4-0.023+0.5)}$$

$$C_2 = 2272 \text{ ppm}$$

6) Final concentration: measured using GC after the equilibrium time has passed

7)  $C_e$  = Final concentration x correction factor

$$C_e = 154 \times \frac{(4-0.023)}{(4-0.023+0.5)}$$

$$C_e = 137 \text{ ppm}$$

8) Adsorbed by activated carbon

$$C_{\text{ppm}} = \frac{(\text{initial vial concentration} - \text{final vial concentration}) \times \text{volume of headspace in the vial}}{\text{volume of carbon}}$$

$$C_{\text{mg/m}^3} = \frac{\text{MW} \times C_{\text{ppm}}}{24.45}$$

$$C_{\text{g/L}} = C_{\text{mg/m}^3} \times 10^{-6}$$

$$\text{Adsorbed (g)} = \frac{(2272-137) \text{ ppm} \times 106.17 \text{ g/mol} \times (4-0.023) \text{ ml} \times 10^{-6} \text{ g/L}}{24.45 \times 1000 \text{ ml/L} \times (4-0.023)}$$

$$= 0.0000415 \text{ g}$$

9) VOC. adsorbed per g of carbon =  $\frac{0.0000415 \text{ g}}{0.011 \text{ g}}$

$$= 0.00377$$

## APPENDIX D

### EXPERIMENTAL DATA AND PLOT



Table D.1 Data table for ethylbenzene tested with bituminous coal based AC

Carbon		VOC injected	Vial (ppm)			VOC adsorbed	Voc adsorbed/carbon
Weight (g)	Volume (ml)	Volume (ml)	Initial Con.	Final Con.	Ce	g	g/g
0.011	0.023	0.5	2272	154	137	0.0000415	0.0038
0.011	0.023	0.55	2471	203	178	0.0000451	0.0041
0.011	0.023	0.6	2666	338	294	0.0000472	0.0043
0.011	0.023	0.65	2857	337	290	0.0000516	0.0047
0.011	0.023	0.7	3044	503	428	0.0000531	0.0048
0.011	0.023	0.75	3227	634	533	0.0000553	0.0050
0.011	0.023	0.8	3406	678	564	0.0000590	0.0054
0.011	0.023	0.85	3582	786	648	0.0000615	0.0056
0.011	0.023	0.9	3754	803	655	0.0000656	0.0060
0.011	0.023	0.95	3922	982	793	0.0000670	0.0061
0.011	0.023	1	4087	1243	993	0.0000669	0.0061
0.011	0.023	1.05	4249	1454	1150	0.0000676	0.0061

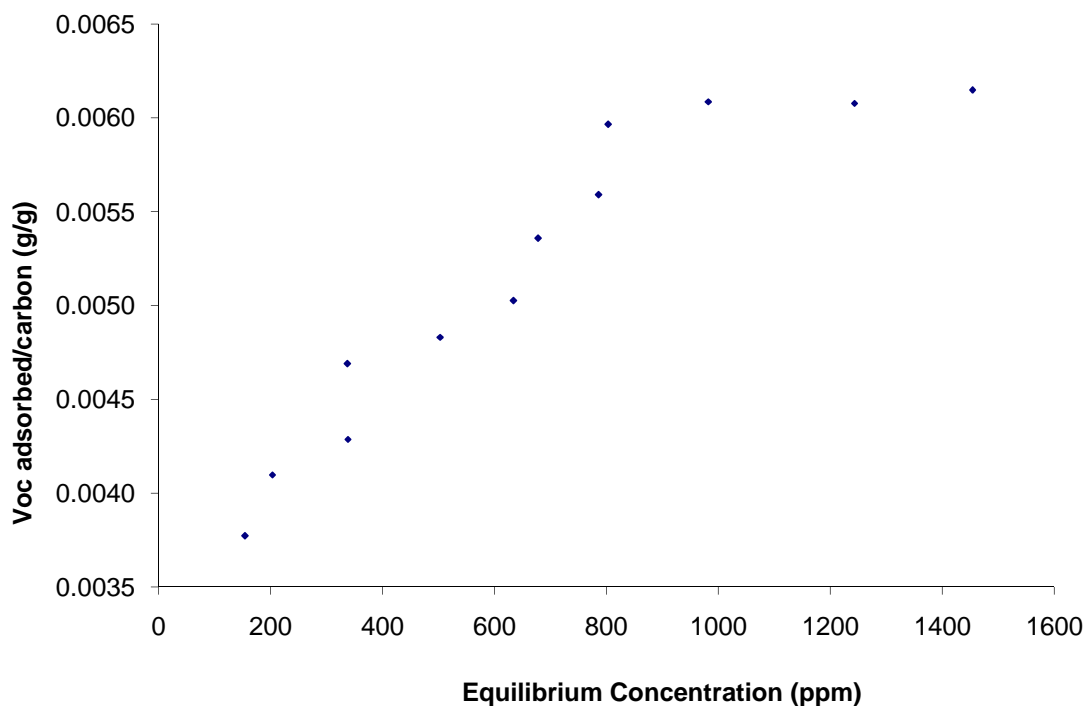


Figure D.1 Isotherm graph for ethylbenzene tested with bituminous coal based AC

Table D.2 Data table for ethylbenzene tested with coconut shell based AC

Carbon		VOC injected	Vial (ppm)			VOC adsorbed	Voc adsorbed/carbon
Weight (g)	Volume (ml)	Volume (ml)	Initial Con.	Final Con.	Ce	g	g/g
0.011	0.023	0.5	2272	34.4	30.6	0.0000436	0.0040
0.011	0.023	0.55	2471	103	90.5	0.0000468	0.0043
0.011	0.023	0.6	2666	204	177	0.0000495	0.0045
0.011	0.023	0.65	2857	356	306	0.0000513	0.0047
0.011	0.023	0.7	3044	512	435	0.0000530	0.0048
0.011	0.023	0.75	3227	672	565	0.0000546	0.0050
0.011	0.023	0.8	3406	789	657	0.0000570	0.0052
0.011	0.023	0.85	3582	896	738	0.0000596	0.0054
0.011	0.023	0.9	3754	945	771	0.0000632	0.0057
0.011	0.023	0.95	3922	1167	942	0.0000638	0.0058
0.011	0.023	1	4087	1423	1137	0.0000638	0.0058
0.011	0.023	1.05	4249	1673	1324	0.0000639	0.0058

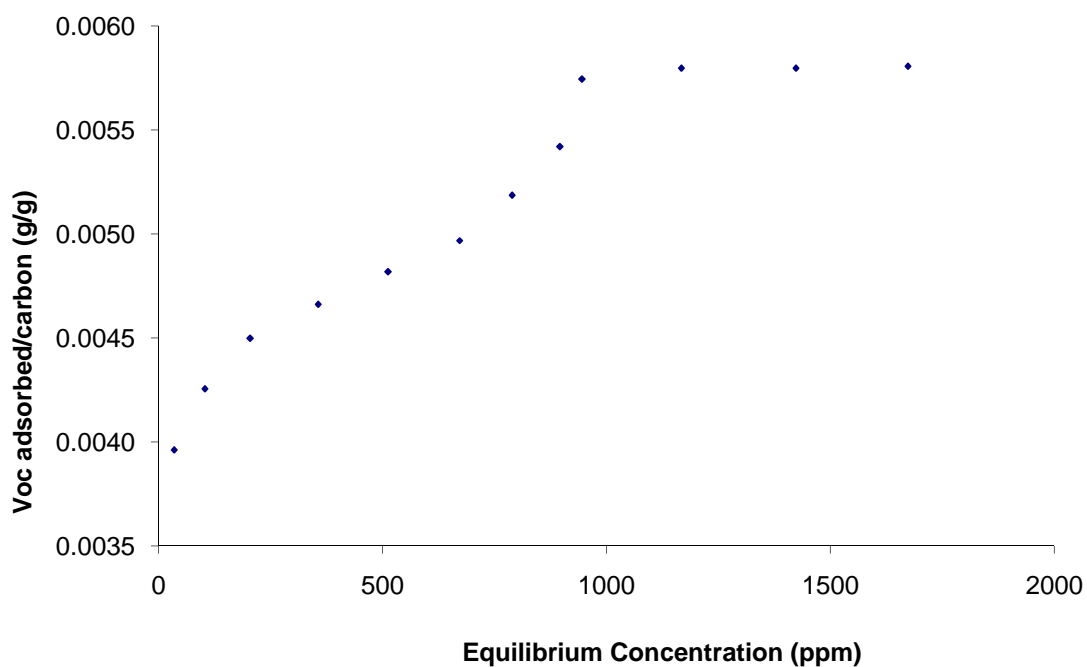


Figure D.2 Isotherm graph for ethylbenzene tested with coconut shell based AC

Table D.3 Data table for methyl ethyl ketone tested with bituminous coal based AC

Carbon		VOC injected	Vial (ppm)			VOC adsorbed	Voc adsorbed/carbon
Weight (g)	Volume (ml)	Volume (ml)	Initial Con.	Final Con.	Ce	g	g/g
0.011	0.023	0.5	2589	73.4	65.2	0.0000333	0.0030
0.011	0.023	0.55	2817	205	180	0.0000352	0.0032
0.011	0.023	0.6	3039	402	349	0.0000363	0.0033
0.011	0.023	0.65	3257	351	302	0.0000403	0.0037
0.011	0.023	0.7	3470	385	327	0.0000433	0.0039
0.011	0.023	0.75	3678	456	384	0.0000459	0.0042
0.011	0.023	0.8	3883	643	535	0.0000472	0.0043
0.011	0.023	0.85	4082	787	648	0.0000489	0.0044
0.011	0.023	0.9	4278	874	713	0.0000513	0.0047
0.011	0.023	0.95	4470	982	793	0.0000534	0.0049
0.011	0.023	1	4658	1062	849	0.0000559	0.0051
0.011	0.023	1.05	4842	1303	1031	0.0000565	0.0051
0.011	0.023	1.1	5023	1607	1259	0.0000564	0.0051

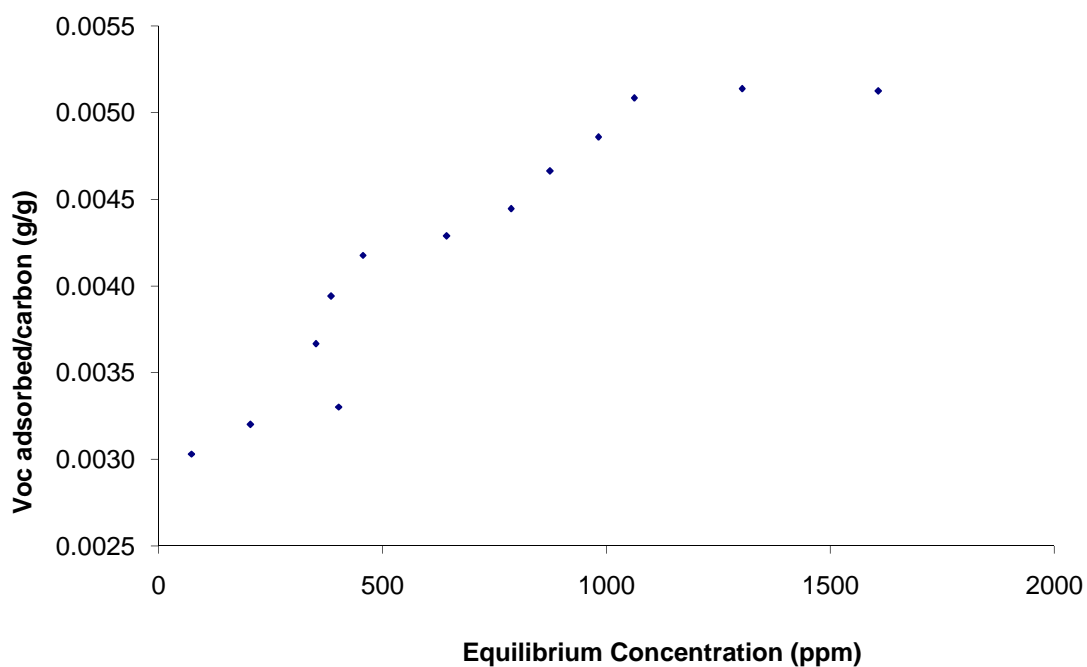


Figure D.3 Isotherm graph for methyl ethyl ketone tested with bituminous coal based AC

Table D.4 Data table for methyl ethyl ketone tested with coconut shell based AC

Carbon		VOC injected	Vial (ppm)			VOC adsorbed	Voc adsorbed/carbon
Weight (g)	Volume (ml)	Volume (ml)	Initial Con.	Final Con.	Ce	g	g/g
0.011	0.023	0.5	2589	54.3	48.2	0.0000336	0.0031
0.011	0.023	0.55	2817	134	118	0.0000360	0.0033
0.011	0.023	0.6	3039	251	218	0.0000381	0.0035
0.011	0.023	0.65	3257	360	309	0.0000402	0.0037
0.011	0.023	0.7	3470	393	334	0.0000433	0.0039
0.011	0.023	0.75	3678	487	410	0.0000456	0.0041
0.011	0.023	0.8	3883	605	504	0.0000476	0.0043
0.011	0.023	0.85	4082	783	645	0.0000489	0.0044
0.011	0.023	0.9	4278	862	703	0.0000514	0.0047
0.011	0.023	0.95	4470	994	802	0.0000533	0.0048
0.011	0.023	1	4658	1093	873	0.0000556	0.0051
0.011	0.023	1.05	4842	1302	1030	0.0000565	0.0051
0.011	0.023	1.1	5023	1614	1264	0.0000563	0.0051

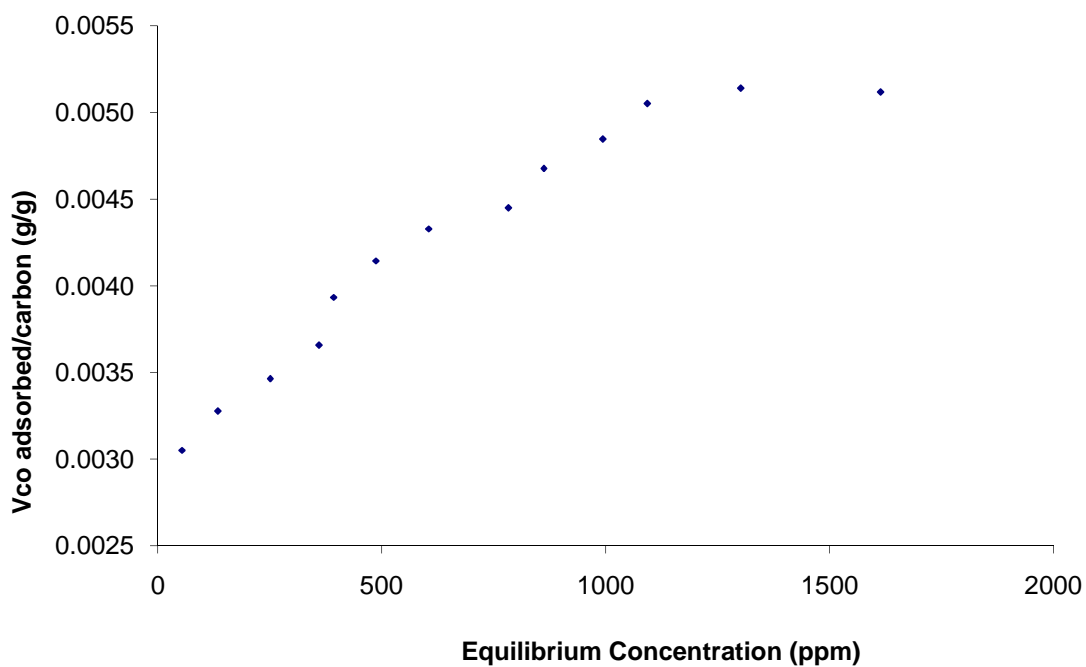


Figure D.4 Isotherm graph for methyl ethyl ketone tested with coconut shell based AC

Table D.5 Data table for *meta*-xylene tested with bituminous coal based AC

<b>Carbon</b>		<b>VOC injected</b>	<b>Vial (ppm)</b>			<b>VOC adsorbed</b>	<b>Voc adsorbed/carbon</b>
<b>Weight (g)</b>	<b>Volume (ml)</b>	<b>Volume (ml)</b>	<b>Initial Con.</b>	<b>Final Con.</b>	<b>Ce</b>	<b>g</b>	<b>g/g</b>
0.012	0.025	0.5	2313	278	247	0.0000401	0.0033
0.012	0.025	0.55	2516	338	297	0.0000436	0.0036
0.012	0.025	0.6	2714	421	366	0.0000467	0.0039
0.012	0.025	0.65	2909	473	407	0.0000503	0.0042
0.012	0.025	0.7	3099	491	417	0.0000544	0.0045
0.012	0.025	0.75	3285	698	587	0.0000554	0.0046
0.012	0.025	0.8	3468	674	561	0.0000603	0.0050
0.012	0.025	0.85	3646	721	594	0.0000640	0.0053
0.012	0.025	0.9	3821	834	680	0.0000665	0.0055
0.012	0.025	0.95	3993	999	806	0.0000681	0.0057
0.012	0.025	1	4160	1131	904	0.0000704	0.0059
0.012	0.025	1.05	4325	1367	1081	0.0000708	0.0059
0.012	0.025	1.1	4486	1634	1280	0.0000707	0.0059

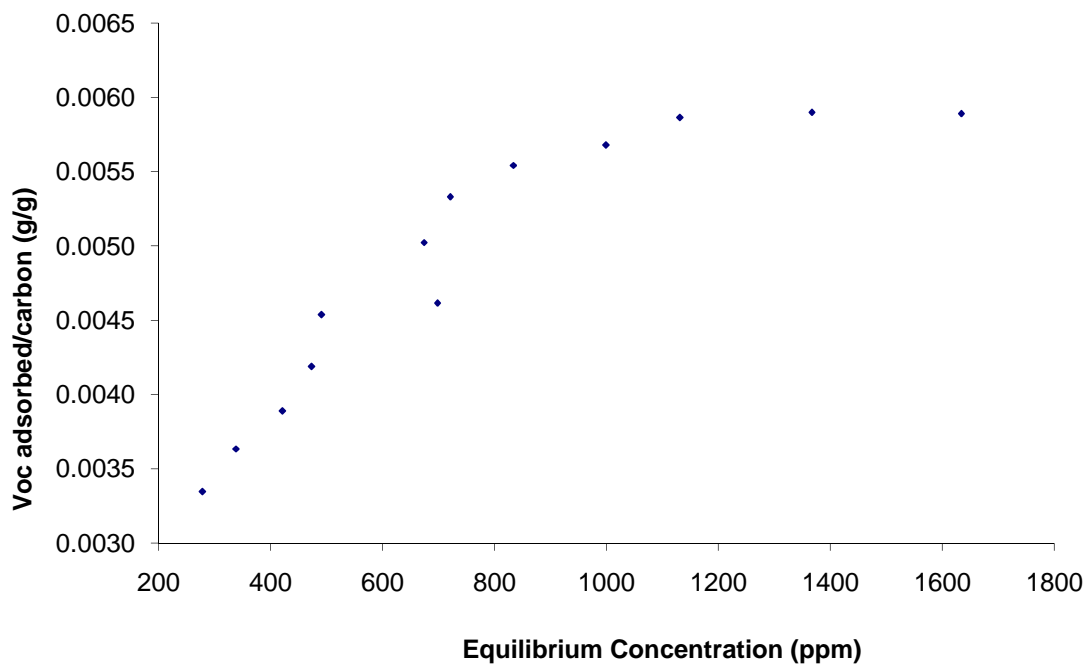


Figure D.5 Isotherm graph for *meta*-xylene tested with bituminous coal based AC

Table D.6 Data table for meta-xylene tested with coconut shell based AC

Carbon		VOC injected	Vial (ppm)			VOC adsorbed	Voc adsorbed/carbon
Weight (g)	Volume (ml)	Volume (ml)	Initial Con.	Final Con.	Ce	g	g/g
0.012	0.025	0.5	2313	247	219	0.0000407	0.0034
0.012	0.025	0.55	2516	331	291	0.0000437	0.0036
0.012	0.025	0.6	2714	489	425	0.0000455	0.0038
0.012	0.025	0.65	2909	510	438	0.0000496	0.0041
0.012	0.025	0.7	3099	597	508	0.0000526	0.0044
0.012	0.025	0.75	3285	684	575	0.0000556	0.0046
0.012	0.025	0.8	3468	743	619	0.0000591	0.0049
0.012	0.025	0.85	3646	787	648	0.0000628	0.0052
0.012	0.025	0.9	3821	925	754	0.0000649	0.0054
0.012	0.025	0.95	3993	1018	822	0.0000678	0.0057
0.012	0.025	1	4160	1276	1020	0.0000679	0.0057
0.012	0.025	1.05	4325	1503	1189	0.0000684	0.0057

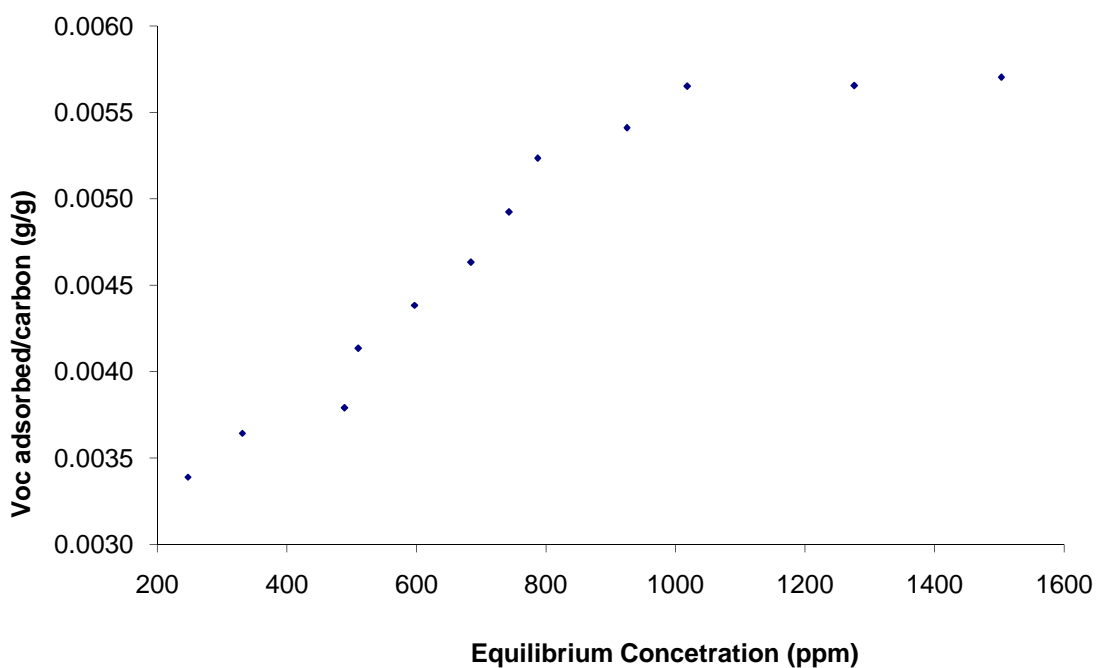


Figure D.6 Isotherm graph for *meta*-xylene tested with coconut shell based AC

Table D.7 Data table for *ortho*-xylene tested with bituminous coal based AC

Carbon		VOC injected	Vial (ppm)			VOC adsorbed	Voc adsorbed/carbon
Weight (g)	Volume (ml)	Volume (ml)	Initial Con.	Final Con.	Ce	g	g/g
0.012	0.025	0.5	2357	357	317	0.0000396	0.0033
0.012	0.025	0.55	2564	414	364	0.0000432	0.0036
0.012	0.025	0.6	2766	428	372	0.0000476	0.0040
0.012	0.025	0.65	2964	532	457	0.0000503	0.0042
0.012	0.025	0.7	3158	601	511	0.0000537	0.0045
0.012	0.025	0.75	3348	628	528	0.0000579	0.0048
0.012	0.025	0.8	3534	701	584	0.0000612	0.0051
0.012	0.025	0.85	3716	699	576	0.0000658	0.0055
0.012	0.025	0.9	3894	760	620	0.0000693	0.0058
0.012	0.025	0.95	4069	797	643	0.0000733	0.0061
0.012	0.025	1	4240	890	711	0.0000762	0.0064
0.012	0.025	1.05	4407	1100	870	0.0000772	0.0064
0.012	0.025	1.1	4572	1367	1071	0.0000772	0.0064

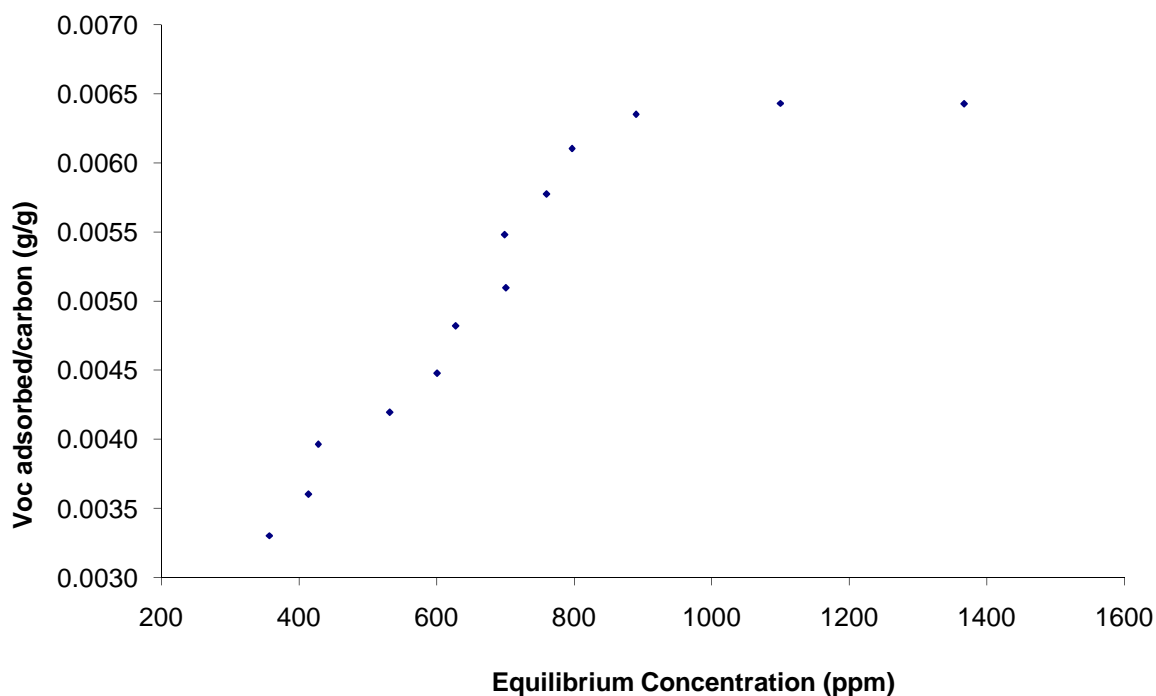


Figure D.7 Isotherm graph for *ortho*-xylene tested with bituminous coal based AC

Table D.8 Data table for *ortho*-xylene tested with coconut shell based AC

Carbon		VOC injected	Vial			VOC adsorbed	Voc adsorbed/carbon
Weight (g)	Volume (ml)	Volume (ml)	Initial Con.	Final Con.	Ce	g	g/g
0.012	0.025	0.5	2357	174	155	0.0000428	0.0036
0.012	0.025	0.55	2564	237	208	0.0000463	0.0039
0.012	0.025	0.6	2766	278	242	0.0000502	0.0042
0.012	0.025	0.65	2964	315	271	0.0000541	0.0045
0.012	0.025	0.7	3158	385	327	0.0000575	0.0048
0.012	0.025	0.75	3348	438	368	0.0000611	0.0051
0.012	0.025	0.8	3534	476	396	0.0000651	0.0054
0.012	0.025	0.85	3716	518	427	0.0000689	0.0057
0.012	0.025	0.9	3894	660	538	0.0000710	0.0059
0.012	0.025	0.95	4069	753	608	0.0000740	0.0062
0.012	0.025	1	4240	982	785	0.0000746	0.0062
0.012	0.025	1.05	4407	1270	1005	0.0000742	0.0062

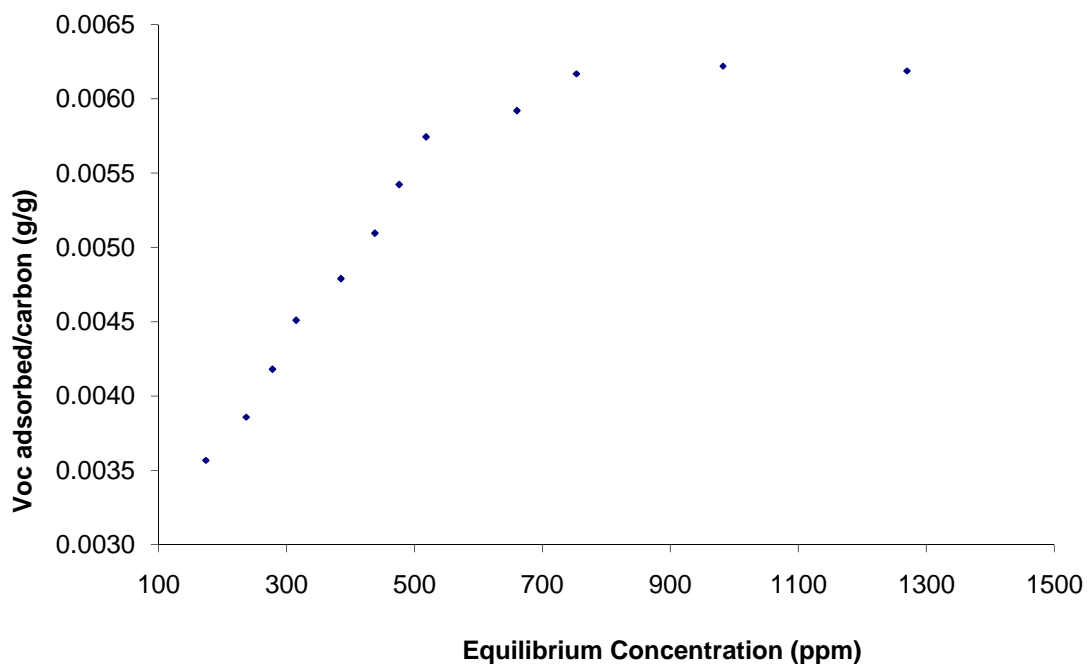


Figure D.8 Isotherm graph for *ortho*-xylene tested with coconut shell based AC



Table D.9 Data table for *para*-xylene tested with bituminous coal based AC

Carbon		VOC injected		Vial (ppm)		VOC adsorbed	Voc adsorbed/carbon	
Weight (g)	Volume (ml)	Volume (ml)	Initial Con.	Final Con.	Ce	g	g/g	
0.012	0.025	0.5	2130	150	133	0.0000388	0.0032	
0.012	0.025	0.55	2318	157	138	0.0000428	0.0036	
0.012	0.025	0.6	2501	234	203	0.0000456	0.0038	
0.012	0.025	0.65	2680	279	240	0.0000490	0.0041	
0.012	0.025	0.7	2855	423	360	0.0000507	0.0042	
0.012	0.025	0.75	3027	402	338	0.0000552	0.0046	
0.012	0.025	0.8	3194	425	354	0.0000589	0.0049	
0.012	0.025	0.85	3359	387	319	0.0000637	0.0053	
0.012	0.025	0.9	3520	400	326	0.0000676	0.0056	
0.012	0.025	0.95	3678	520	420	0.0000697	0.0058	
0.012	0.025	1	3833	645	515	0.0000717	0.0060	
0.012	0.025	1.05	3984	850	672	0.0000723	0.0060	
0.012	0.025	1.1	4133	1087	851	0.0000723	0.0060	

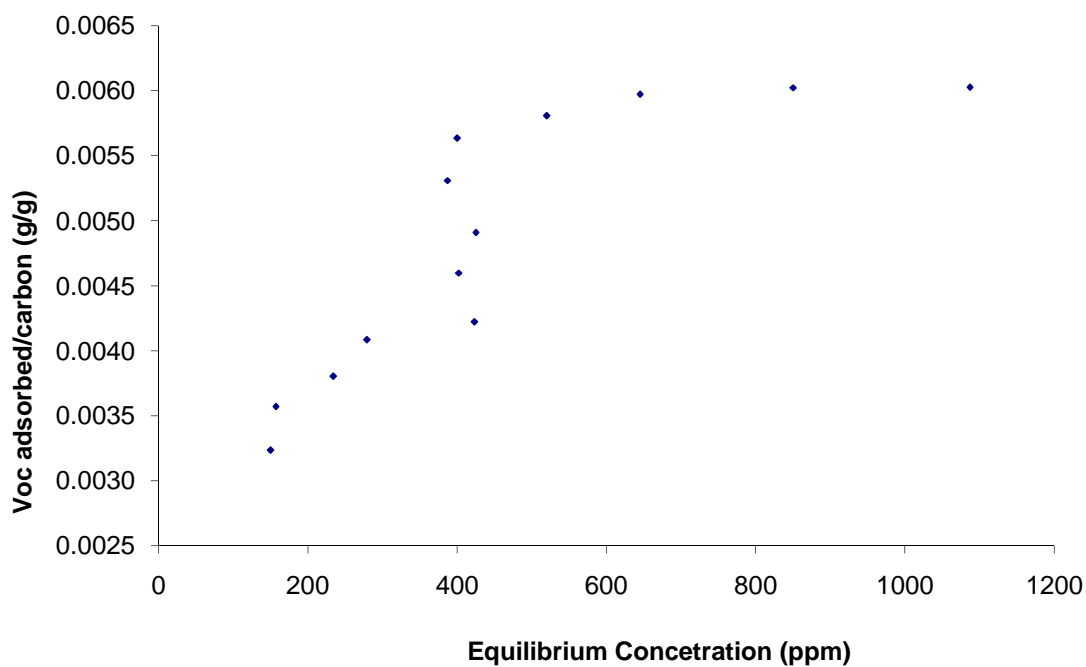


Figure D.9 Isotherm graph for *para*-xylene tested with bituminous coal based AC

Table D.10 Data table for *para*-xylene tested with coconut shell based AC

Carbon		VOC injected	Vial (ppm)			VOC adsorbed	Voc adsorbed/carbon
Weight (g)	Volume (ml)	Volume (ml)	Initial Con.	Final Con.	Ce	g	g/g
0.012	0.025	0.5	2130	20	17.8	0.0000411	0.0034
0.012	0.025	0.55	2318	83	72.9	0.0000441	0.0037
0.012	0.025	0.6	2501	103	89	0.0000479	0.0040
0.012	0.025	0.65	2680	184	158	0.0000506	0.0042
0.012	0.025	0.7	2855	187	159	0.0000547	0.0046
0.012	0.025	0.75	3027	285	240	0.0000572	0.0048
0.012	0.025	0.8	3194	302	251	0.0000610	0.0051
0.012	0.025	0.85	3359	276	227	0.0000656	0.0055
0.012	0.025	0.9	3520	398	325	0.0000676	0.0056
0.012	0.025	0.95	3678	549	443	0.0000692	0.0058
0.012	0.025	1	3833	790	631	0.0000692	0.0058
0.012	0.025	1.05	3984	1024	810	0.0000693	0.0058

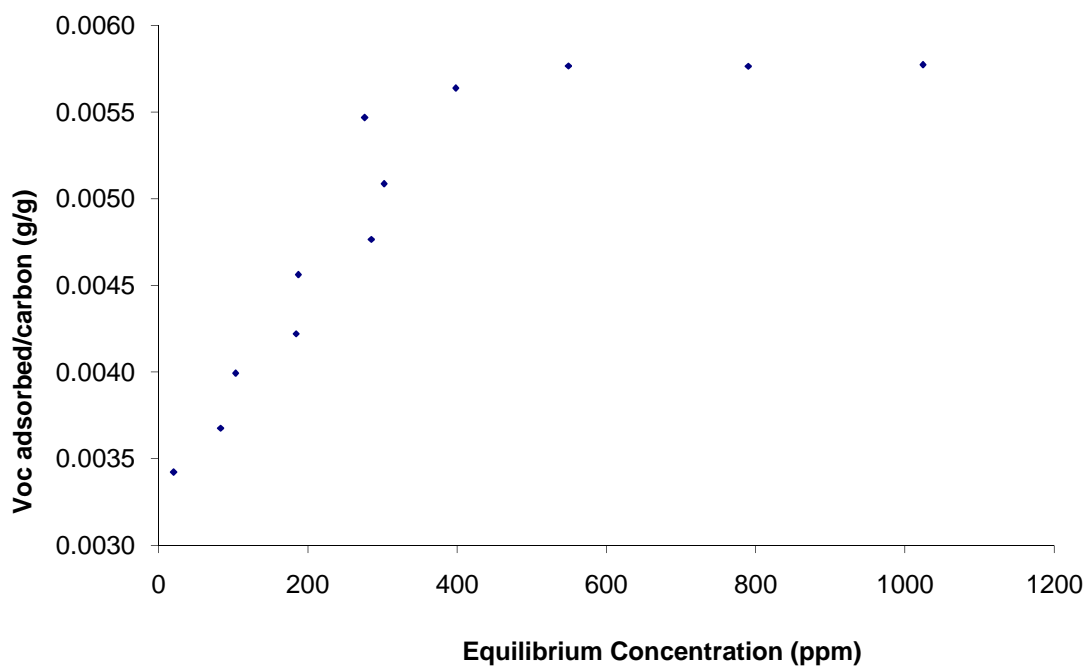


Figure D.10 Isotherm graph for *para*-xylene tested with coconut shell based AC

Sample: Data table and graph for ethylbenzene tested with bituminous coal based AC

Table D.11 Freundlich isotherm (linear)

$Q_e$	$C_e$	$\log(Q_e)$	$\log(C_e)$
0.0038	137	-2.4233	2.136
0.0041	178	-2.38746	2.251242
0.0043	294	-2.36783	2.467893
0.0047	290	-2.3288	2.461887
0.0048	428	-2.31595	2.631158
0.0050	533	-2.2987	2.727061
0.0054	564	-2.27089	2.751632
0.0056	648	-2.25249	2.811302
0.0060	655	-2.22431	2.81612
0.0061	793	-2.21563	2.899086
0.0061	993	-2.21622	2.997061
0.0061	1150	-2.21123	3.060813

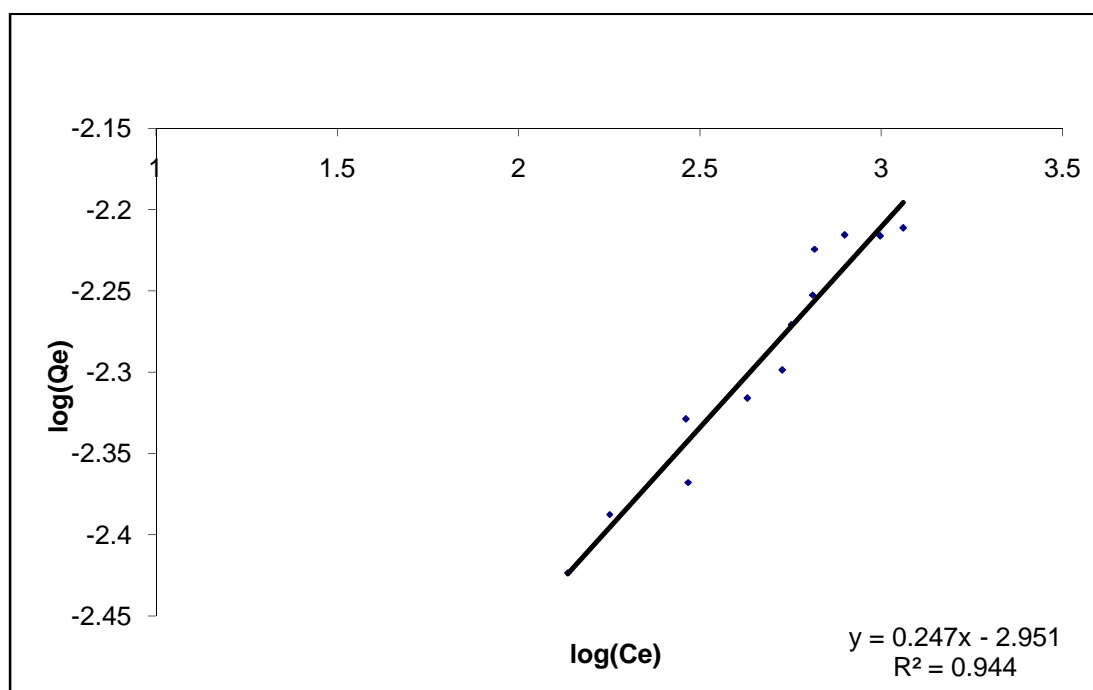


Figure D.11 Freundlich isotherm graph (Linear)

Table D.12 Langmuir Isotherm (Linear equation 1)

$Q_e$	$C_e$	$1/Q_e$	$1/C_e$
0.0038	137	265.0339	0.00731
0.0041	178	244.0416	0.005607
0.0043	294	233.2524	0.003405
0.0047	290	213.2078	0.003452
0.0048	428	206.9909	0.002338
0.0050	533	198.9277	0.001875
0.0054	564	186.5895	0.001772
0.0056	648	178.8496	0.001544
0.0060	655	167.614	0.001527
0.0061	793	164.2967	0.001262
0.0061	993	164.5205	0.001007
0.0061	1150	162.6415	0.000869

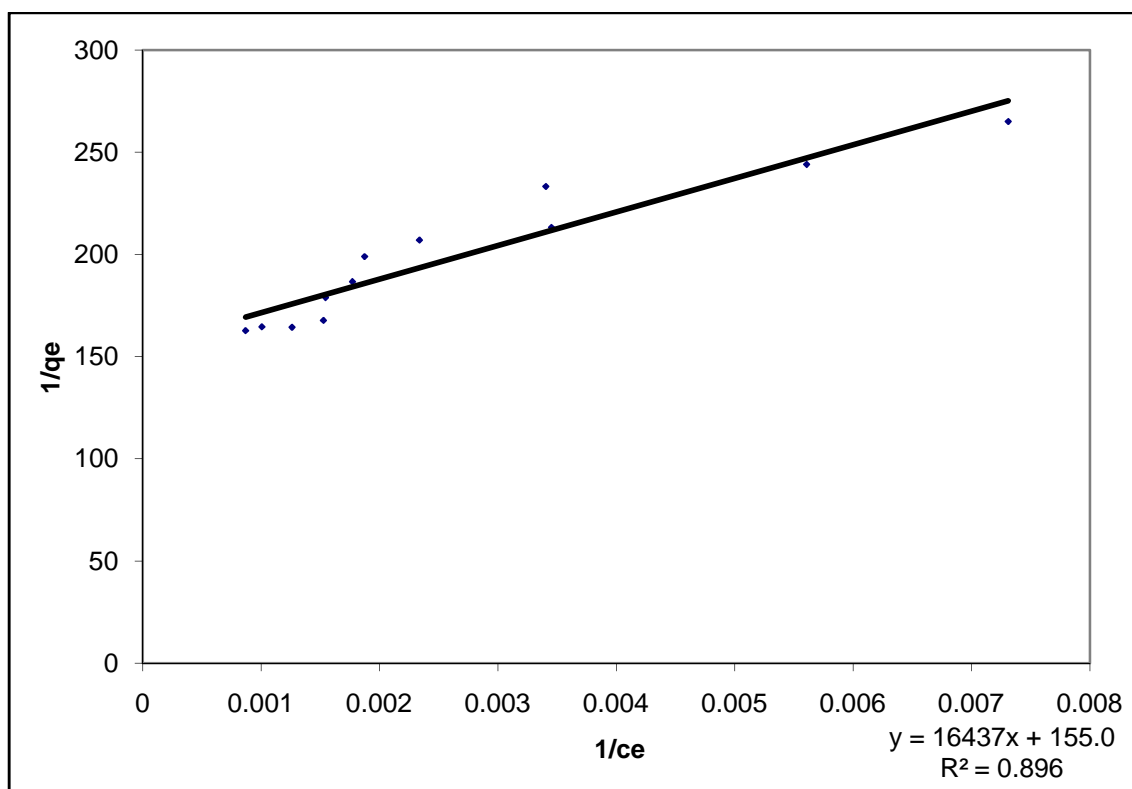


Figure D.12 Langmuir Isotherm graph (Linear equation 1)

Table D.13 Langmuir isotherm linear (linear equation 2)

$Q_e$	$C_e$	$C_e/q_e$
0.0038	137	36256.98
0.0041	178	43521.73
0.0043	294	68504.43
0.0047	290	61757.59
0.0048	428	88533.74
0.0050	533	106109.9
0.0054	564	105321.9
0.0056	648	115821.8
0.0060	655	109756.5
0.0061	793	130231.2
0.0061	993	163410.8
0.0061	1150	187087.3

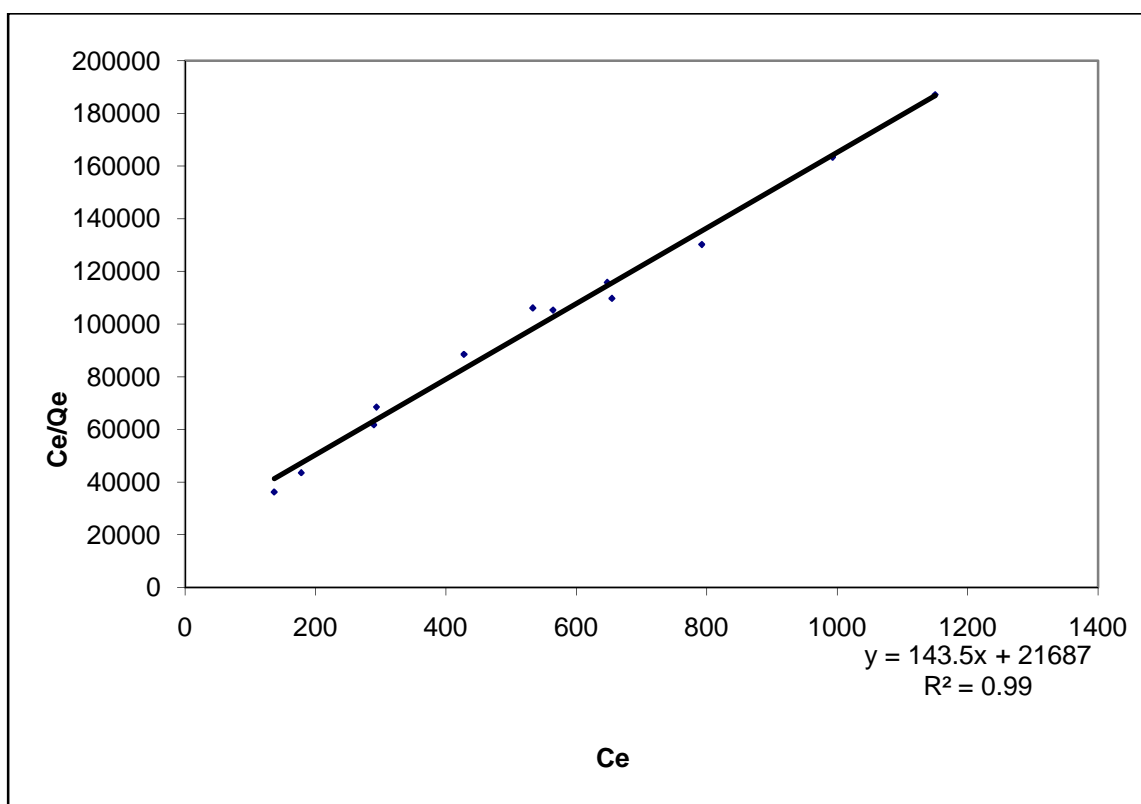


Figure D.13 Langmuir isotherm graph linear (linear equation 2)

Table D.14 Summary of results non-linear form

Rank	Model	StdError	Residual Sum	Residual Avg.	RSS	R <sup>2</sup>	Ra <sup>2</sup>
1	$a \cdot x^b$	0.00024	-3.00E-06	-2.50E-07	5.78E-07	0.924771	0.917248
2	$a \cdot b \cdot x / (1 + b \cdot x)$	0.000296	5.26E-05	4.39E-06	8.75E-07	0.886174	0.874791

Table D.15 Equilibrium time for VOC tested with BPL and OVC (lower concentration)

Time	g Voc adsorbed/g carbon									
	ethylbenzene		Methyl ethyl ketone		<i>ortho</i> -xylene		<i>para</i> -xylene		<i>meta</i> -xylene	
	OVC	BPL	OVC	BPL	OVC	BPL	OVC	BPL	OVC	BPL
0	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
10	0.0012	0.0009	0.0013	0.0009	0.0016	0.0008	0.0012	0.0009	0.0010	0.0008
20	0.0025	0.0017	0.0024	0.0017	0.0024	0.0014	0.0020	0.0019	0.0023	0.0012
30	0.0035	0.0025	0.0026	0.0023	0.0030	0.0024	0.0028	0.0025	0.0027	0.0021
40	0.0039	0.0028	0.0029	0.0029	0.0034	0.0027	0.0030	0.0028	0.0030	0.0025
50	0.0040	0.0037	0.0031	0.0030	0.0036	0.0032	0.0031	0.0031	0.0033	0.0031
55	0.0040	0.0038	0.0031	0.0030	0.0036	0.0033	0.0033	0.0032	0.0034	0.0032
60	0.0040	0.0038	0.0031	0.0030	0.0036	0.0033	0.0034	0.0032	0.0034	0.0033
65		0.0038				0.0033	0.0034	0.0032	0.0034	0.0033
70							0.0034			0.0033

Table D.16 Equilibrium time for VOC tested with BPL and OVC (higher concentration)

Time	g voc adsorbed/g carbon			
	Methyl ethyl ketone		<i>ortho</i> -xylene	
	OVC	BPL	OVC	BPL
0	0.0000	0.0000	0.0000	0.0000
10	0.0021	0.0019	0.0024	0.0015
15	0.0031	0.0030	0.0043	0.0040
20	0.0040	0.0039	0.0053	0.0049
25	0.0049	0.0048	0.0060	0.0056
30	0.0050	0.0050	0.0061	0.0060
35	0.0051	0.0051	0.0062	0.0062
40	0.0051	0.0051	0.0062	0.0064
45	0.0051	0.0051	0.0062	0.0064
50				0.0064

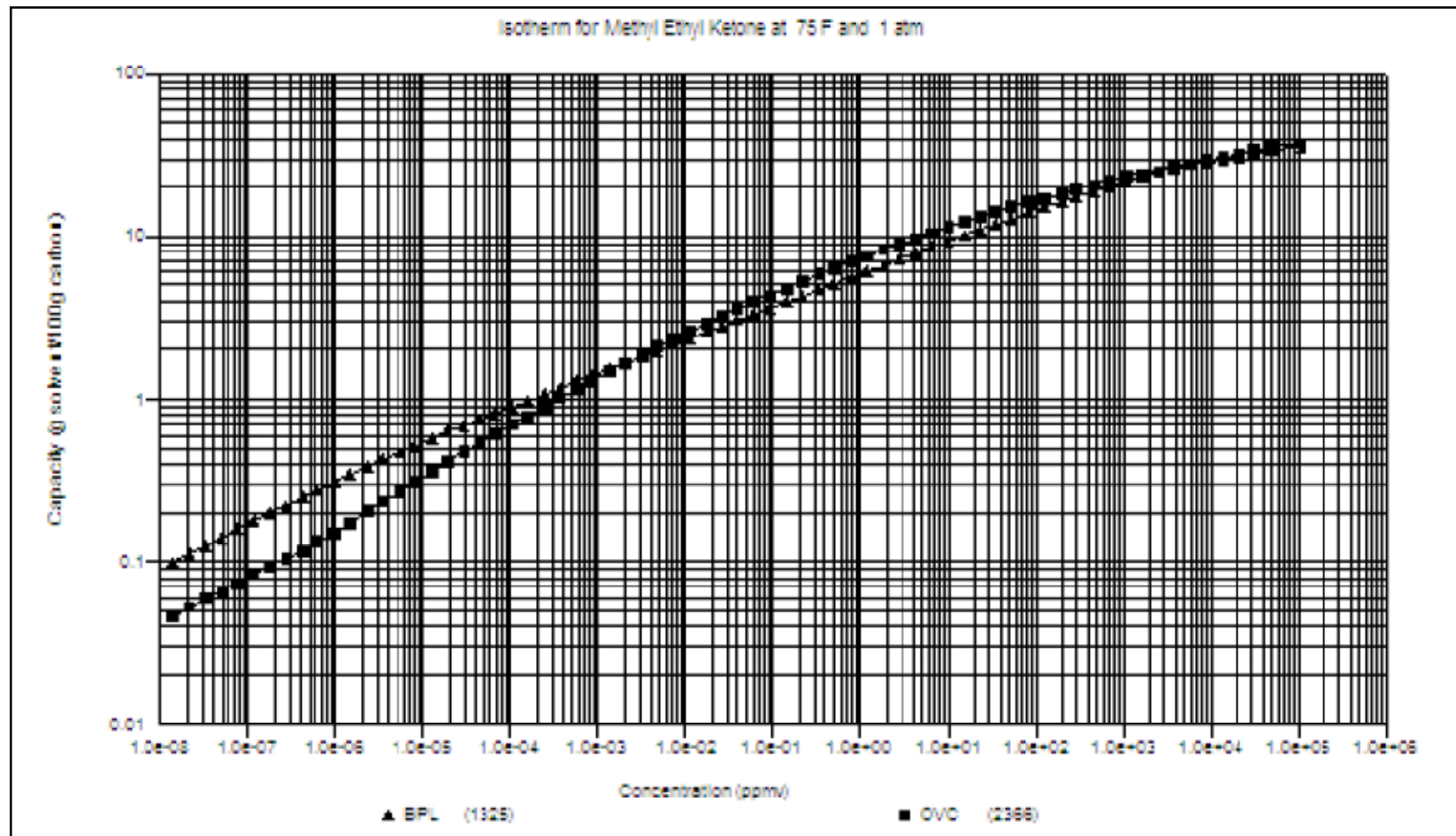


Figure D.14 Manufacturer's isotherm graph for MEK



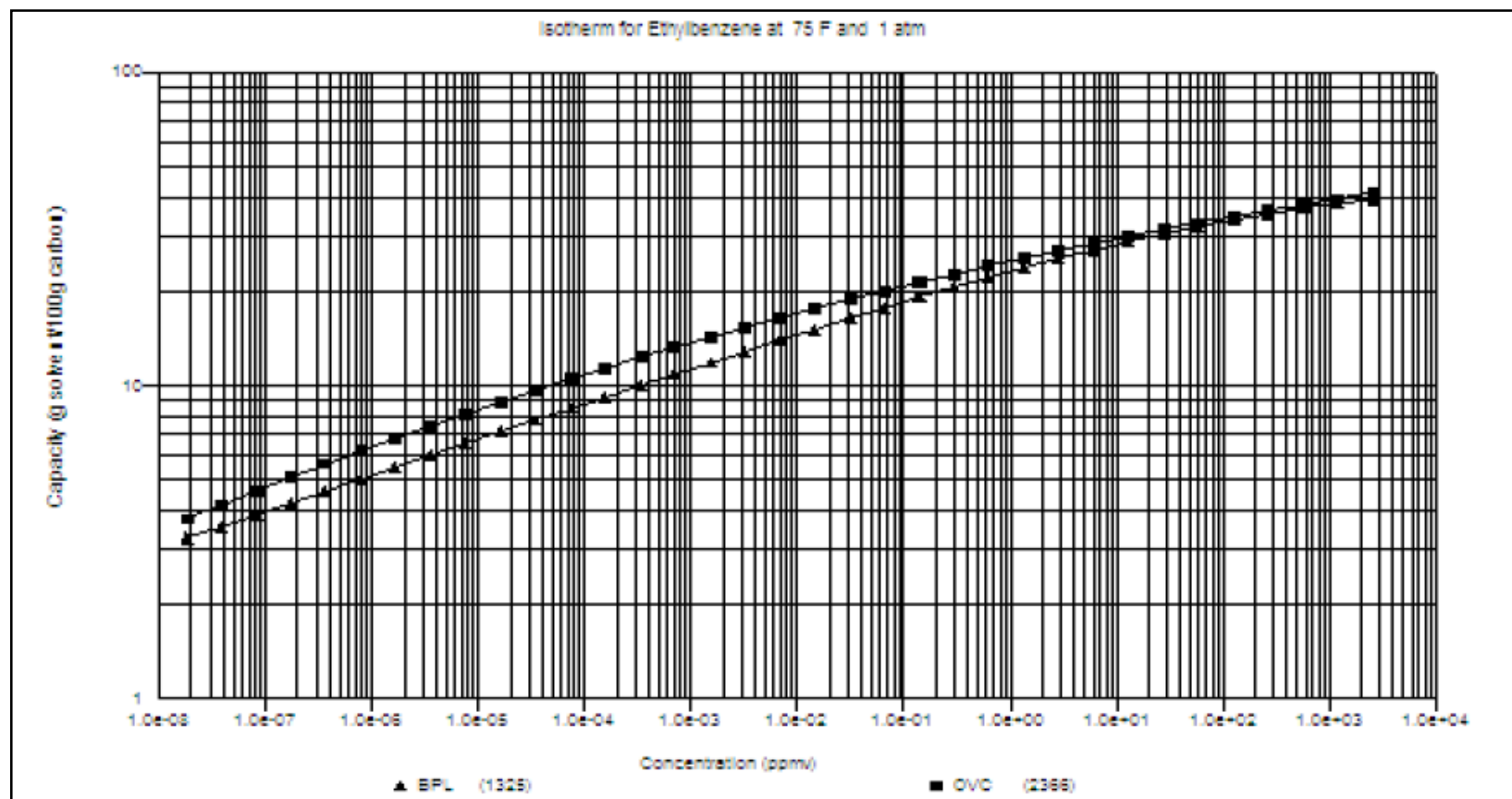


Figure D.15 Manufacturer's isotherm graph for ethylbenzene

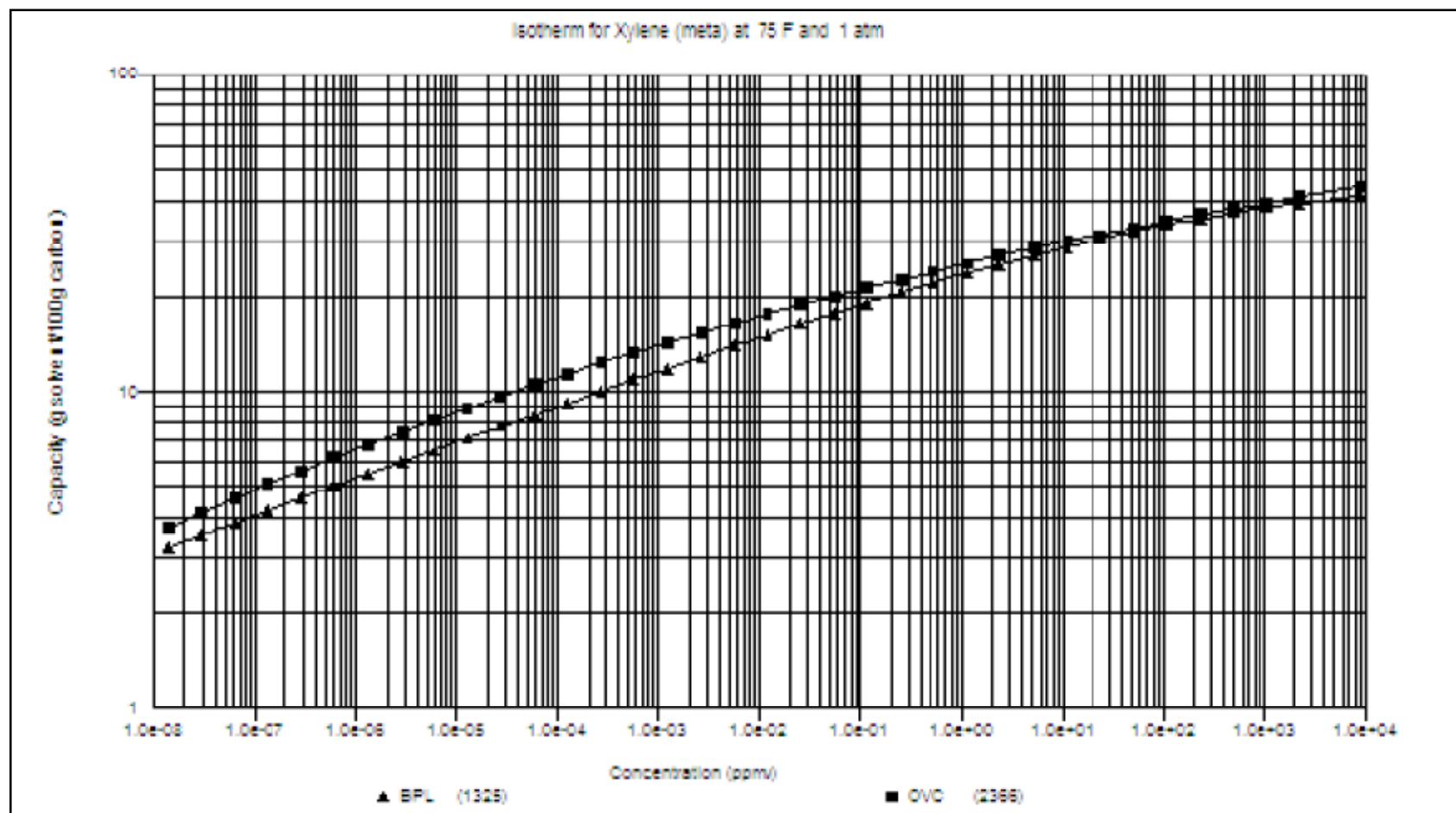


Figure D.16 Manufacturer's isotherm graph for meta-xylene

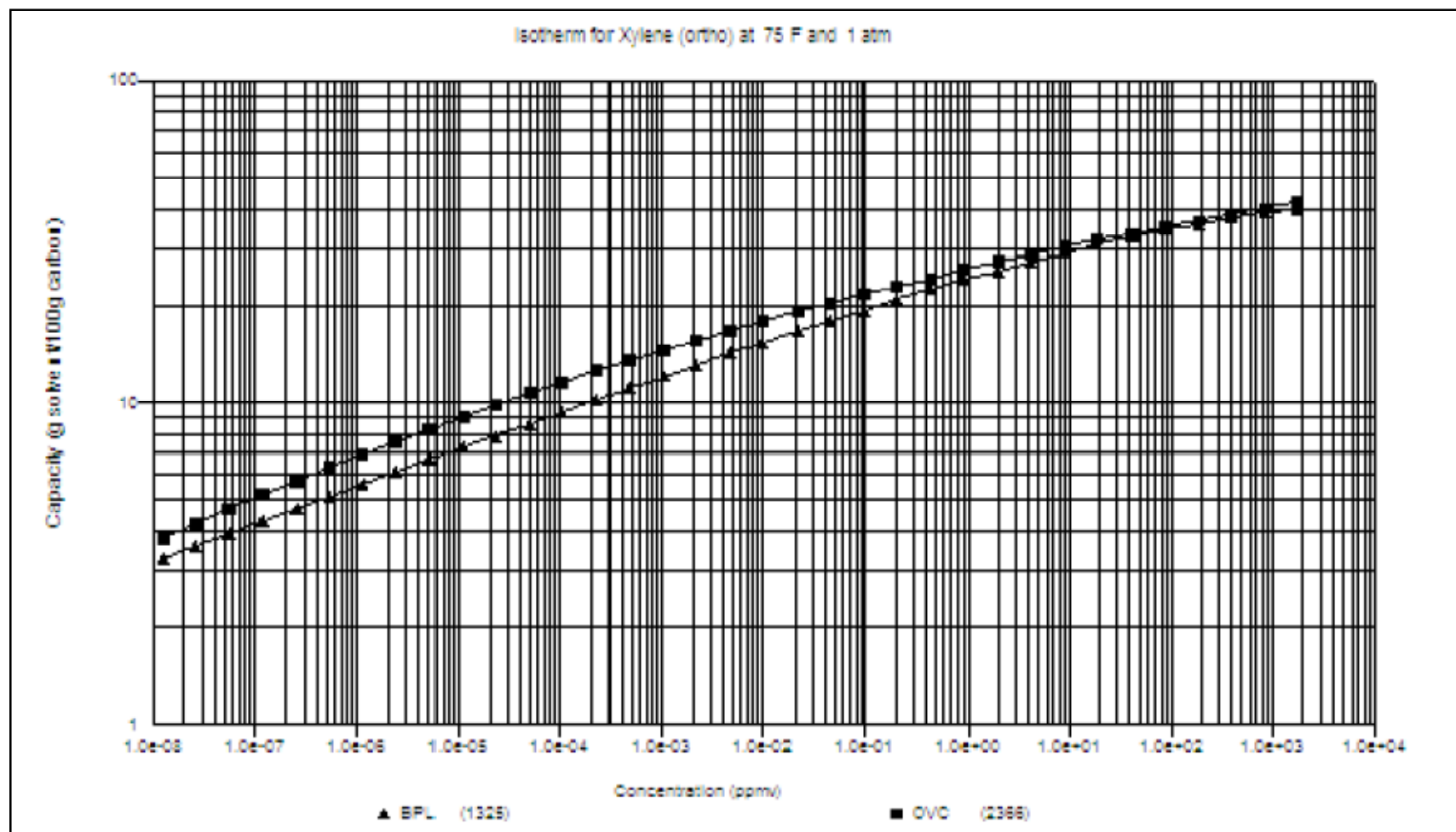


Figure D.17 Manufacturer's isotherm ortho-xylene

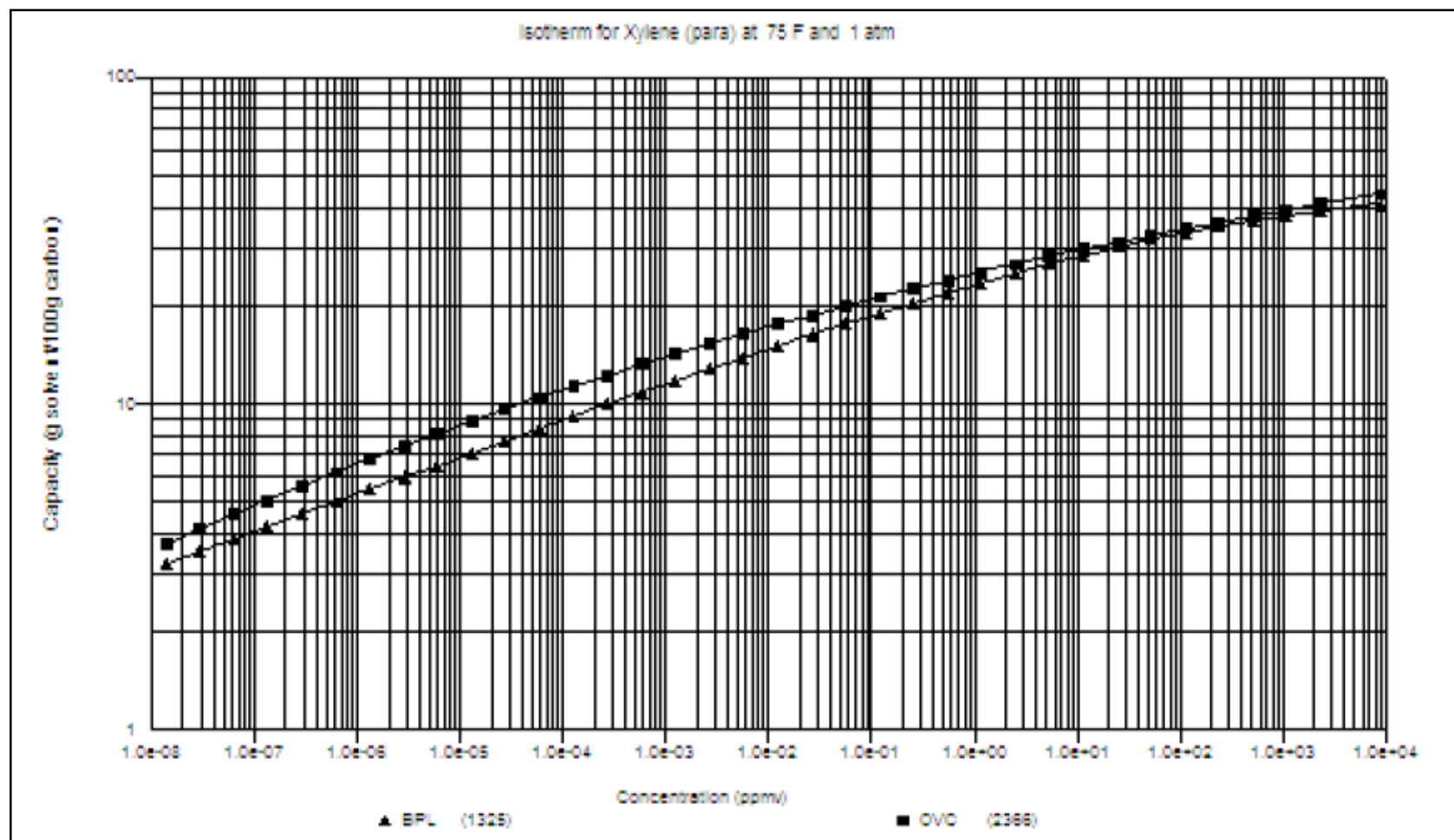


Figure D.18 Manufacturer's isotherm for para-xylene

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## BIOGRAPHICAL INFORMATION

Annaprabha Athappan was born on February 26, 1981 in Madurai, India. Madurai is a small town in the southern part of India. It is well known for Goddess Meenakshi and its temple. She grew up with her siblings Prakash, Ashok, Poorani, and Meenu. Her mother Mrs. Thenmoli Athappan has completed her teaching professional degree but decided to stay with kids at home. Her father Dr. P.R. Athappan is a Professor & Head, Department of Inorganic Chemistry and Dean (Industrial Consultancy) in Madurai Kamaraj University (MKU), India. His interest is in bioinorganic chemistry. She admired her father and became interested in obtaining her doctorate. She finished her school in St. Joseph higher secondary and got a bachelors degree in Civil and Environmental engineering in 2002 at P.S.N.A College of Engineering and Technology in Dindigul, Tamilnadu, India.

She got married on December 2002 with Mr. Saravanan Nachimuthiah and moved to the United States. His interest and motivation in fulfilling her dream degree and make her independent, made her to join in masters program at University of Texas at Arlington (UTA) on may 2005. She delivered a baby boy on March 2006 and they named him as Sanjiv Prakash Saravanan. She has been studying as a part time student since then. She started doing her research under Dr. Melanie L. Sattler in May 2006 on

adsorption. Finally, she graduated with her master's degree in Civil and Environmental engineering from UTA December 2008.