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**M.S. Thesis**

**May 2014**

**Simultaneous adsorption of 11 volatile organic compounds by an activated carbon made from polystyrene sulfonic acid-based organic salt**

**By Alejandro Smith**

**Spring 2014**

**Advisor: Professor Pengfei Zhang**

**Submitted in partial fulfillment of the request for the degree of Master of Sciences in the College of Liberal Arts and Sciences of the City College of the City University of New York**

## **Abstract**

Activated carbon is used in water treatment worldwide due to its ability to adsorb many different contaminants from water. The high adsorption capacity of activated carbon is linked to its high internal surface area and micro/meso- porosity. In this work an activated carbon obtained from polystyrene sulfonic acid-based organic salt was examined to simultaneously adsorb eleven volatile organic compounds from aqueous solution. Adsorption data were modeled with different isotherms to determine the equilibrium adsorptive capacities for these compounds. The performance of the polymer-based activated carbon was then compared with that of a commercial wood-based activated carbon. The results indicate that the polymer-based activated carbon has almost twice the adsorption capacity than the wood-based activated carbon.

## **Acknowledgment**

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## 1 Introduction

Volatile organic compounds (VOCs) in the environment are a major health issue worldwide because of their impact on human health and quality of life. Most of these chemicals are used as precursors to fabricate other chemicals; many have applications in pharmaceutical manufacturing, production of rubber and plastic, textile industry, building construction and automobile parts; some are essential components of floor waxes, paints and varnishes, several pesticides and resins [1, 2, 3, 4].

One of the most important groups of VOCs to be addressed in drinking water treatment include: benzene, carbon tetrachloride, 1,2-dichloroethane, 1,2-dichloropropane, dichloromethane, tetrachloroethylene (PCE), trichloroethylene (TCE), vinyl chloride, aniline, benzyl chloride, 1,3-butadiene, 1,1-dichloroethane, nitrobenzene, oxirane methyl, 1,2,3-trichloropropane and urethane [5]. This group of VOCs has a great impact on human health when inhaled or ingested. Acute health effects can be manifested as nervous system damage, pulmonary edema, and others, while chronic health effects include cancer, birth defects, immune systems deficiencies, and others [6, 7]. The carcinogenicity for some of these VOCs including benzene, carbon tetrachloride, 1,2-dichloroethane, 1,2-dichloropropane, dichloromethane, PCE, TCE, and vinyl chloride have been well determined; the remaining eight compounds are suspected carcinogens [5].

The production of these chemicals for human use has increased drastically during last century. Although most peaked in production at the end of the last century, they still are produced in very large quantities. Today the production of these compounds ranges from hundreds to thousands of tons per year (e.g., PCE, TCE, carbon tetrachloride, and 1, 2, 3-trichloropropane) to millions of tons per year (e.g., 1, 3-butadiene and dichloromethane) [8, 9, 10].



Contamination of drinking water sources is often linked to liquid and solid wastes discharged into water bodies or soils, from septic tanks, municipal landfills, industrial processes, and others [11, 12, 13]. Once released into the ground, these chemicals can infiltrate the soil, reach water table, and eventually discharge into streams, making groundwater and surface water improper and dangerous for human consumption, agriculture, recreation and other uses [11, 13]. Water bodies can be naturally contaminated with VOCs by minerals and organic matter dissolved in ground or in atmosphere. However, the extensive use of VOCs nowadays and the improper handling of these compounds have led to the increasing concern about the contamination of drinking water sources with VOCs and their negative impact on human health [5].

Due to the enormous problem of water sources contamination by VOCs around world, several treatment technologies for water purification have been employed, including reverse osmosis, air stripping, and activated carbon adsorption. Adsorption is a process that involves the migration of impurities into the porous cavities of an adsorbent; once inside, molecules are attracted to the internal surface via various forces, with the weak Van der Waals attraction as the most common [14, 18, 19]. Adsorption onto activated carbon is known as one of the most effective methods for water purification. Activated carbon is a unique material that has the ability of adsorbing large amounts of impurities from liquid phase, due to its large internal surface area and a high degree of porosity [14, 16]. Activated carbon can be made by carbonizing any material with high carbon content such as wood, coconut shells, coal, among others, and then activating it by a chemical or physical process. The affinity of the final product for a specific group of compounds depends on the way how it was made, the raw material used, and the activation process [14, 15]. Today the global annual production of activated carbon is around 1.2 million tons, with a huge variety of

different carbons produced. Activated carbon has become one of the preferred materials for purification of drinking waters everywhere [15, 16].

A novel type of activated carbon was produced by Prof. Bandosz's group at the CCNY Chemistry Department. It is made by the carbonization of a commercially available poly-(styrene sulfonic acid-*co*-maleic acid) salt containing iron as a metal cation, and has very high surface area and porosity, and super adsorption capacities for toxic gases [17].

The objectives of this study are two: 1) determine the adsorptive capacity of Bandosz's group polymer based activated carbon (PBAC) for eleven different VOCs (carbon tetrachloride, 1,2-dichloroethane, dichloromethane, 1,1-dichloroethane, 1,2-dichloropropane, 1,2,3-trichloropropane, PCE, TCE, 1,3-butadiene, benzene, and benzyl chloride) by performing batch adsorption experiments, and 2) compare the adsorptive capacity to that of a commercial wood-based activated carbon (WBAC). Since the PBAC also contained some reduced iron the potential reductive dechlorination of the chlorinated compounds was also examined.

## **2 Materials and Methods**

### **2.1 Materials**

The PBAC was made by the carbonization of a polystyrene sulfonic acid-based organic salt using a horizontal furnace with nitrogen as an inert gas; it was heated with a rate 50 °C /min and held at 800 °C for 40 min [17]. The resultant material has a well-developed porous structure (micro- and mesopores), and the porous structure was further enhanced by washing the material with hydrochloric acid and cleaning with distilled water. The final material has the appearance of

foam and possesses a low density, a high degree of porosity and a large surface area. The WBAC was obtained from Westvaco (WVA 900). 1, 1-dichloroethane, 1, 2-dichloropropane and 1, 2, 3-trichloropropane were purchased from Supelco, 1,3-butadiene was purchased from Restek Corp, and the rest of the compounds were purchased from Sigma-Aldrich. The purity of the compounds is over 99.8% except for 1, 3-butadiene, which is provided by the vendor as a 2000 ppm solution in methanol. Methanol used for stock solution preparation was purchased from J. T. Baker.

## **2.2 Methods**

### **2.2.1 Batch Adsorption**

Batch adsorption experiments were performed to determine the adsorptive capacity of the PBAC for VOCs. Five samples were made by weighting 8 mg of the activated carbon into five different 10.5 mL amber glass vials and mixing with 10.5 mL solution containing different concentrations of the 11 VOCs (250, 500, 1000, 2500, or 5000 ppb). Samples were shaken in an orbital shaker at room temperature for 15 hours, and a headspace analysis was done using a gas chromatograph/mass spectrometer (GC/MS) with a headspace autosampler. Due to limited amount of PBAC available, only duplicate experiments were run for each solution concentration.

Similar batch adsorption experiments were also performed with the WBAC (at six different VOC concentrations: 100, 250, 500, 1000, 2500, and 5000 ppb). Triplicate experiments were run for each concentration.

### **2.2.2 Gas Chromatography/Mass Spectrometer**

The equilibrium concentrations of the 11 compounds were determined using headspace GC/MS (A Shimadzu QP2010 Plus GC/MS with an AOC-5000 autosampler) following the published methods of Caro et al. and EPA method 524.2 [5]. The supernatant (5 mL) from the adsorption vial was transferred to a sealed 10 mL autosampler vial through a gas tight syringe with a needle. The autosampler vials were then placed into the heated six-position incubator in the autosampler for preconditioning (80 °C for 10 min). Afterwards a heated gastight syringe was moved over the incubator and the headspace sample was withdrawn and injected to the GC. After injection the hot syringe was automatically cleaned by purging with nitrogen gas. An HP-5MS capillary column (30 m×0.25 mm i.d., 0.25 µm film thicknesses) was used for separation. The oven temperature was initially maintained at 40 °C for 3 min, and increased to 95 °C at a rate of 15 °C/min and held for 2 min. After that, the temperature was increased to 200 °C at a rate of 25 °C/min and held for additional 3min. Mass spectra were obtained at 70 eV in the electron impact ionization mode. The MS detector was operated in full scan mode between m/z 45 and 200 if sensitivities were good enough for quantization, otherwise the selected ion monitoring (SIM) mode was used.

Calibration curves were produced by using external standards of 20, 40, 200, 500, 2000, and 5000 ppb for all compounds.

### **2.2.3 Ion Chromatography**

In order to witness possible reductive dechlorination of the chlorinated compounds, two samples with the highest compound concentrations and the PBAC were analyzed for chloride using ion chromatography (IC). A DIONEX IC system with an AS40 automated sampler, LC25 chromatographic oven, GS50 gradient pump, and a CD25 conductivity detector was employed.

The chloride anion was separated using an IonPAC AS14A analytical column (5 $\mu$ m, 3x150 mm). The sample injection volume was 25  $\mu$ L and the flow rate was 0.5 mL/min. The eluent solution used was a mixture of 0.8 mM of Na<sub>2</sub>CO<sub>3</sub> and 1 mM of NaHCO<sub>3</sub>. The experiment was carried at room temperature. A calibration curve was produced using external chloride standards of 0.01, 0.05, 0.1, and 0.15 mM.

#### **2.2.4 Equilibrium Isotherms**

If the adsorbent and adsorbate are in contact for enough time equilibrium will be established between them. The equilibrium can be described by the so-called adsorption isotherm, a curve relating the equilibrium amount of solute adsorbed onto the surface of an adsorbent, to the concentration of the solute remaining in the aqueous phase [14, 15]. The amount adsorbed at equilibrium can be calculated from the following equation:

$$q_e = (C_0 - C_e)V/m \quad (1)$$

where  $q_e$  (mg/g) is the amount adsorbed at equilibrium,  $C_0$  (mg/L) and  $C_e$  (mg/L) are the initial and equilibrium concentrations in solution, respectively,  $V$  (L) is the volume of the solution, and  $m$  (g) is the mass of the adsorbent. The equilibrium data were fitted to Langmuir, Freundlich and Langmuir-Freundlich isotherm (or Sips) to find the best isotherm that represents the adsorption process.

Langmuir isotherm is commonly used for the application of activated carbon in water treatments. It assumes that once a site is occupied no further adsorption takes place, and that all adsorption sites have the same probability to be filled. This isotherm is reduced to the linear isotherm at low concentrations and it predicts a monolayer sorption capacity at higher concentrations [19, 20, 21].

Langmuir isotherm equation is given by:

$$q_e = mK_L C_e / (1 + K_L C_e) \quad (2)$$

Where  $K_L$  (L/mg) is the adsorption constant, and  $m$  (mg/g) is the monolayer adsorptive capacity.

Freundlich isotherm is an empirical expression largely used for modeling adsorption processes; it considers heterogeneous adsorption on the adsorbent surface. At low concentrations Freundlich isotherm is also linear, at higher concentrations it becomes curved reflecting lower adsorption while sites are filled. However, this isotherm does not predict a maximum capacity as Langmuir does, so there is no limit on adsorption [19, 20, 21].

Freundlich isotherm equation is given by the expression

$$q_e = K_F C_e^{1/n} \quad (3)$$

Where  $K_F$  is a constant and  $n$  is the affinity term.

The Langmuir-Freundlich isotherm (or Sips) is a versatile isotherm expression that can simulate both Langmuir and Freundlich behaviors. At low concentrations it reduces to Freundlich isotherm, at high concentrations it predicts a maximum single layer capacity of adsorption, characteristic of Langmuir isotherm [21, 23].

The Langmuir-Freundlich isotherm equation has the following form:

$$q_e = mK_s C_e^r / (1 + K_s C_e^r) \quad (4)$$

Where the parameter  $m$  (mg/g) is related to the monolayer maximum adsorptive capacity,  $K_s$  (L/mg) is an affinity constant and  $r$  is the index of heterogeneity ( $0 < r \leq 1$ ).

### 3 Results and Discussion

#### 3.1 Isotherms and Adsorption Capacities

An example of adsorption isotherms for TCE and carbon tetrachloride with the two activated carbons is presented in Figure 1. It is evident that the PBAC has much higher adsorption capacities for these two VOCs than the WBAC. For instance, at the highest contaminant loading, the amount of TCE adsorbed by PBAC is about 9.5 mg/g, 1.6 times the amount adsorbed by WBAC (~ 6.0 mg/g). Likewise, the maximum amount of carbon tetrachloride adsorbed by the PBAC (~ 10.2 mg/g) is also about 1.6 times the amount adsorbed by WBAC (~ 6.6 mg/g). This is indeed the case for all 11 VOCs examined here (see Appendix).

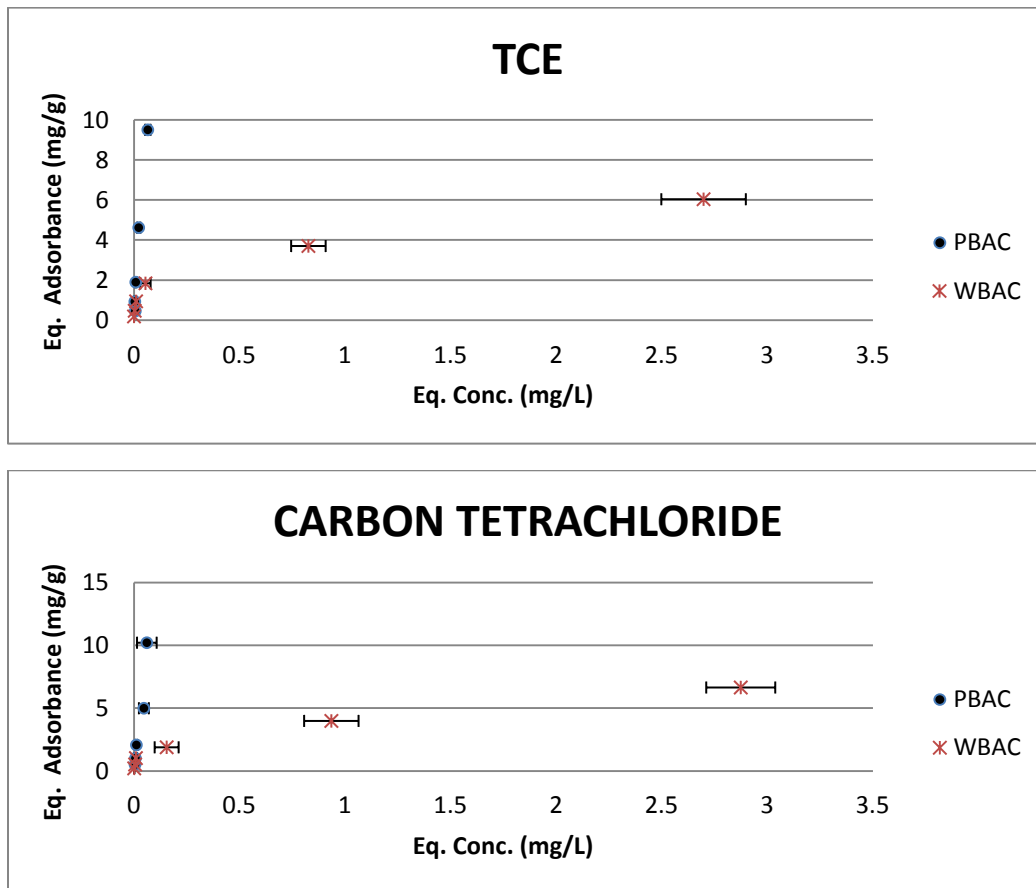


Figure 1: Comparison between PBAC and WBAC for the adsorption of TCE and carbon tetrachloride.

For a given sample at a given solution concentration, the amount of each compound adsorbed was added one by one to create the TOTAL amount adsorbed (Table 1). Likewise, the amount of each compound remaining in the solution at equilibrium was also added to yield TOTAL equilibrium concentration in solution (Table 1).

Table 1: TOTAL amount adsorbed ( $q_e$ ) and TOTAL equilibrium solution concentration ( $C_e$ ) for PBAC and WBAC.

TOTAL PBAC		TOTAL WBAC	
$q_e$ (mg/g)	$C_e$ (mg/L)	$q_e$ (mg/g)	$C_e$ (mg/L)
3.5	$0.2 \pm 0.04$	1.8	$0.06 \pm 0.004$
8.2	$0.4 \pm 0.04$	4.4	$0.3 \pm 0.02$
16.9	$0.6 \pm 0.05$	7.9	$1.3 \pm 0.03$
49.1	$2.2 \pm 0.4$	13.9	$3.6 \pm 0.3$
82.0	$4.7 \pm 0.3$	28.7	$13.3 \pm 0.4$
		51.3	$31.3 \pm 1.4$

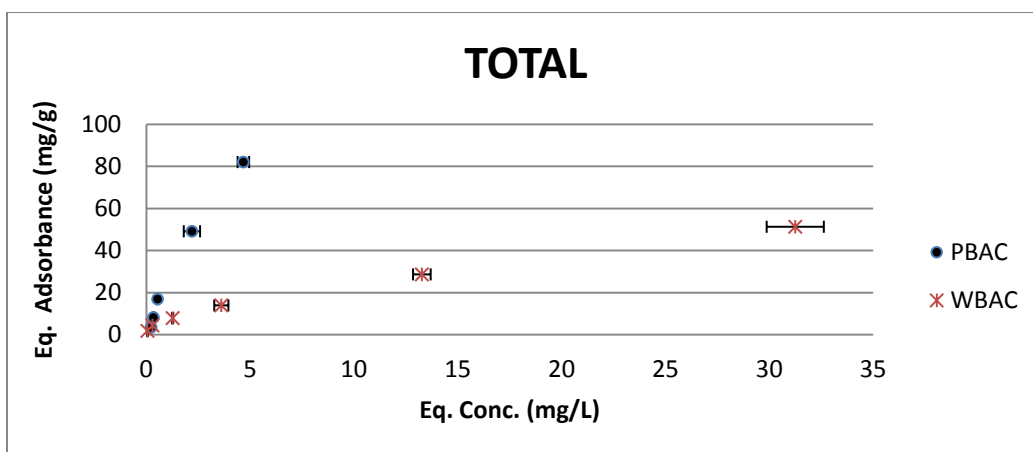


Figure 2: Plot of total amount adsorbed against total equilibrium solution concentration for both PBAC and WBAC.



A plot of TOTAL amount adsorbed against TOTAL equilibrium solution concentration, for both activated carbons, is shown in Fig 2. The total maximum amount of VOCs adsorbed by the PBAC is about 82 mg/g, 1.6 times of that adsorbed by the WBAC (51 mg/g).

The isotherm data were fitted with the different models using a non-linear regression with the STATGRAPHIC Centurion XVI.I modeling program to obtain the isotherm parameters.

The Langmuir isotherm assumes monolayer adsorption onto a surface containing a finite number of adsorption sites; once a site is filled no further sorption can take place at that specific site. This indicates that the surface reaches a saturation point where the maximum adsorption of the surface will be achieved [19, 20, 21].

The fitted parameter values ( $m$ ,  $K_L$  and correlation coefficient  $R^2$ ) for the Langmuir isotherm are listed in Table 3. The parameter  $K_L$  can be used to calculate a constant known as Separation Factor (SF) defined by equation (5) below.

$$SF = 1/(1+K_L C_0) \quad (5)$$

If  $SF > 1$  then the isotherm is considered unfavorable, when  $SF = 1$  it is linear, and if  $0 < SF < 1$  then the isotherm is favorable [26, 27]. The SF values are also listed in Table 2.

It can be seen from Table 2 that the  $m$  values from PBAC are higher than  $m$  values from WBAC, indicating higher monolayer loading for all compounds [19, 20, 21]. For the majority of the compounds (e.g., 1,2,3-trichloropropane (26.20 mg/g for PBAC and 8.87 mg/g for WBAC), TCE (36.85 mg/g PBAC and 5.45 mg/g WBAC), carbon tetrachloride (23.06 mg/g PBAC and 8.04 mg/g WBAC), and benzene (14 mg/g PBAC and 3.44 mg/g WBAC)) the maximum loading is four to five times higher for PBAC with respect to WBAC. The Separation Factor for PBAC and

WBAC lies between 0 and 1 (Table 2) indicating favorable adsorption with both activated carbons [26, 27]. The correlation coefficient  $R^2$  values are above 0.90 for all but one compound (dichloromethane), with a few of them as high as 0.99. The  $R^2$  value for dichloromethane with WBAC is 0.855 (Table 2).

Table 2: Langmuir parameters for each compound for both PBAC and WBAC

Langmuir Isotherm Compound	PBAC				WBAC			
	$K_L$ (L/mg)	SF	m (mg/g)	$R^2$	$K_L$ (L/mg)	SF	m (mg/g)	$R^2$
1,2,3trichloropropane	8.9	0.3	26.2	0.98	1.1	0.8	8.9	0.93
1,2dichloropropane	1.5	0.7	14.3	0.93	0.2	0.9	4.6	0.90
1,1dichloropropane	0.9	0.8	18.9	0.96	0.2	0.9	4.8	0.93
TCE	5.2	0.4	36.8	0.97	8.0	0.3	5.5	0.91
PCE	25.6	0.1	15.5	0.97	30.1	0.1	9.9	0.99
Benzyl chloride	28.1	0.1	13.2	0.94	13.5	0.2	8.9	0.96
1,3butadiene	44.2	0.08	8.4	0.99	1.1	0.7	7.9	0.93
1,2dichloropropane	5.9	0.4	21.4	0.98	1.3	0.8	3.1	0.95
Carbon tetrachloride	5.9	0.2	23.1	0.99	1.4	0.8	8.0	0.95
Benzene	18.8	0.	14.0	0.99	1.6	0.7	3.4	0.92
Dichloromethane	0.2	0.9	16.2	0.99	0.7	0.9	1.0	0.85
TOTAL	0.1	0.9	208.7	0.99	0.04	0.9	87.2	0.97

The isotherm data with Langmuir fitting for the TOTAL VOCs of each activated carbon can be seen in Fig 3.

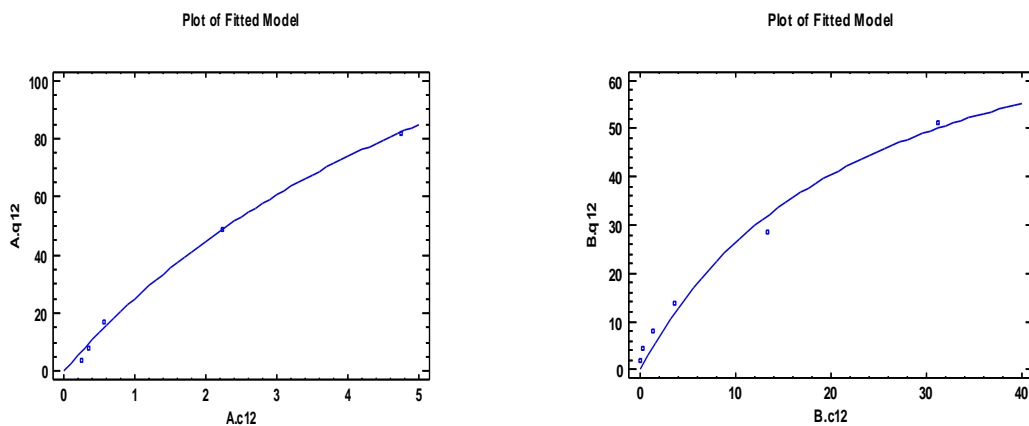


Fig 3: Total amount of VOCs adsorbed (Y axis, mg/g) vs total equilibrium solution concentration (X axis, mg/L) with Langmuir isotherm (Left: PBAC; right: WBAC).

Freundlich equation is an empirical expression that provides a relation between concentrations of a solute on the adsorbent surface to the concentration of the solute in liquid phase [19, 20 21].

The fitted parameter values for the Freundlich isotherm ( $K_F$ ,  $n$  and  $R^2$ ) are listed in Table 3.

The parameter  $K_F$  is an indicator of the adsorptive capacity, with units of  $\text{mg/g}(\text{L/mg})^{1/n}$ . When the concentration  $C_e$  is equal to 1 mg/L then  $K_F$  (mg/g) becomes the adsorptive capacity (see equation (3)). In Table 3 it can be seen that for all the compounds, PBAC has much greater values for this parameter than does WBAC, indicating that PBAC has a higher capacity of adsorb these volatile compounds.

The parameter  $n$  is related to the energetic heterogeneity of the adsorbent surface. The greater the deviation of this parameter is from one, the wider the distribution of bound energies [19, 20, 21, 27]. It can be seen from Table 3 that PBAC has lower values for this parameter than does WBAC, suggesting that PBAC has a more homogeneous surface. The correlation coefficient  $R^2$

showed values over 0.96 for most of the compounds except for PCE, benzyl chloride and 1,2-dichloropropane, which have  $R^2$  values between 0.93 and 0.95.

Table 3: Freundlich parameters for each compound for both PBAC and WBAC

Freundlich Isotherm Compound	PBAC			WBAC		
	$K_F$	n	$R^2$	$K_F$	n	$R^2$
1,2,3trichloropropane	12.3	1.3	0.96	4.4	2.2	0.98
1,2dichloropropane	8.9	1.8	0.97	0.9	1.7	0.95
1,1dichloropropane	9.7	1.4	0.98	0.8	1.6	0.96
TCE	105.6	1.1	0.97	4.2	2.8	0.98
PCE	45.7	1.7	0.95	10.6	3.0	0.92
Benzyl chloride	62.8	1.5	0.93	13.4	2.1	0.99
1,3butadiene	93.2	1.3	0.99	3.9	2.0	0.96
1,2dichloropropane	51.9	1.2	0.99	1.6	2.5	0.99
Carbon tetrachloride	46.9	1.3	0.99	4.2	2.3	0.99
Benzene	79.1	1.2	0.98	1.9	2.5	0.98
Dichloromethane	1.9	1.1	0.99	0.3	2.1	0.92
TOTAL	20.9	1.1	0.99	6.4	1.7	0.99

The isotherm data with Freundlich fitting for the TOTAL VOCs of each activated carbon can be seen in Fig 4.

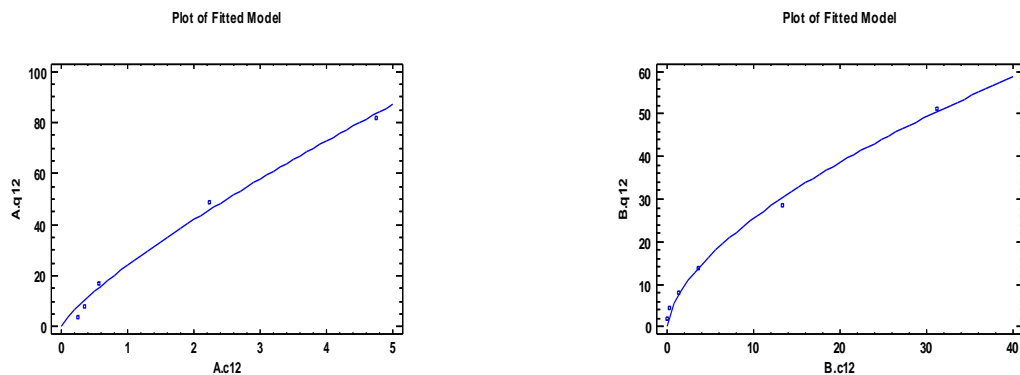


Fig 4: Total amount of VOCs adsorbed (Y axis, mg/g) vs total equilibrium solution concentration (X axis, mg/L) with Freundlich isotherm (Left: PBAC; right: WBAC),

The Langmuir-Freundlich isotherm is a combination of both equations. At low concentrations this isotherm behaves as Freundlich equation, and at high concentrations it predicts a monolayer adsorptive capacity as does Langmuir (see equation 4) [21, 22]. The parameters of this isotherm, the adsorptive capacity  $m$ , the parameter  $r$ , the affinity constant  $K_s$ , as well as the correlation coefficient  $R^2$  for the TOTAL VOCs are listed in Table 4. The parameter  $r$  ( $0 < r < 1$ ) reflects surface heterogeneity (close to one for homogeneous material).

The Langmuir-Freundlich isotherm fit the isotherm data well, with correlation coefficients as high as 0.94 for most of compounds. However, some fitted parameter values do not match with experience. For instance, the adsorptive capacities ( $m$ ) for some of the compounds were over 2000 mg/g, which is too high to make sense in a real world.

Table 4: Lagmuir-Freundlich isotherm parameters TOTAL for both activated carbons.

Isotherm Parameters	PBAC	WBAC
$m$ (mg/g)	2810.6	2506.6
$K_s$ (L/mg)	0.007	0.003
$r$	0.9	0.6
$R^2$	0.99	0.98

All 11 VOCs examined here are considered as hydrophobic compounds, with moderate to high values of octanol-water partition coefficients ( $K_{ow}$ , Table 5). The hydrophobic surface of the activated carbon would preferably adsorb hydrophobic compounds, thus the  $K_{ow}$  values can be regarded as an indicator of the tendency of adsorption onto activated carbon [23, 24].

Table 5: log  $K_{ow}$  values and maximum amount adsorbed for each compound.

Compound	Log( $K_{ow}$ )	PBAC max. $q_e$ (mg/g)	WBAC max. $q_e$ (mg/g)
1,2,3-Trichloropropane	2.27	8.9	6.3
1,2-Dichloroethane	1.47	7.3	2.3
1,1-Dichloroethane	1.79	7.1	2.2
TCE	2.71	9.5	6.0
PCE	2.67	10.5	9.6
Benzyl Chloride	2.30	7.2	6.9
1,3-Butadiene	1.99	3.3	3.2
1,2-Dichloropropane	1.97	7.5	1.7
Carbon Tetrachloride	2.73	10.2	6.6
Benzene	2.13	5.7	2.8
Dichloromethane	1.25	2.9	0.7

A plot of the maximum amount adsorbed for each compound against its log  $K_{ow}$  value is presented in Figure 5. There is a nice positive linear relationship between maximum  $q_e$  and log  $K_{ow}$ , suggesting that the adsorption is driven mainly by hydrophobic interactions.

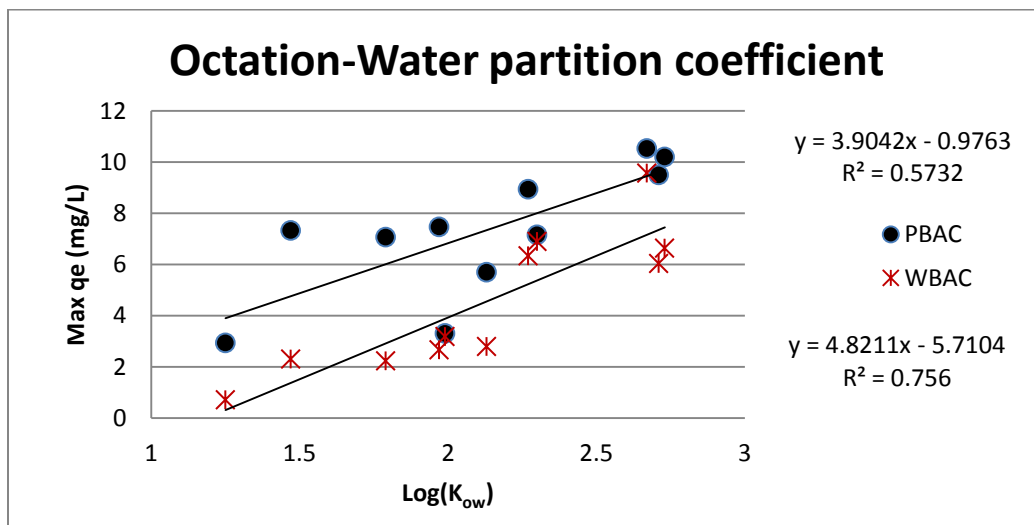


Figure 5: Maximum amount adsorbed vs. log  $K_{ow}$  for both activated carbons.

### 3.2 Pore Size Distribution and Pore Volume

The pore size distribution and volume are fundamental to characterize the adsorption process. Adsorption capacities are generally linked to the kind of porosity structure and surface area that the material has. The volume of micropores and mesopores is essential to adsorb a target contaminant, e.g., large molecules need wider pores.

The structural parameters were collected from the nitrogen adsorption isotherm; they are presented in Table 6 and Figure 6.

Table 6: Structural parameters for both carbons, PBAC (CPS-Fe-950) and WBAC (WVA-900). [17].

AC	$S_{\text{BET}}$ ( $\text{m}^2/\text{g}$ )	$V_t$ ( $\text{cm}^3/\text{g}$ )	$V_{\text{meso}}$ ( $\text{cm}^3/\text{g}$ )	$V_{<0.7\text{nm}}$ ( $\text{cm}^3/\text{g}$ )	$V_{<1\text{nm}}$ ( $\text{cm}^3/\text{g}$ )
CPS-Fe-950	950	0.655	0.327	0.164	0.216
WVA-900	1519	1.265	0.923	0.095	0.096

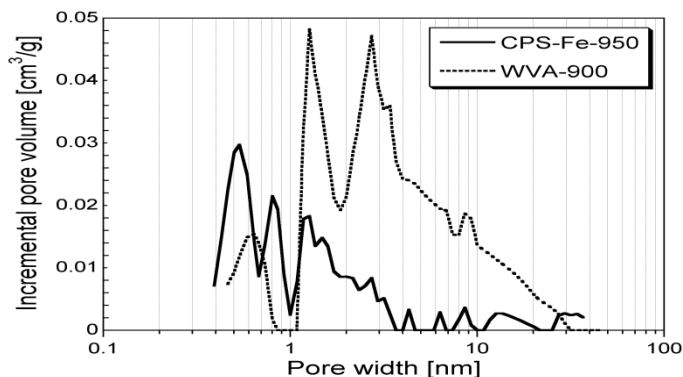


Figure 6: Pore size distribution for both carbons (solid line: PBAC; dotted line: WBAC) [17]. It can be seen from this table and Figure 6 that PBAC has a higher pore volume of micropores than WBAC, especially in the range between 0.4 nm and 1 nm (about twice of WBAC). The mesopore distribution (20 Å to 500 Å) is much better for WBAC having almost three times more

mesopore volume than PBAC (Table 6). The surface area was larger for WBAC as well as the total pore volume [17].

The molecular diameters for all compounds were calculated using the software ChemBioOffice version 12 from Cambridgesoft. It was found that all the VOCs examined here have an average diameter of less than 4 Å. Therefore these molecules could be preferentially adsorbed to the micropores of < 10 Å, explaining the high adsorption capacities of the PBAC for these compounds.

### **3.3 Reductive Dechlorination**

The PBAC contained reduced iron, used in the precursor, on its surface in the form of clusters [17], which could potentially interact with chlorinated hydrocarbons (reductive dechlorination). The reductive dechlorination may happen in any of three paths: direct reduction at the activated carbon surface, reduction by ferrous iron, or reduction by hydrogen [28, 29]. After run the ion chromatograph a mass balance was carried out to determine the percentage of the chlorinated compounds that was degraded. The total amount of chlorine in the VOCs in solution was 2.424 μmol. The amount of chloride detected was 0.036 μmol, suggesting that only around 1.5 % of the chlorinated molecules were degraded.

## **Conclusions**

Batch adsorption experiments were carried out to examine the adsorption capacities of PBAC and WBAC for VOCs. PBAC has almost twice the capacity than the WBAC. This is due to the



fact that PBAC has well-developed micropores suitable for the adsorption of compounds with small diameters, such as the VOCs examined here. The WBAC has a high mesopore volume but low micropore volume, making it less effective in capturing these VOCs.

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## Appendices

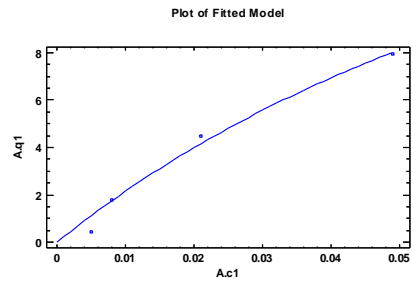
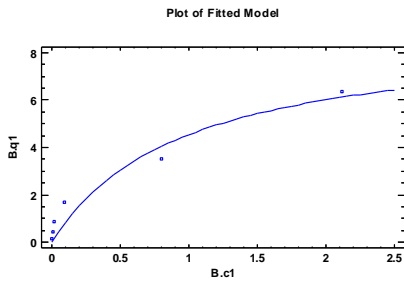
### Appendix I: Compound Properties

Compound	Formula	MW (g/mol)	CAS No
Benzene	C <sub>6</sub> H <sub>6</sub>	78.11	71-43-2
Carbon Tetrachloride	CCl <sub>4</sub>	153.82	56-23-5
1,2-Dichloroethane	C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	98.96	107-06-2
Dichloromethane	CH <sub>2</sub> Cl <sub>2</sub>	84.93	75-09-2
Tetrachloroethylene	C <sub>2</sub> Cl <sub>4</sub>	165.83	127-18-4
Trichloroethylene	C <sub>2</sub> HCl <sub>3</sub>	131.40	79-01-6
Benzyl Chloride	C <sub>7</sub> H <sub>7</sub> Cl	126.58	100-44-7
1,3-Butadiene	C <sub>4</sub> H <sub>6</sub>	54.09	106-99-0
1,1-Dichloroethane	C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	98.96	75-34-3
1,2-Dichloropropane	C <sub>3</sub> H <sub>6</sub> Cl <sub>2</sub>	112.99	78-87-5
1,2,3Trichloropropane	C <sub>3</sub> H <sub>5</sub> Cl <sub>3</sub>	147.43	96-18-4

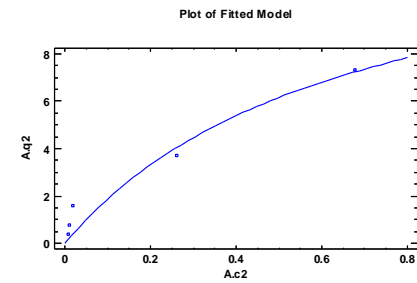
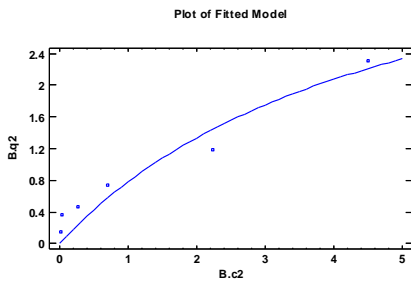
Appendix II: Adsorption isotherms.

**A. LANGMUIR ISOTHERM.**

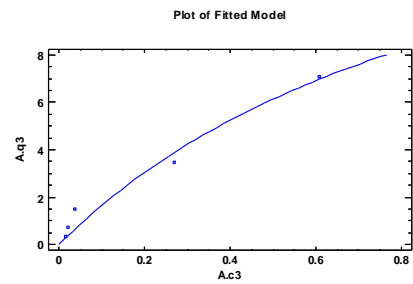
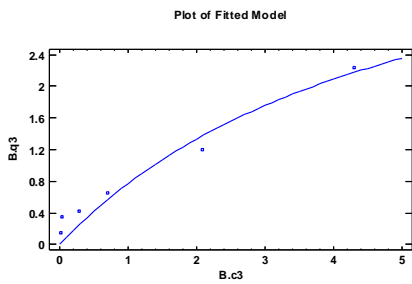
**Left Column for WBAC and Right Column for PBAC**



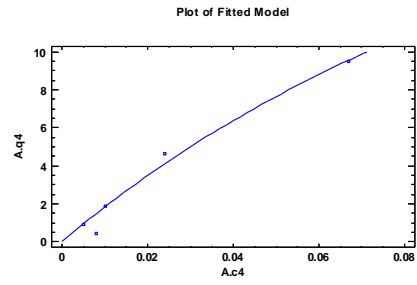
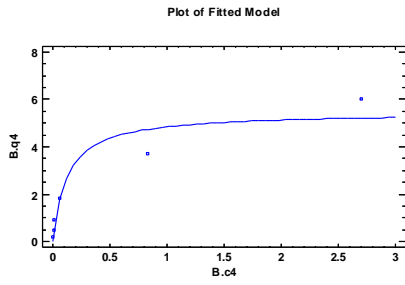
1,2,3-Trichloropropane



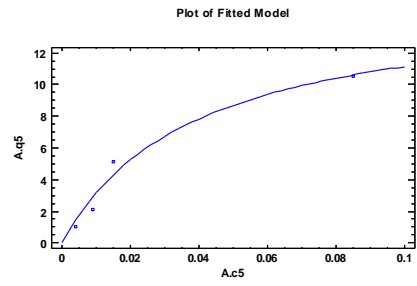
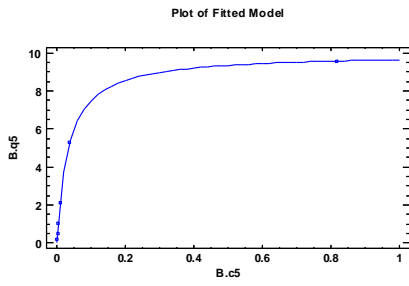
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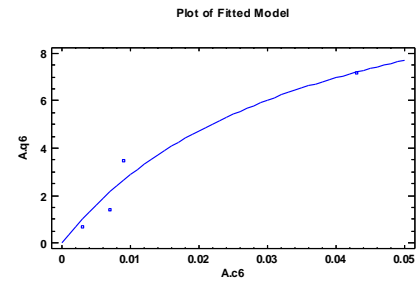
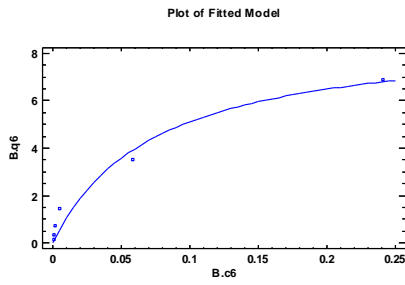
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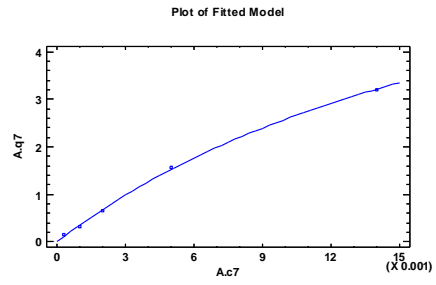
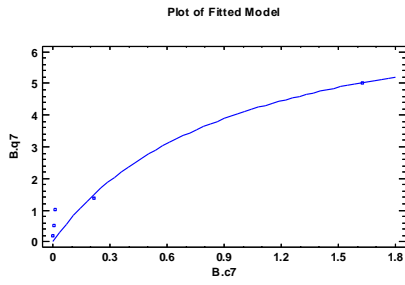
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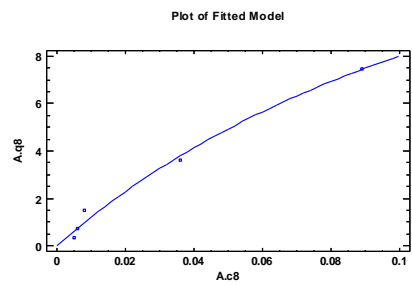
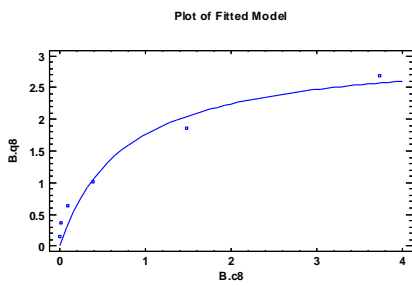
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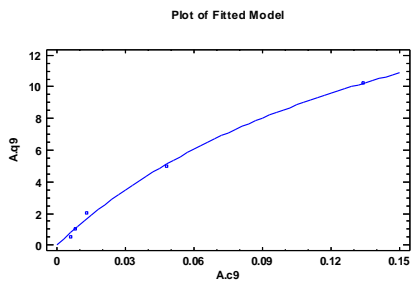
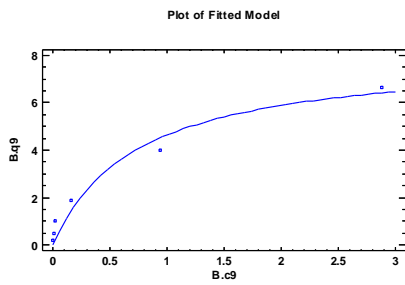
Benzyl Chloride



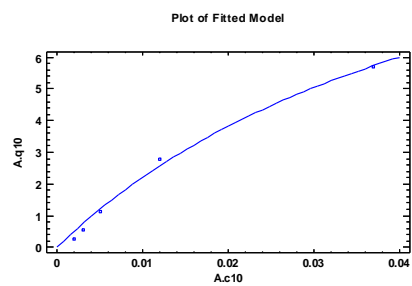
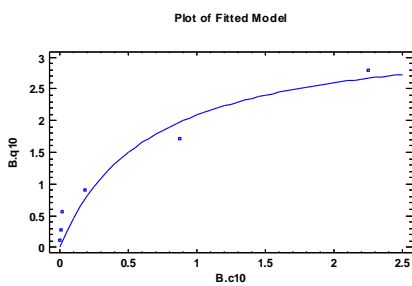
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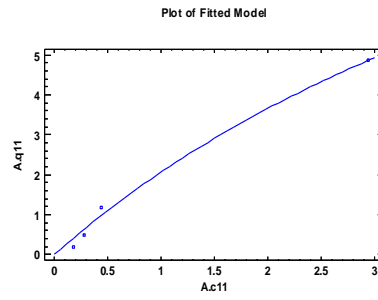
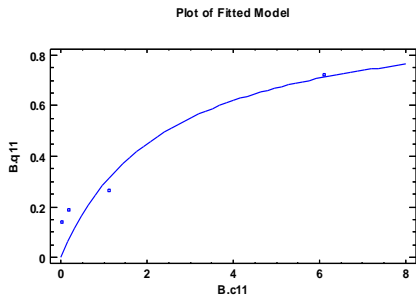
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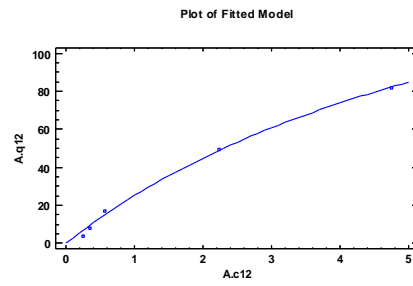
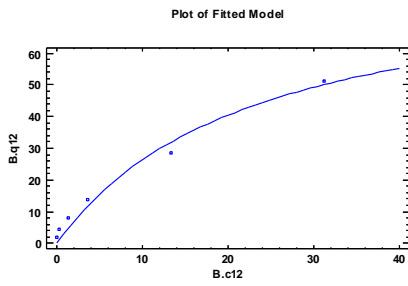
### Carbon Tetrachloride



## Benzene



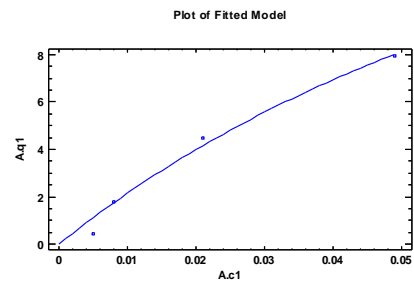
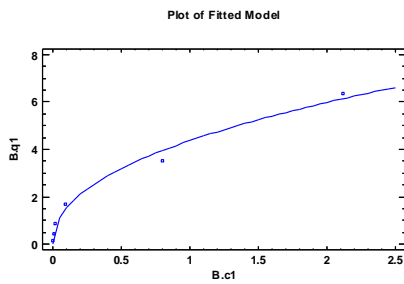
## Dichloromethane



## TOTAL

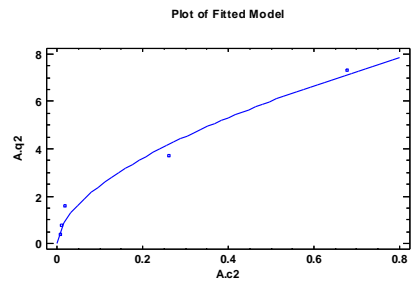
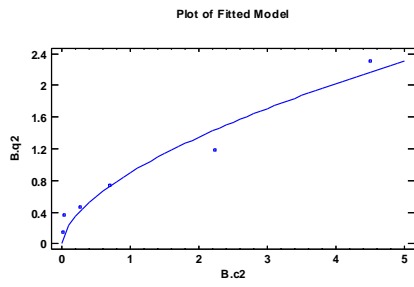
### B. FREUNDLICH ISOTHERM.

Left Column for WBAC and Right Column for PBAC

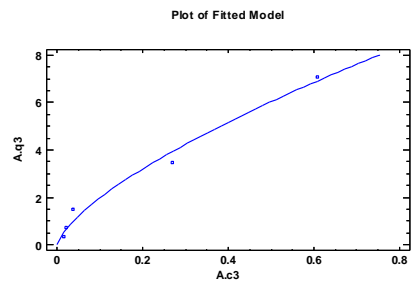
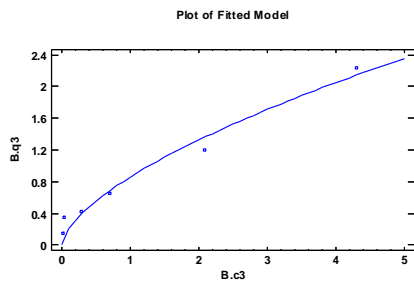


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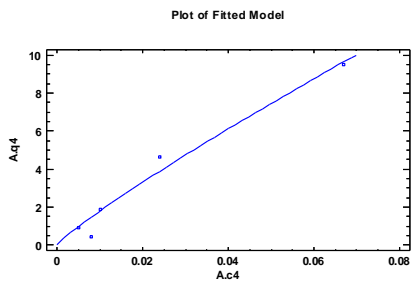
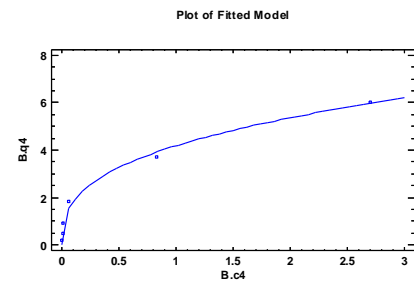




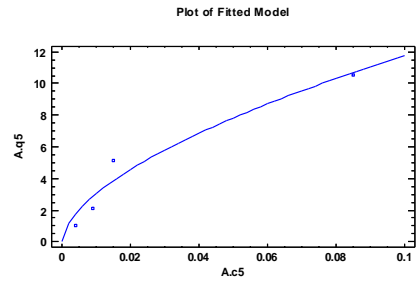
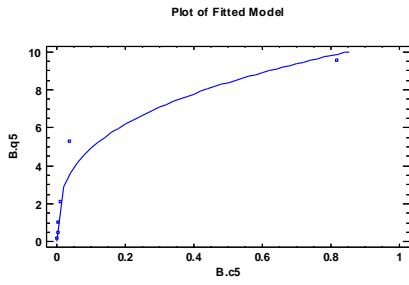
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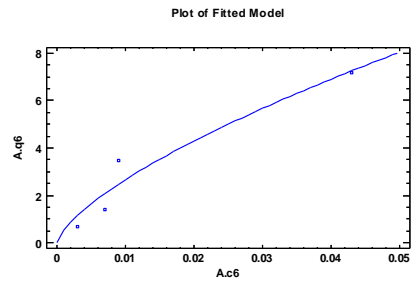
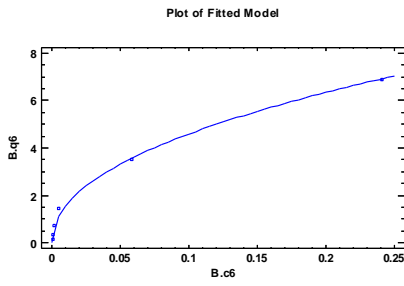
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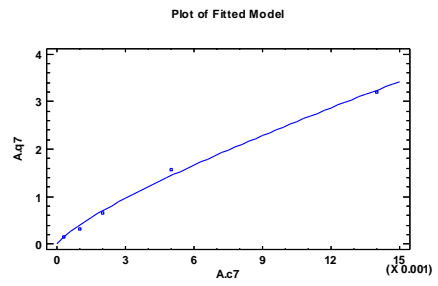
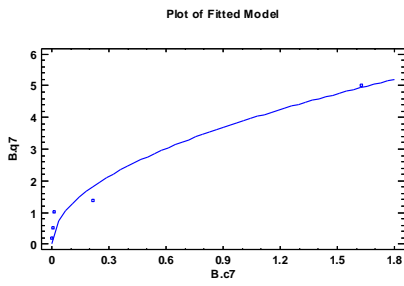
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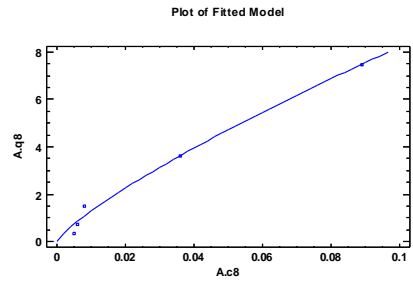
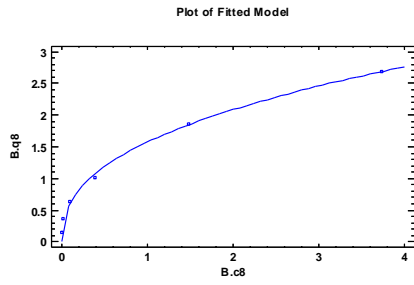
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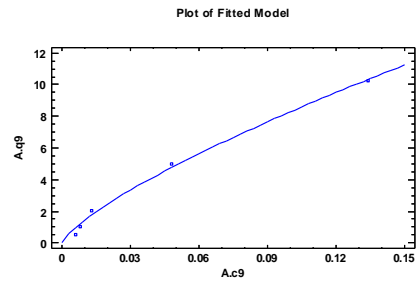
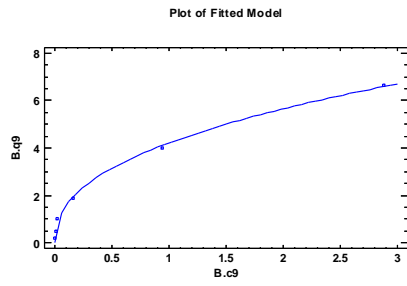
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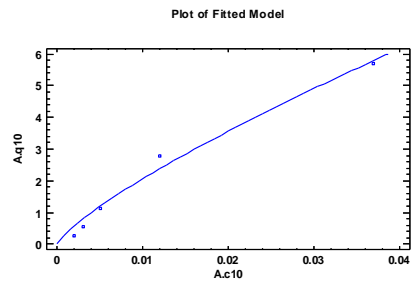
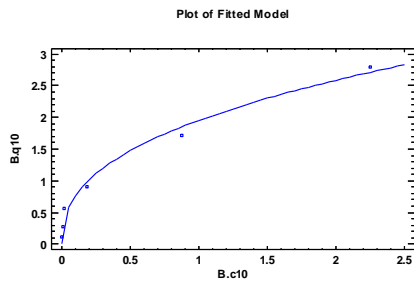
1,3-Butadiene



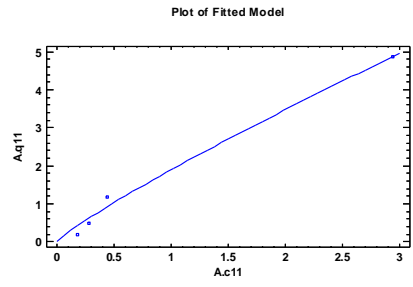
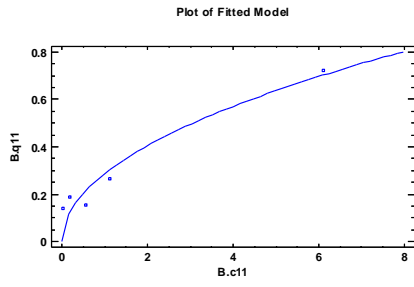
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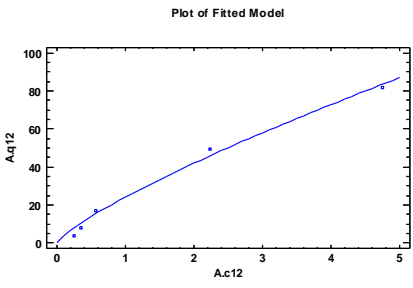
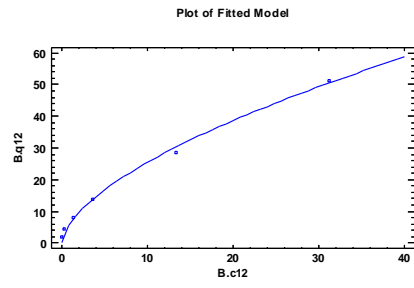
## Carbon Tetrachloride



## Benzene



Dichloromethane



TOTAL