FINAL PROGRESS REPORT

Adsorption of Gas Phase Contaminant Mixtures

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A. Specific Aims

This project seeks to study the effect of multiple gas-vapor mixtures on the activated carbon adsorption breakthrough time and pattern. Activated carbon cartridges used for respiratory protection are tested in most cases for a single component at relatively high concentration. Because in the real working conditions a multitude of contaminants of various concentrations may be present, the performance of personal protective equipment must be evaluated for individual gases and vapors as well as for mixtures.

The aim of this project is to study experimentally the adsorption of various low concentration gases, vapors and gas-vapor mixtures on activated carbon and to develop suitable models able to predict the adsorption performance (efficiency) of activated carbon cartridges under various conditions.

The scope of the project is to improve the understanding of the activated carbon adsorption process by studying the adsorption characteristics of activated carbon samples exposed to individual gases and vapors and binary mixtures. Specifically this research seeks to evaluate under dynamic conditions the change in the adsorption characteristics when more than one component is adsorbed and to develop simplified, applicable models to predict breakthrough from limited experimental single component adsorption data. The experimental part of the project consists in conducting a series of experiments in which various organic vapors (toluene, dichlormethane, and ethanol), gases (sulfur dioxide, and radioactive xenon), and mixtures are passed through fixed columns of activated carbon. Adsorption of mixtures is being studied considering both simultaneous and sequential adsorption of various concentrations of gases and vapors. The main adsorption models presented in the literature are also being evaluated and simplified models for the adsorption of mixtures will be developed based on the prevailing theories and correlated with the obtained experimental data.

The activities conducted during the the project were: (1) Update the literature review on multi-component adsorption experiments and modeling with papers published in the past few years. (2) Design, construct and test the adsorption experimental apparatus used in single component adsorption and binary adsorption tests. (3) Collect single component and binary gas-vapor adsorption data using simultaneous injection into the air stream. (4) Analysis of the adsorption data and development or improve adsorption models.

B. Studies and Results

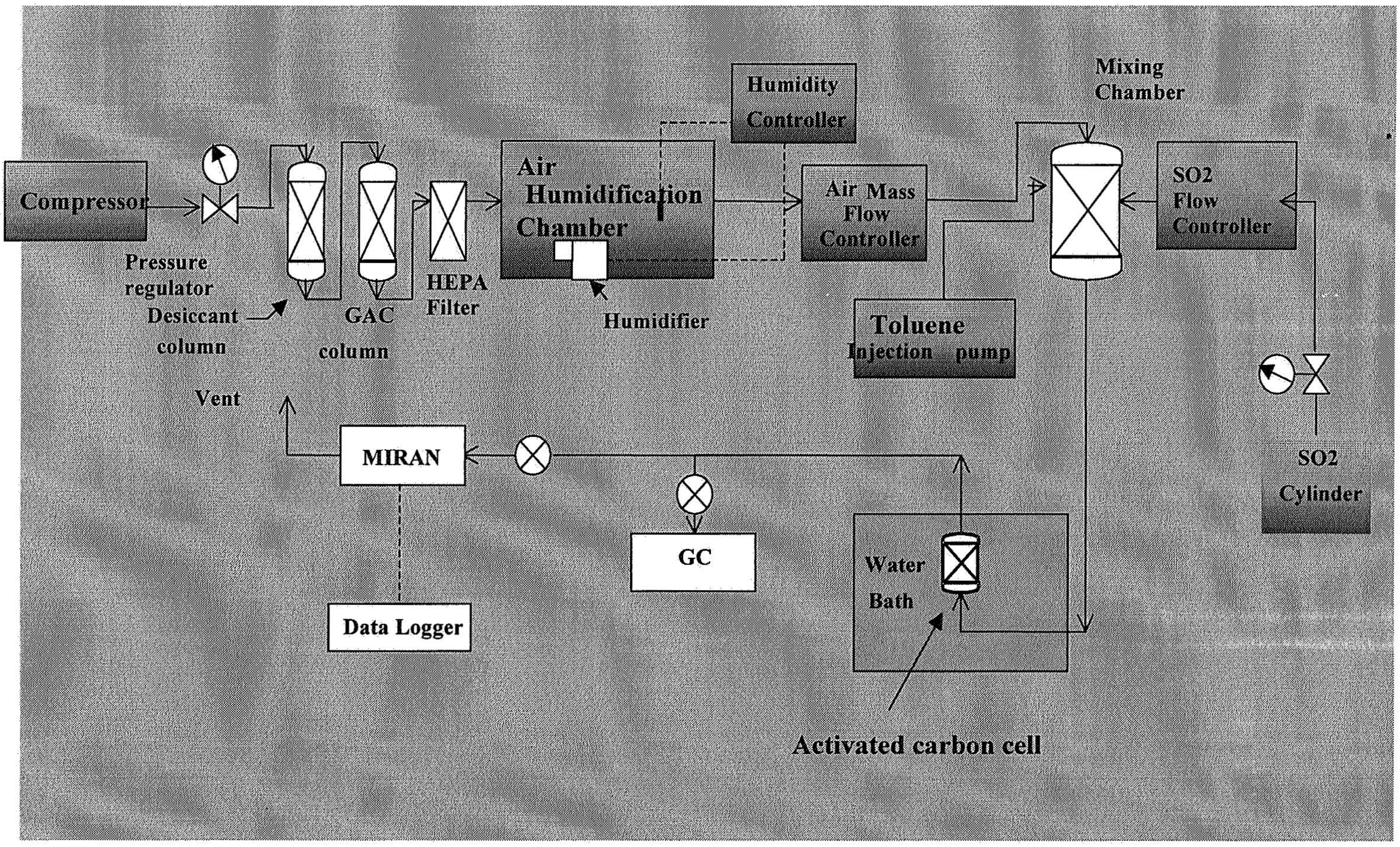
A summary of the work conducted during the project is described next.

Literature Review

Most of the literature review was conducted in the first year of the study. During the past few years, a number of articles were published regarding the adsorption of organic vapors, gases and mixtures onto activated carbon. All these articles were examined by the principal investigator. A particular attention was dedicated to examine the review material obtained from Dr. Gerry Wood from LANL: "Review of models for adsorption of single vapors, mixtures of vapors, and vapors at high humidities on activated carbon for applications including predicting service lives of organic vapor respirator cartridges." This material summarizes experimental data and modeling of activated carbon adsorption using a large database obtained from various studies. The principal investigator will use this material as the main reference to compare data and results obtained in the multiple component adsorption experiment.

Experimental Apparatus

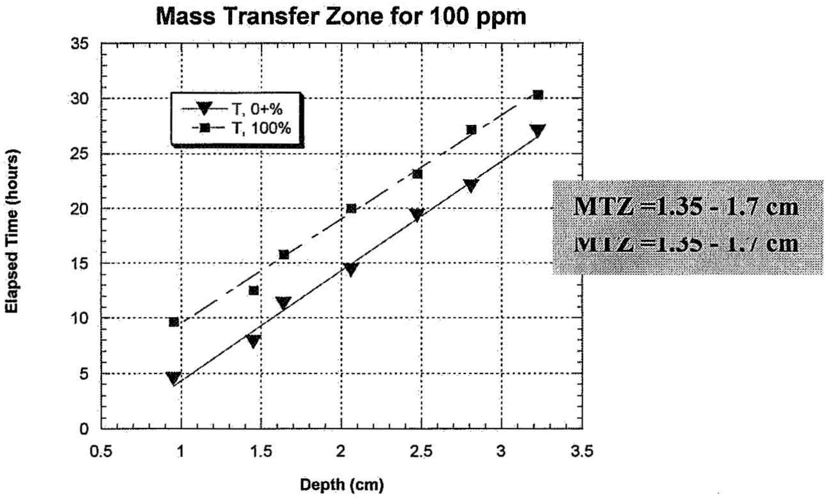
The construction and testing of the experimental apparatus designed to study the adsorption of various gases, vapors and mixtures was accomplished and is basically the same as the one described in the initial proposal. A block diagram of the apparatus as it is currently used is given bellow.



A few changes have been made to the experimental apparatus from the initially proposed design, which are summarized in the following description:

a. Humidification of the air stream at the desired relative humidity has been achieved by passing the clean, dried air through a large chamber (~100 Liters) which has inside a small humidifier unit. The humidifier is controlled by a humidity controller placed outside the chamber which starts the humidifier every time the humidity measured inside the chamber differs more than 3% from the setting. With this system the air stream was humidified at 50 ± 3%, and respectively 85 ± 5% relative humidity.
b. For the injection of liquid compounds into the mixing chamber, a digital syringe pump was purchased allowing the achievement of precise injection rates of the contaminant into the air stream. For ethanol the needle of the syringe was heated to allow continuous, uniform evaporation of the liquid inside the mixing chamber.
c. A new mass flow controller has been also purchased to allow the injection of the gas compounds into the mixing chamber from a pressurized gas cylinder.
d. The simultaneous use of multiple adsorption cells was not entirely successful because small differences in the airflow was observed due to not precisely symmetric geometry of the split, which led to differences in the upstream concentrations. A few adsorption tests were performed using multiple cells, but the majority of the tests were conducted using just a single cell.
e.

As mentioned in the previous reports the activated carbon column was optimally dimensioned using a series of adsorption tests. To choose an optimum diameter, breakthrough curves were obtained for three different column diameters for toluene in air passing through the column at the same linear velocity. Similar curves were obtained for the 2-cm and 3-cm diameter columns, but slightly different for the 4-cm diameter column. We decided to use the 2-cm diameter column for all the adsorption tests. To determine the optimum bed height a number of tests were conducted using toluene, in which the beginning and the end of the breakthrough was plotted against different carbon



bed heights. The mass transfer zone for various challenging concentrations was determined in this way.

A summary of the test conditions used for most of the adsorption experiments is shown in the following paragraph:

Experimental Conditions

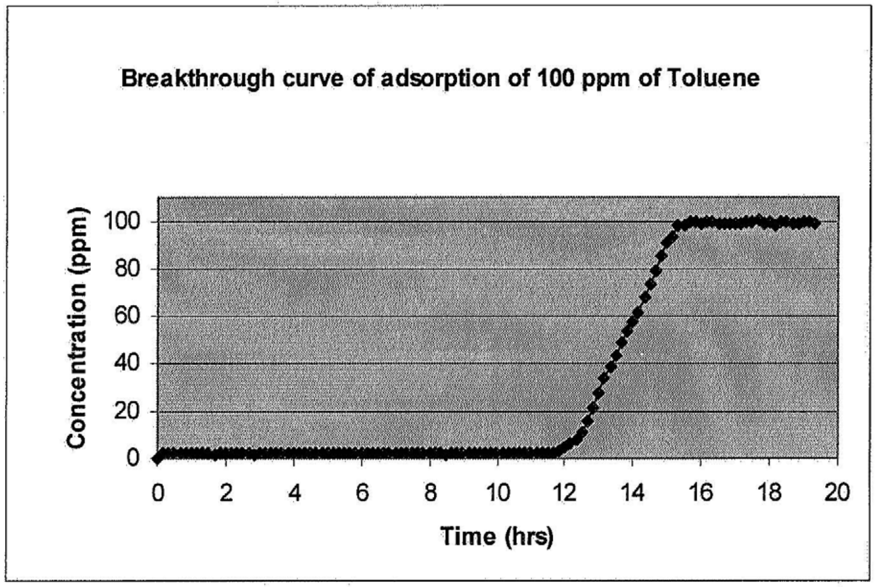
Air Flow Rate = 3 L/min
Carbon bed dimensions:
Diameter = 2 cm;
Depth = 1.8 cm (most tests)
Carbon bed weight = 2 g (most tests);
Linear velocity = 16 cm/s
Test temperature = 23 °C
Relative humidity: 15 % - dry;
50% - normal;
85% - humid

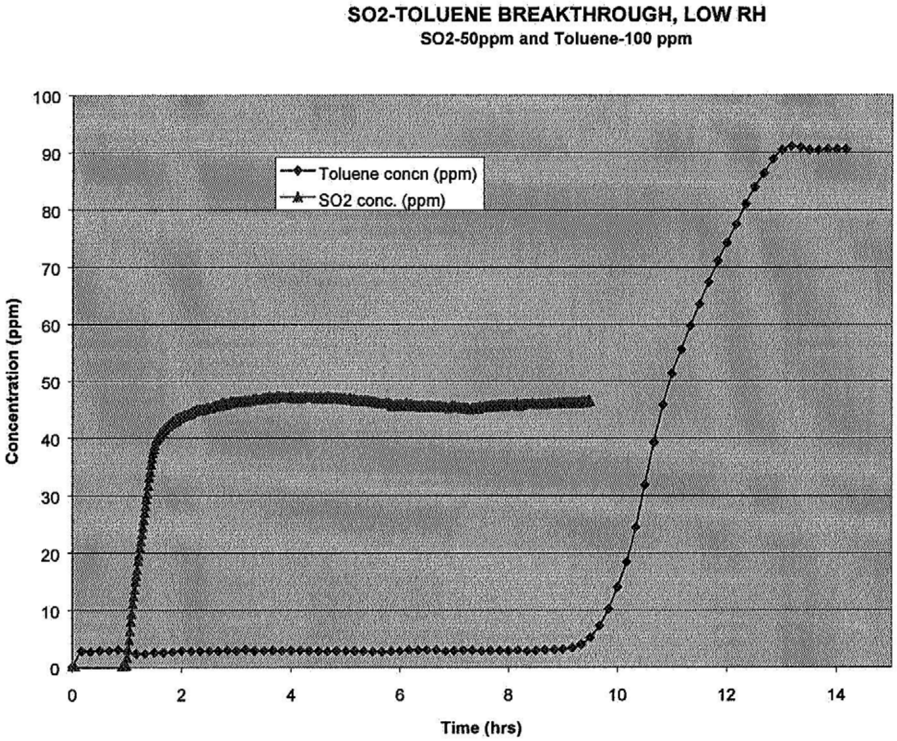
These conditions were similar with those used in the 1980s at the Los Alamos National Laboratory to collect a large number of adsorption data.

Results and Data Analysis

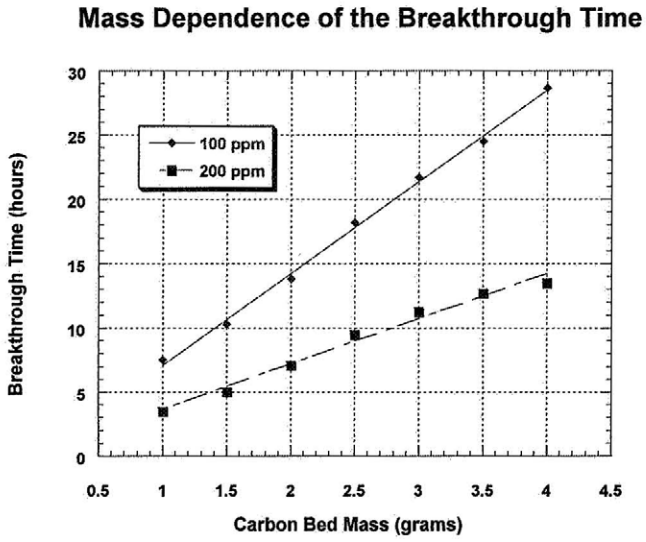
Complete single component adsorption data were obtained for toluene, sulfur dioxide, and ethanol. Adsorption tests for dichloromethane were also obtained but because of calibration problems at high relative humidity these tests were conducted only at low relative humidity. For the simultaneous adsorption configuration, complete binary adsorption data were obtained for toluene - sulfur dioxide mixtures. For ethanol – sulfur dioxide mixtures and toluene-ethanol mixtures complete sets of data were also obtained for all conditions. Breakthrough curves were also obtained for radioactive xenon, but because of difficulties to obtain Xe-133 gas after stricter regulations of radioactive materials were set, the data set for Xenon is not complete. Because there were no relevant differences in the breakthrough data at dry and normal conditions (50% RH) it has been decided that only a limited number of experiments will be conducted at 50% relative humidity. High relative humidity (85 %) showed to have an important effect on the breakthrough for single components as well as for mixtures.

As typical examples for the adsorption data collected, the breakthrough curves for 100 ppm toluene and 100 ppm toluene – 50 ppm sulfur dioxide mixture are shown here.


Breakthrough curve of adsorption of 100 ppm of Toluene
Concentration (ppm)
0
20
40
60
80
100
0
2
4
6
8
10
12
14
16
18
20
Time (hrs)


SO2-TOLUENE BREAKTHROUGH, LOW RH
SO2-50ppm and Toluene-100 ppm
Toluene concn (ppm)
SO2 conc. (ppm)
Concentration (ppm)
0
10
20
30
40
50
60
70
80
90
100
0
2
4
6
8
10
12
14
Time (hrs)

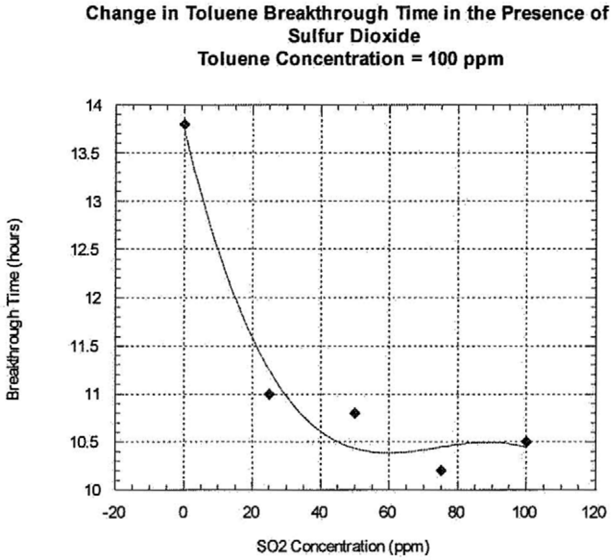
As a result of the literature search and at the suggestion of one of the mentors a change in the experimental protocol and data analysis occurred. Most activated carbon adsorption data in the literature are obtained by producing breakthrough curves at fixed challenging concentrations and variable bed weights. Applying the modified Wheeler equation this method gives the equilibrium adsorption capacity. This parameter is used then to produce adsorption isotherms based on the Dubinin-Radushkevich model. However, a disadvantage of this method is that it does not characterize the behavior of the adsorption bed for various challenging concentrations. It has been decided that at each challenging concentration a few tests to be conducted for variable bed weights, so that the equilibrium bed capacity would be determined for each challenging concentration. This addition obviously increases the number of tests to be conducted, but it is considered essential for obtaining data to be used in the modeling of binary component adsorption. A typical plot of the breakthrough time versus bed capacity is given below for two challenging concentrations. The linearity of these plots shows that the application of the modified Wheeler equation can precisely determine the equilibrium adsorption capacity.


Mass Dependence of the Breakthrough Time

Both for single components and for mixtures the following parameters were obtained from the breakthrough curves:

a. The stoichiometric breakthrough time – represents the breakthrough time when 50% of the challenging concentration is achieved.
b. The bed capacity (loading) - represents the total mass of the adsorbed contaminant when 100% breakthrough is achieved.
c. The equilibrium adsorption capacity
d. The mass transfer rate coefficient

One part of the data analysis consists in examining how these parameters change from the condition when a single component is adsorbed versus the binary adsorption. Because the breakthrough time represents the most important safety feature of a respirator cartridge determining its service life, the modification of the breakthrough time was examined carefully for each condition. The following figure represents the decrease in the stoichiometric breakthrough time for the adsorption of toluene when various concentrations of sulfur dioxide are co-adsorbed. The toluene challenging concentration was 100 ppm and these data were taken under dry condition. Similar plots were obtained for various other combinations of gas-vapor mixtures. Predicting quantitatively the decrease in the breakthrough time when another compound is adsorbed was the main task of the next year of this project.

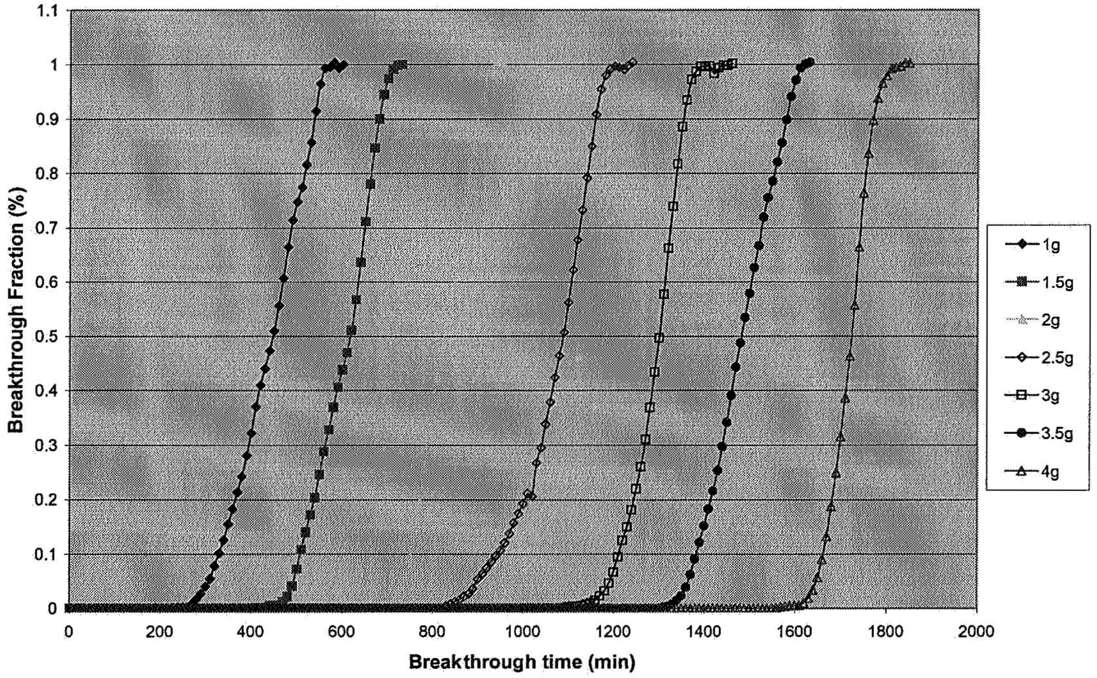


Toluene adsorption

A typical family of breakthrough curves for low RH toluene at a concentration of 100 ppm and an activated carbon bed weight between 1g and 4 g is shown bellow. The curves are plotted with breakthrough time as abscissa and breakthrough fraction as ordinate. These curves show a consistent "S"-shaped pattern with increasing activated carbon bed weight.

Breakthrough adsorption experiments at low concentration for estimating the life of respiratory cartridges take long time. As an optimization measure, adsorption capacity calculations are typically carried out at 10% of breakthrough time. In this study, adsorption capacity was calculated using three different approaches using the Modified Wheeler Equation to check for the consistency of results using each approach. The modified Wheeler equation is shown below:

Figure 5: Breakthrough Curves for Low RH Toluene at 100 ppm concentration



$$t_b = \left(\frac{W_e W}{C_0 Q}\right) - \left(\frac{W_e \rho_b}{K_v C_0}\right)\ln\left[\frac{(C_0 - C_x)}{C_x}\right]$$

where: t_b = breakthrough time (min) at selected penetration fraction

W_e = adsorption capacity (g /g of activated carbon)

W = weight of activated carbon (g)

C_0 = challenge concentration of vapor or gas (g/cm^3)

C_x = effluent concentration of gas or vapor (g/cm^3)

Q = Volumetric flow rate (cm^3/min)
k_v = overall adsorption rate coefficient (min^{-1})
ρ_b = bulk density of activated carbon bed (g/cm^3)

a) Plotting 10% breakthrough time t_b (min) versus varied activated carbon bed weight W (g) at fixed breakthrough fraction C_x/C_0 and applying the Modified Wheeler Equation (Varied bed mass method).

b) Plotting $\ln[(C_0 - C_x)/C_x]$ versus breakthrough time t_b (min) for varying C_x/C_0 using a single breakthrough curve at a fixed bed weight and contaminant concentration, and applying the Modified Wheeler Equation. The breakthrough fraction ranges were chosen from 10% to 50% (Log Method).

c) Fitting the breakthrough curve using advanced statistical software (Sigma Plot) and applying the Modified Wheeler Equation.

Adsorption capacities calculated by the above mentioned approaches are described below

Adsorption Capacity of Toluene

Concentration (ppm)	Adsorption Capacity (mg/g)		
	Varied mass	Log Method	Curve fitting
46.0	338.9	276.2	290.8
98.0	492.5	471.9	487.0
150.0	554.6	349.5	399.3
193.0	561.5	448.2	469.8

Adsorption capacities estimated using the varied bed mass method could be more accurate because they are based only on the 10% breakthrough time assuming a perfect sigmoid curve. Further, at 10% breakthrough times, resistance to the contaminant while it travels through the mass transfer zone is not considered. In the log method, adsorption capacity varies depending on the shape of breakthrough curve. The results obtained matche with the previous theory proposed by Wood that the error margin in estimating adsorption capacity increases at higher concentrations when using the log method.

The third approach of fitting the breakthrough curve using a statistical software is better than the log method as it takes into account the complete breakthrough pattern and also minimizes errors in estimating breakthrough times manually.

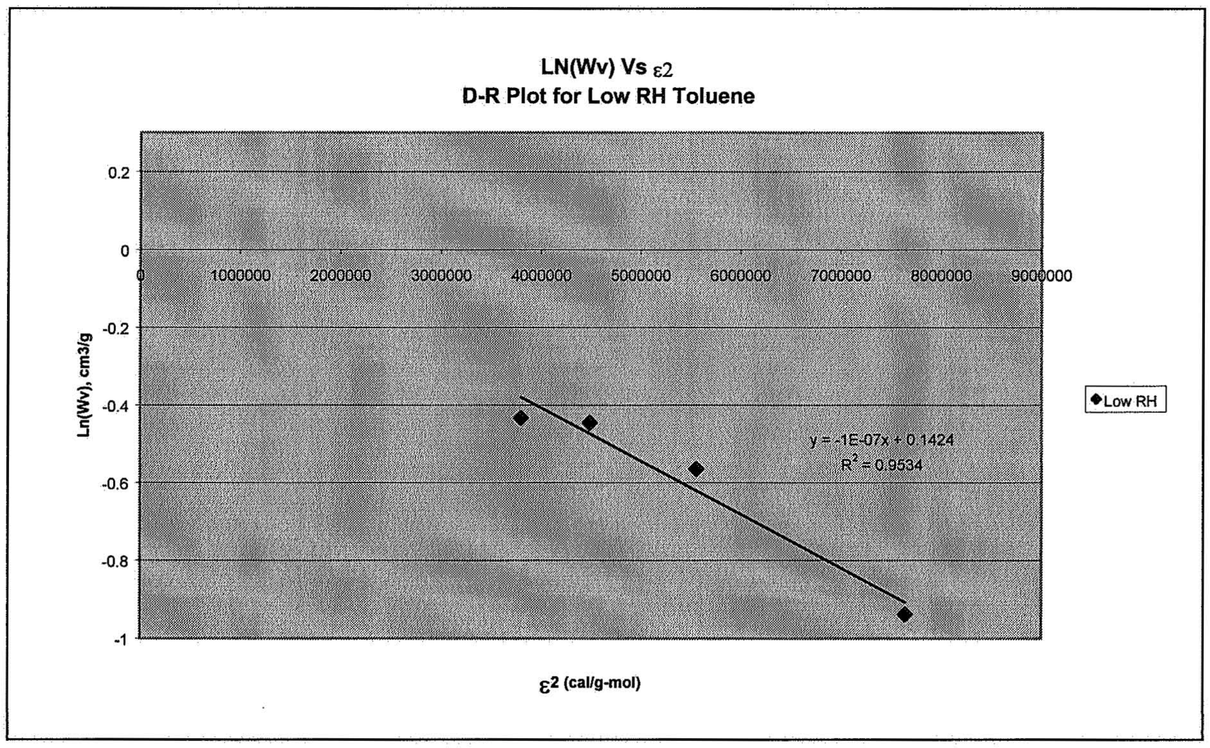
The adsorption capacities obtained from the varied bed mass method were used to estimate the pore volume, W_0 and structural constant, k, using the Dubinin-Radushkevich (D-R) equation:

$$LnW_v = LnW_0 - k\left(\frac{\varepsilon^2}{\beta^2}\right)$$

where: W_v = adsorption capacity (g /g of activated carbon)
W_0 = micropore volume (cm^3/g)
ε = Polanyi adsorption potential (cal/g-mol)
β = Affinity Coefficient
k = Structural constant

Adsorption potential was calculated as described by the Polanyi equation (equation 4), using the relative vapor pressure as defined by the partial pressure (P) and saturation pressure (P_s) of the vapor (toluene).

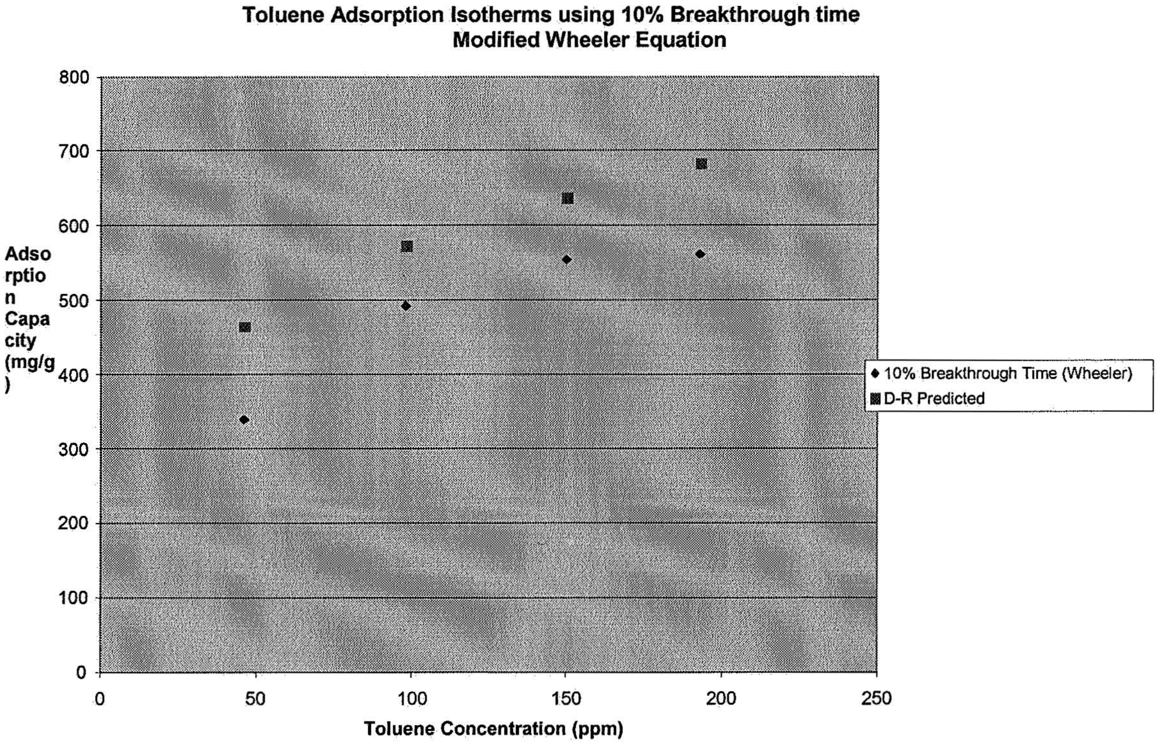
Saturation pressure of toluene at the different experimental concentration was calculated by the Antoine equation. The volume of toluene adsorbed onto activated carbon, W_v (cm^3/g) at various concentrations was estimated using the adsorption capacity calculated by the modified wheeler equation. The affinity coefficient for toluene (β) was taken as 1 with reference to benzene vapor. Characteristic curves obtained by plotting Ln (W_v) versus ε^2 and the corresponding regression lines are shown. The slope of this line is –k, the structural constant, and the ln (W_v) axis intercept is ln(W_0). From this Y-intercept, W_0, the maximum adsorption space of activated carbon for toluene was calculated.



D-R parameters

Wo	**1.153038**	**cm3/g**
K	**1.00E-07**	

Adsorption capacity for toluene at various concentrations was re-estimated using the D-R parameters, W_0 and k.

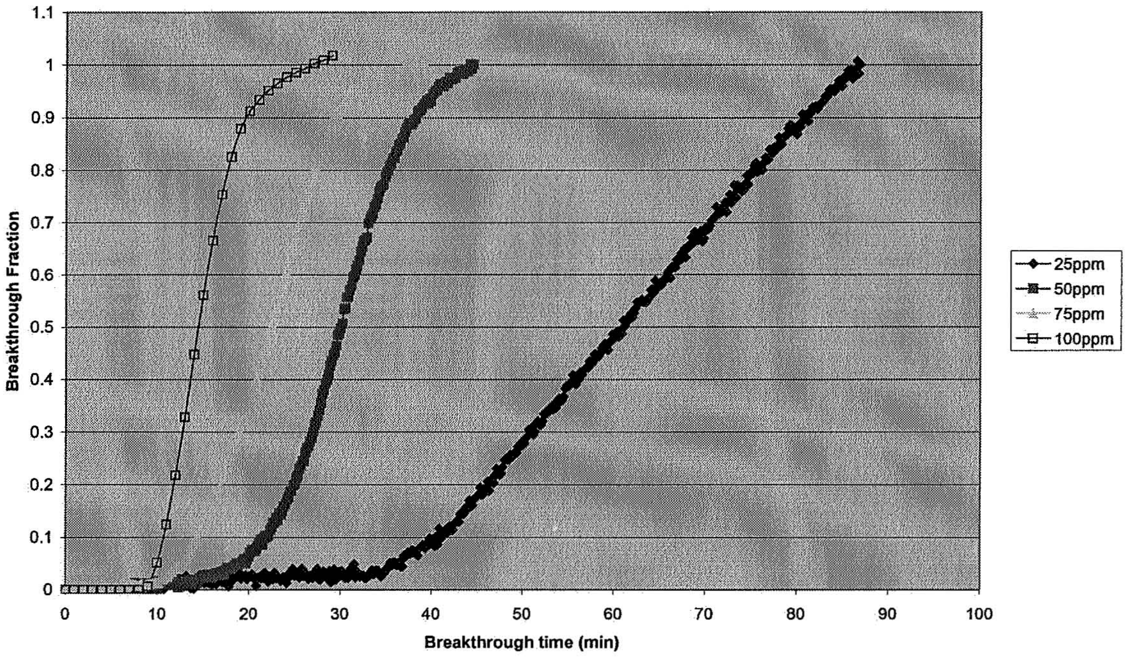


The predicted D-R isotherms have higher adsorption capacities as the D-R parameters were estimated from the best fit of the experimental adsorption capacities ($R^2 = 95.34\%$). Re-fitting the experimental data minimizes errors between various data points. The comparison shows that both the experimental and predicted adsorption isotherms curves depresses at higher concentrations, indicating that the activated carbon has reached a saturation adsorption capacity. The negative curvatures of the isotherms indicate that the doubling of vapor concentration decreases the breakthrough time less than half. According to the Modified Wheeler Equation, breakthrough time t_b is proportional to W_e/C_0. This explains the increase in W_e with concentrations though t_b decreases faster than $1/C_0$. The adsorption capacities for toluene and other similar organic vapors found in the literature varied from those obtained from this research. Differences in adsorption capacities obtained could be attributed to differences in experimental conditions, type of adsorbent used and contaminant concentrations.

Sulfur Dioxide Adsorption

A typical family of breakthrough curves for low RH Sulfur dioxide at an activated carbon bed weight of 1g and at varied SO_2 concentrations is shown bellow. The curves are plotted with breakthrough time as abscissa and breakthrough fraction as ordinate. These curves are asymmetrical at lower concentrations but move closer to "S"-shaped pattern at higher concentrations

Figure 9: Breakthrough curves for Sulfur dioxide at different concentrations
Activated Carbon Bed Weight - 1g



Adsorption capacity of sulfur dioxide was estimated varied bed mass method of the Modified Wheeler Equation at 10% breakthrough times. Lodewyckx and Verhoeven have applied the modified Wheeler successfully to estimate the adsorption capacity of an inorganic compound like chlorine. Adsorption capacities of SO_2 calculated by the modified Wheeler equation are listed. D-R parameters were estimated as described earlier. β was taken as 1 with reference to Nitrogen. D-R parameters for single component SO_2 are also listed.

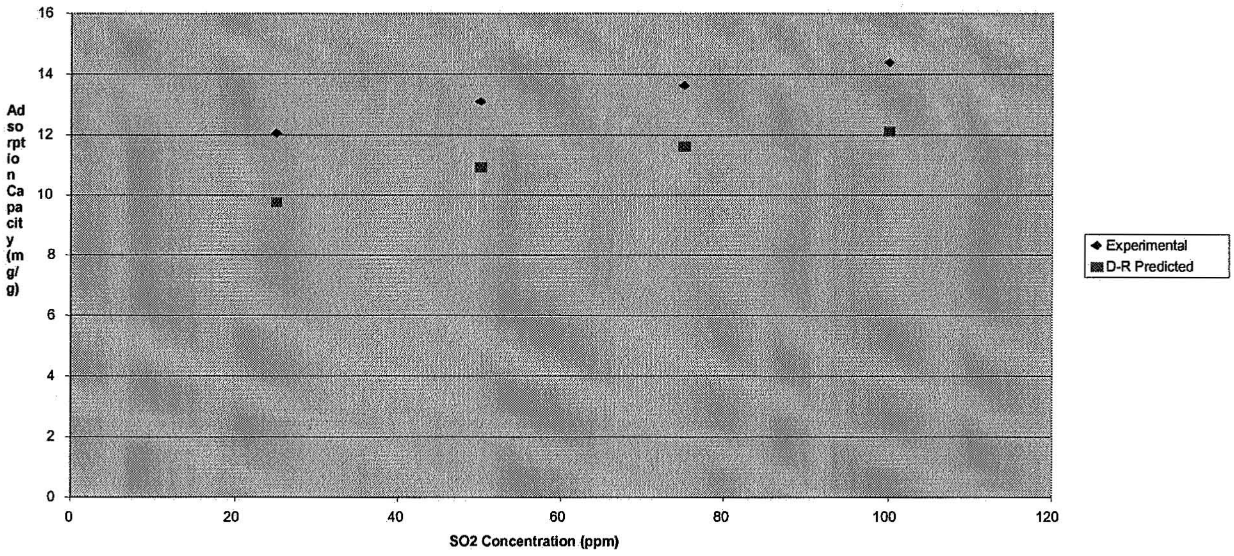
Adsorption Capacity of SO_2

SO_2 Concn. (ppm)	Adsorption Capacity (mg/g)
25	12.043
50	13.098
75	13.629
100	14.374

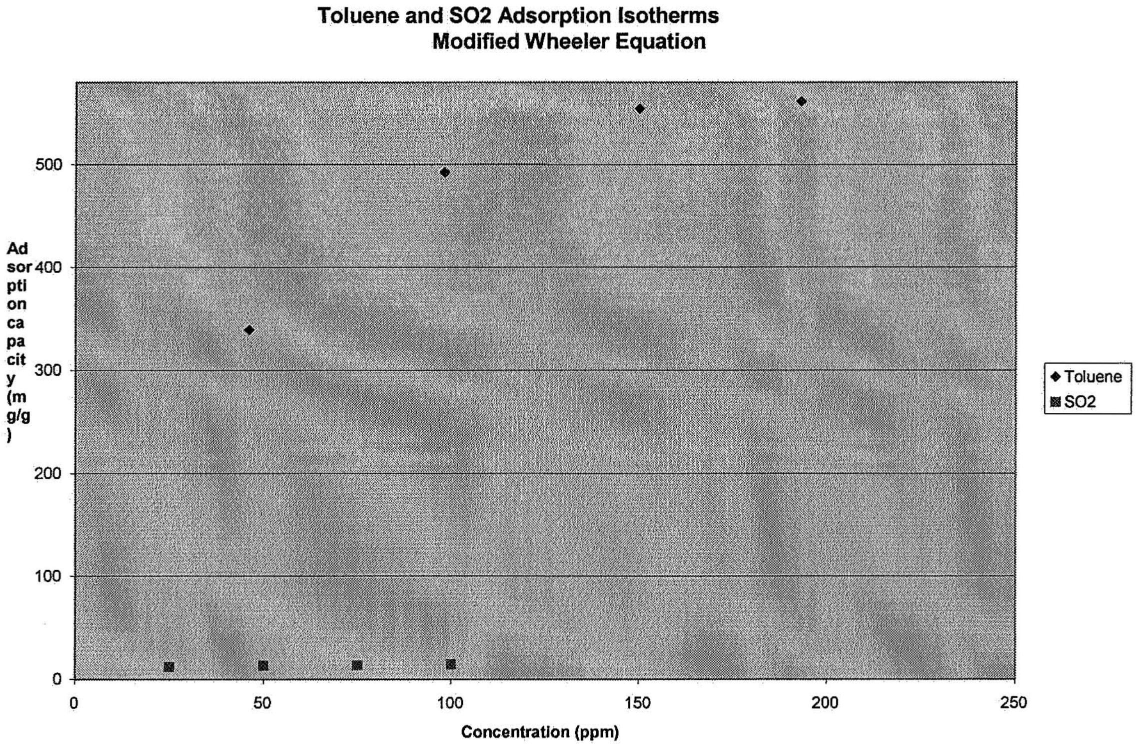
D-R parameters for SO_2

Wo	**0.01915484**	**cm3/g**
K	**2.00E-08**	

SO2 Adsorption Isotherm (10% breakthrough time)
Modified Wheeler Equation

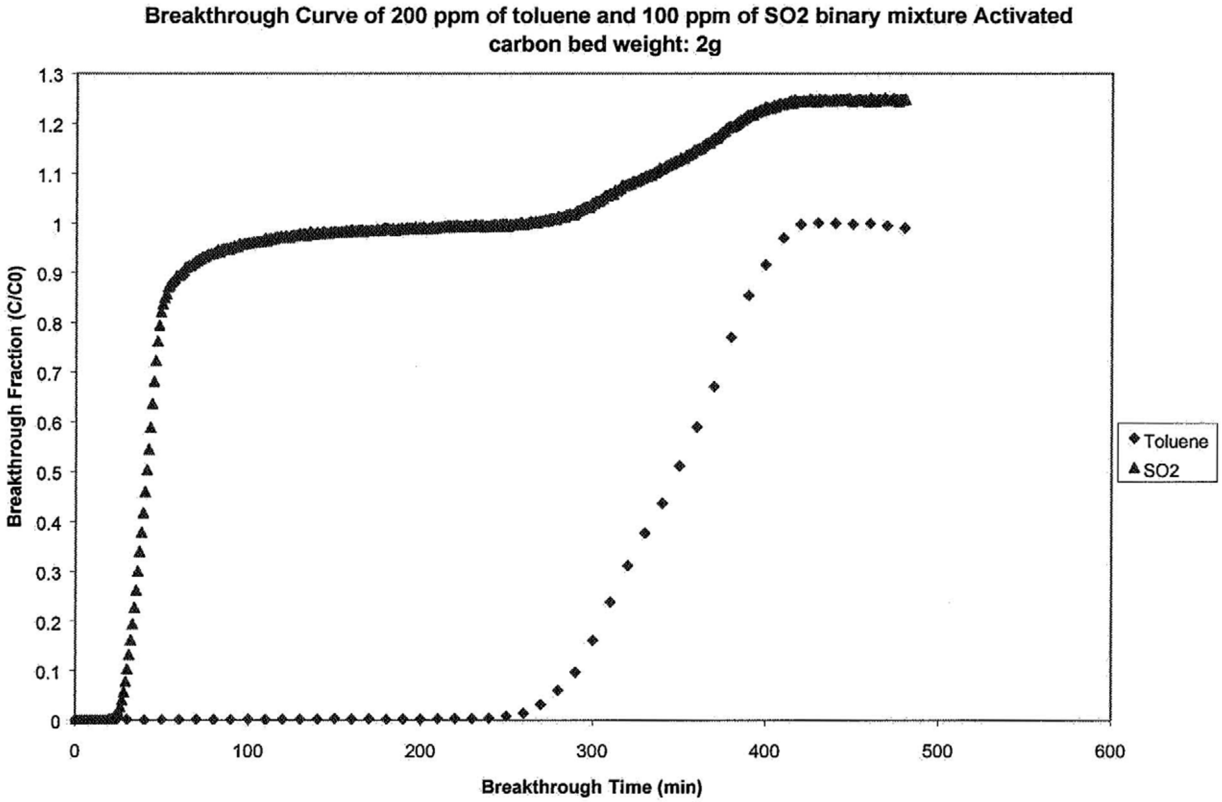


The above figure shows a plot experimental isotherms calculated using the modified Wheeler equation and predicted isotherms estimated using the D-R parameters, W_0 and k. The predicted D-R isotherm is more accurate than the experimental adsorption isotherm as discussed earlier. The isotherms show that this activated carbon has a low affinity for SO_2 gas. That is, adsorption capacities are lower at higher concentrations indicating the low saturation capacity of this activated carbon for SO_2 as compared to toluene. These adsorption capacities are also lower compared to that in the literature. This is because the reported results were obtained at concentrations higher than experimental concentrations used in this study. However, the results obtained by C. Martin et al., who conducted their SO_2 adsorption experiments at a concentration range of 2.5 to 100 ppm closely matches with those obtained in this research. The adsorption capacities for SO_2 ranged from 0.5 mg/g to 9.5 mg/g for their experimental range of concentrations. Though they used different type of activated charcoal in their experiments, the affinity of SO_2 gas to both these carbons show similarity. Comparison of SO_2 and toluene adsorption isotherms is graphically described in the figure below. Adsorption capacity of activated carbon for toluene is more than 20 times higher as compared to SO_2. That is, toluene will take a longer time to breakthrough this activated carbon compared to SO_2. These results are significant in terms of respiratory protection.

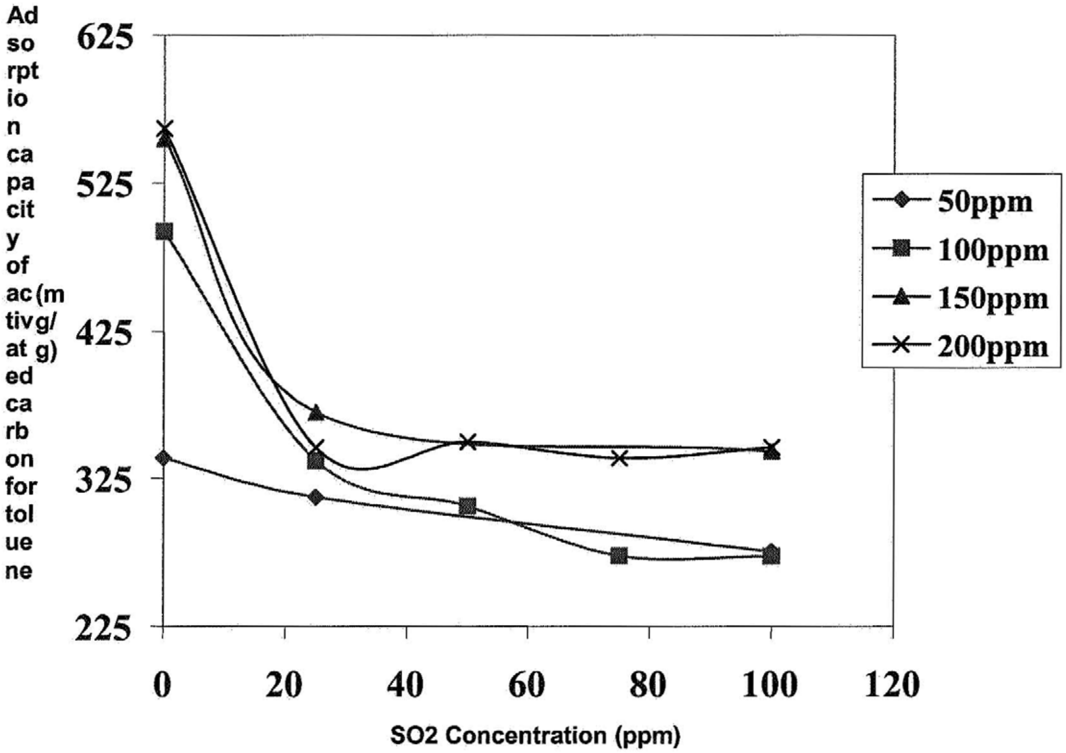


Adsorption of Binary Mixture of SO_2 and Toluene

Breakthrough curves of 200 ppm SO_2 and 100 ppm toluene at 2g activated carbon weight are shown in the figure bellow. The curves are plotted with breakthrough time as abscissa and breakthrough fraction as ordinate. The breakthrough curve, however, does not have the similar shape as that of other organic vapor binary mixtures. In this plot, it is clearly evident that SO_2 is the weakly adsorbed component (first to breakthrough) and toluene is the strongly adsorbed. There is an increase in SO_2 concentration when toluene starts to breakthrough. Once toluene breaks through completely, both components seem to have attained equilibrium and continue to maintain their final saturation concentrations.



Adsorption capacity of both toluene and SO_2 was estimated using modified Wheeler equation. Plots showing the effect of SO2 adsorption on the adsorption capacity of toluene are shown bellow. The percent change in adsorption capacity of toluene due to the presence of SO_2 is also shown.



Effect of Sulfur dioxide Adsorption on the Adsorption Capacity for Toluene
Activated Carbon Weight -2g, Varied Toluene Concentrations

Adsorption Capacity for Toluene in SO_2-Toluene Mixtures

Toluene (ppm)	SO2 (ppm)	We (mg/g) for toluene in SO_2-Toluene mixtures	Percent decrease in W_e for pure toluene
50	25	312.196	8.55%
50	100	275.285	23.11%
100	25	336.683	46.27%
100	50	306.05	60.91%
100	75	272.637	80.63%
150	25	369.606	50.05%
150	100	343.024	61.68%
200	25	345.5	62.52%
200	50	349.463	60.68%
200	75	338.36	65.95%
200	100	345.805	62.37%

As the data indicate, adsorption capacity of toluene decreases with the increase in sulfur dioxide concentration. The overall decrease in toluene adsorption capacity ranged from 8.55 % to 80.63% for all experimental combinations of toluene-SO_2.
The decrease in toluene adsorption capacity is higher at higher SO_2 concentrations.

Effect of toluene in the Adsorption capacity of SO_2

Plots showing the effect of SO2 adsorption on the adsorption capacity of toluene are shown bellow. The percent change in the adsorption capacity of toluene due to the presence of SO_2 are shown in Table 8.

Adsorption Capacity for SO_2 in SO_2-Toluene Mixtures

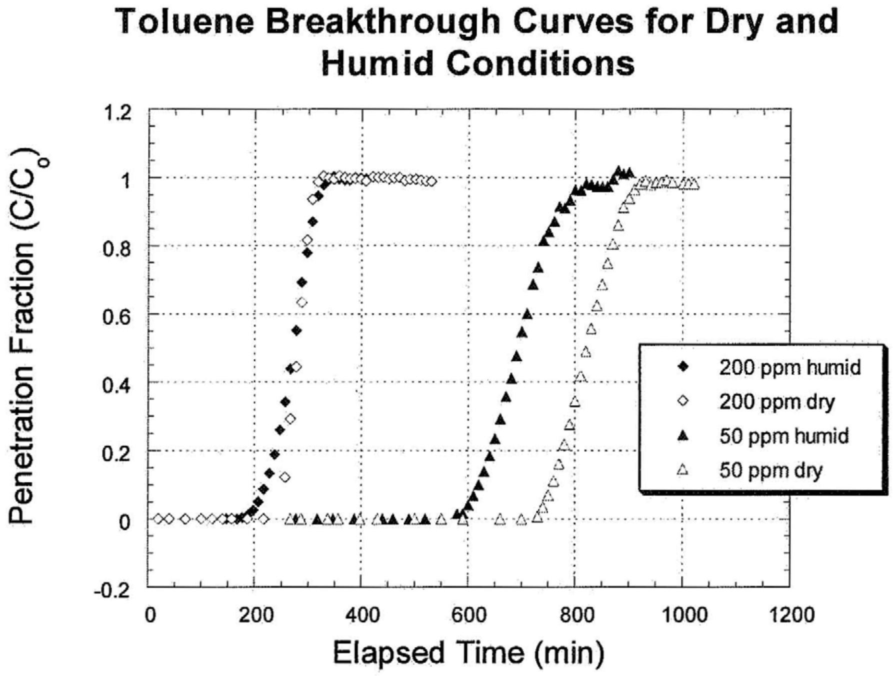
SO2 (ppm)	Toluene (ppm)	We (mg/g) for SO2 in So2-Toluene mixtures	Percent increase in We for Pure SO2
25	100	15.259	52.79%
25	150	8.799	73.42%
25	200	19.05	53.81%
25	250	17.073	11.58%
50	100	15.859	17.41%
50	200	17.535	9.56%
75	100	19.28	29.31%
75	200	17.502	10.16%
100	50	16.305	11.84%
100	100	24.158	32.51%
100	200	23.006	51.57%

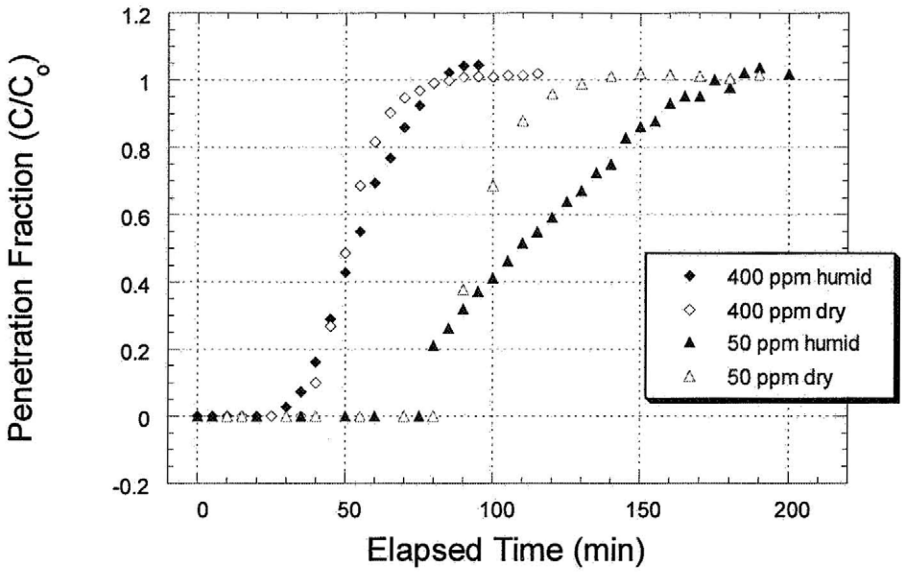
As the data indicate, the adsorption capacity of SO_2 increases with increase in toluene concentration. The overall increase in SO_2 adsorption capacity varied from 9.56 % to 73.42% for all experimental combinations of toluene-SO_2. The changes in SO_2 breakthrough curve pattern, however, tends to prove that the adsorption of toluene-SO_2 binary mixtures on activated carbon are different compared to binary mixtures consisting of organic vapors alone.

Dynamic adsorption experiments were conducted for toluene, SO_2 and SO_2-Toluene mixtures at 50-250 ppm concentration ranges for toluene and 25-100 ppm concentration ranges for SO_2. Adsorption capacity of all the experiments was estimated from breakthrough times using modified Wheeler equation. Adsorption capacity of toluene was estimated by three different approaches using the modified Wheeler equation. It was found that the varied bed mass method using 10% breakthrough time gave more accurate results compared to log method or curve fitting. The former method assumes a perfect sigmoid breakthrough curve while the latter two approaches depend on the shape of the breakthrough curve. It was found that the adsorption capacity of toluene was 20 times higher than sulfur dioxide. Toluene adsorption capacities of the experimental concentrations ranged from 330 – 560 mg/g while SO_2 adsorption capacities ranged from 12-15 mg/g. Breakthrough curves of binary mixtures of toluene and SO_2 is different from that of organic vapor mixtures. The concentration of weakly adsorbed SO_2 increases during toluene breakthrough and attains equilibrium with toluene. Investigating the adsorption capacities of binary mixtures showed that the adsorption capacity of toluene decreases with increase in SO_2 concentration. The same reverse phenomenon was observed when looking at the adsorption capacity of SO_2. Adsorption capacity of SO_2 increased in the presence of toluene. The results are still inconclusive because of low affinity of this activated carbon for SO_2. Further study is needed with different types of impregnated activated carbon to conclude these results.

Humidity influence on Toluene and Ethanol adsorption

Breakthrough curves for toluene and ethanol under dry and humid conditions were obtained. The influence of humidity on the breakthrough curves for a few particular challenging concentrations is shown in the next two plots.





Ethanol Breakthrough Curves for Dry and Humid Conditions

The adsorption capacity for each individual case was determined by fitting the breakthrough curve with the Wheeler equation. The influence of the humidity on the breakthrough capacity is shown in the next table:

Experimental adsorption capacities for toluene and ethanol

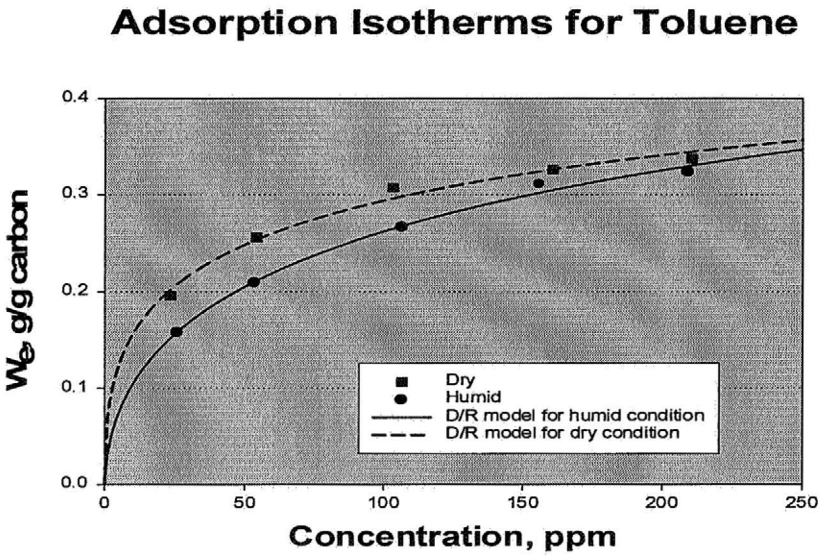
Toluene

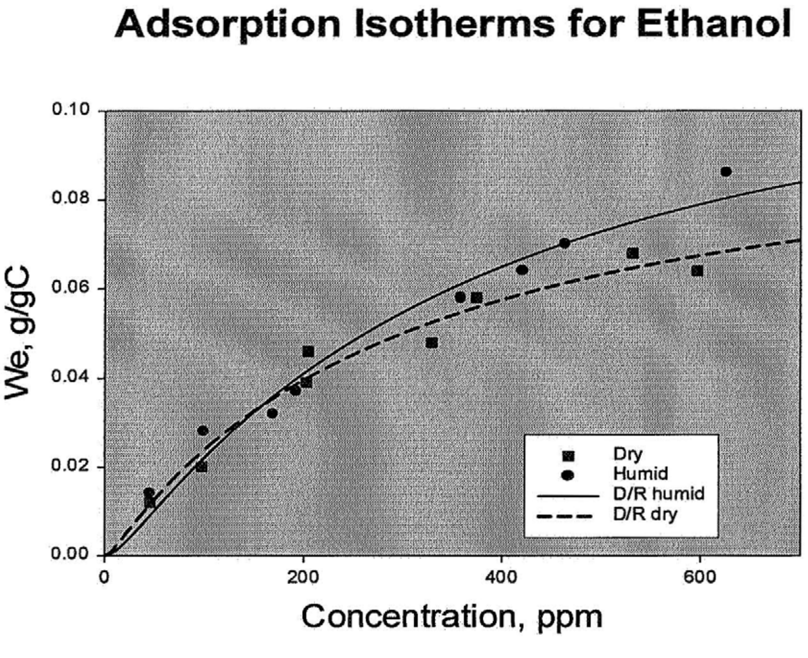
Nominal Conc. ppm	W_e dry mg g^{-1}	W_e humid mg g^{-1}	% Difference
25	196	158	24.05
50	256	209	29.75
100	307	262	28.48
150	326	311	9.50
200	337	323	8.86

Ethanol

Nominal Conc. ppm	W_e dry mg g^{-1}	W_e humid mg g^{-1}	% Difference
45	12	14	-16.7
100	20	28	-40
200	43	35	18.8
360	53	61	-15.1
550	66	78	-18.2

The influence of the relative humidity on the adsorption isotherms for both ethanol and toluene is shown bellow:

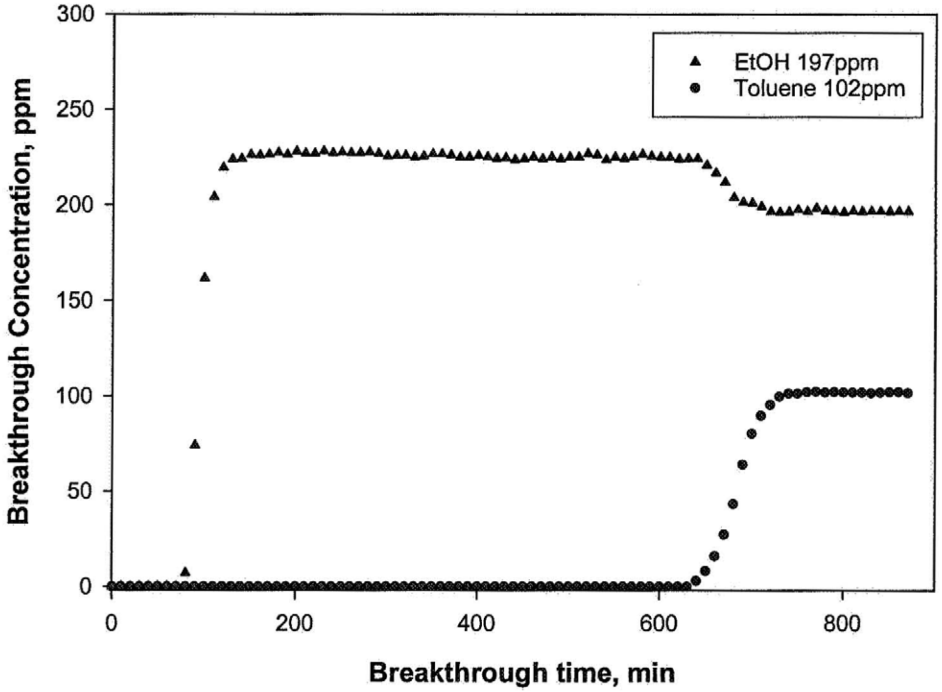

Adsorption Isotherms for Toluene

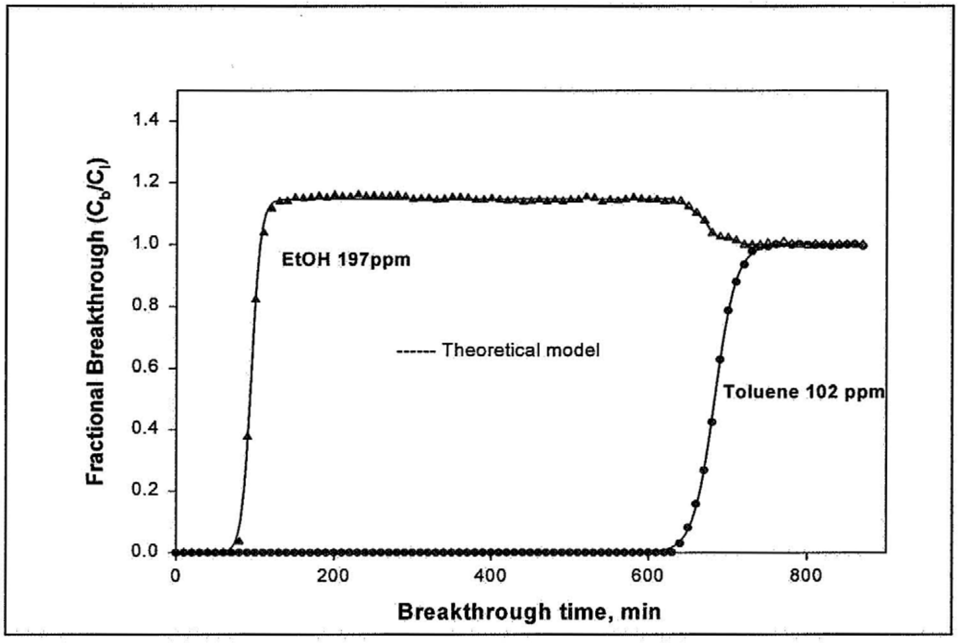

Adsorption Isotherms for Ethanol

The conclusion of the relative humidity influence on the adsorption capacity for toluene and ethanol is that humidity interferes with the adsorption in both cases. However, it has opposite effects: inhibits the adsorption of toluene on activated carbon and enhances the adsorption of ethanol. This latest effect could be explained by the fact that ethanol is adsorbed also on the water droplets resulting from the condensation of water inside the pores of the charcoal. Additional adsorption surfaces are created, enhancing the adsorption. As expected in the case of non-polar toluene, water vapors occupy the micropore volume inhibiting the adsorption onto activated carbon.

Toluene-Ethanol binary mixtures

For the toluene-ethanol mixture a large number of tests were conducted for various combinations of the mixture. Results are shown here for a fixed toluene challenging concentration: 100 ppm and variable ethanol concentration: 200, 400, and 550 ppm, as well as for a fixed ethanol concentration: 200 ppm and variable toluene concentration: 100, 150, and 200 ppm. The Yoon –Nelson model was used to determine the adsorption parameters in the mixture adsorption.





The lines in the above figure represent the breakthrough concentration obtained by applying this model. The parameters given by the model are expressed in the following table.

Experimental parameters in binary systems

Conc.(ppm)		Toluene				Ethanol	
Toluene	Ethanol	W_e (g/gC)	k' (min^{-1})	k	τ(min)	W_{e1}*	W_{e2}**
102	200	0.342	0.032	18.7	587	0.042	0.010
103	415	0.333	0.058	32.8	520	0.080	0.058
103	537	0.337	0.037	20.8	570	0.101	0.085
149	197	0.353	0.033	13.1	411	0.037	0.002
206	192	0.385	0.056	18.2	325	0.035	0.009

*: maximum adsorption capacity for region 1, g/gC)
** : final adsorption capacity for region 2, g/gC).