Theoretical Physics

Analysis of respiratory filters by the Wheeler-Jonas equation

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Abstract

Within the Swedish Armed Forces different types of filters are used in respirators, vehicles and naval ships to protect against chemical agents. The filters are to protect against a variety of chemicals. The Swedish armed forces has a need for a predictive model describing breakthrough times through such filters. There are several known models for carbon filtering and the one most used is the Wheeler-Jonas (WJ) equation[3]. In this thesis focus lies on filters made with activated carbon, the kind of filters used in gas masks and especially "skyddsfilter 90". The task is to find a model among the existing models for carbon filtering breakthrough times and determine if it can predict penetration times of different compounds both organic and inorganic in "skyddsfilter 90" and if so suggest such a model. The time of resistance in a filter depends on both the type of chemical, concentration and the rate of flow through the filter. These are some of the parameters used in the WJ equation. The investigation will show that the WJ equation is applicable to most of the chemical agents that is of interest to military use and that it can be used for carbon filters of varying size. However for filters made with different materials further research is needed. The work demonstrates how to use the model correctly, how to test its applicability and when possible calculations based on given data is performed.

(Abstrakt på svenska)

Inom den svenska försvarsmakten används olika typer av filter i gasmasker, fordon och marina fartyg. Dessa filter ska skydda mot olika kemiska ämnen. Den svenska försvarsmakten har ett behov av en matematisk modell som kan prediktera genombrottstiden genom sådana filter. Det finns flera kända sådana modeller för filtrering genom filter gjorda av aktivt kol och den mest använda är Wheeler-Jonas ekvationen (WJ) ekvationen[3]. I denna avhandling ligger fokus på filter gjorda av aktivt kol, den typ av filter som används i gasmasker och speciellt skyddsfilter 90. Uppgiften är att finna en modell bland dessa existerande modeller och avgöra om den kan prediktera genombrottstider för organiska och inorganiska ämnen genom skyddsfilter 90 och i så fall föreslå en sådan modell. Motståndstiden i ett filter beror båda på typ av ämne, koncentration och flödeshastighet genom filtret. Dessa är några av de parametrar som används i WJ ekvationen. Undersökningen kommer visa att WJ ekvationen är applicerbar för att modellera de flesta ämnen som är intressanta i militärt avseende och kan användas för kolfilter av varierande storlek. För filter gjorda av andra material behövs vidare studier. Denna avhandling visar hur man använder modeller korrekt, hur man testar dess applicerbarhet och när det är möjligt görs beräkningar baserade på given data.

Contents

Chapter 1

Introduction

Within the Swedish Armed Forces different types of filters are used in respirators, vehicles and naval ships to protect against chemical agents. The filters are to protect against a variety of chemicals both organic and inorganic. It is very difficult if not impossible to conduct experiments which accounts for every possible environment, compound and type of filter and therefore there is a need for a mathematical model that can predict penetration time through filters. In this thesis the application of such a model called the WJ equation to the Swedish armed forces own respiratory filter "skyddsfilter 90" is investigated. The aim is to find out if it is applicable to the case of both organic and inorganic compounds using readily available parameters that are obtained from a breakthrough test. Such a breakthrough test is provided by Totalforsvarets forskningsinstitut (FOI) (see Tab. 3.2) and it is a measure of breakthrough times through "skyddsfilter 90" for six different compounds at varying concentration. Although lacking data, for example only one or two data points are provided for each compound making a regression analysis difficult, conclusions should be possible to draw from studying the type of compound and previous research[3][5]. It is also desirable to be able to calculate penetration times without experimental data because such an experiment might be expensive or not possible to conduct at the time it is needed. In this thesis theoretical models for estimating the parameters are also investigated. Also a way of testing the applicability of the model for further work with compounds not mentioned in this thesis is explained. Previous research shows that the WJ equation is a model that fits these requirements[5] and hence this is the model of interest in the thesis. It is known that the WJ equation models the adsorption of organic compounds on activated carbon beds[4]. Recently it has been shown to be applicable also in the case of some inorganic compounds[1][2][3]. We are also interested in studying the relationship between breakthrough time and inlet concentration when all other parameters are held constant. Hence a simplified model for this special case is desired and such a model is given by the Nelson-Harder expression[11].

Chapter 2

Background Material

In order to deal with the problem of a predictive model for filter penetration time we need a model for a filter made with activated carbon that uses parameters readily available from data. Such a model is the WJ equation[4]. The WJ equation models physisorption in the case of organic compounds but recently it has been proven to be useful also for some inorganic adsorbents and for chemisorption[1][2].

Some understanding of the processes adsorption, absorption, physisorption and chemisorption is needed to digest this work so a short introduction to these concepts are given here.

Adsorption is a surface based process where the adsorbate creates a layer on the surface of the adsorbent, in this case, the activated carbon[7]. The adsorption process differs from absorption in which the absorbate is dissolved or absorbed by the absorbent. Hence absorption involves the whole volume of the absorbent. Figure 2.1 shows the difference between physisorption and chemisorption where in the first case no bonds in the molecule are broken and in the second case bonds are broken and new ones are formed with the material of the adsorbent.

Physisorption or physical adsorption is the process where the electronic structure of the atom or molecule is not broken upon adsorption[16]. The major force behind physisorption is the van der waals force.

Chemisorption is a process that involves a chemical reaction between the adsorbate and the adsorbent[17]. The process separates atoms in a molecule and those in turn form new bonds with the material of the adsorbent. The major force behind chemisorption is the electrostatic force.

Carbon filtering is a method where a bed of activated carbon is used to filter a variety of chemicals including organic compounds and non organic compounds[6]. Carbon filtering uses the method of adsorption both chemisorption and physisorption. The typical size of particles that can be removed by carbon filters ranges between 0.5-50 μm and this is what makes it such a useful filtering material.

The Swedish Armed Forces own filter "Skyddsfilter 90" is made with activated carbon and this narrows down the search for a predictive model to models describing carbon filtering. The data provided is from a breakthrough test as described in the introduction and a literature study reveals that the best model to consider is the WJ equation[3][5][4][18]. This model has been thoroughly researched and uses readily available parameters.

Chapter 3

Investigation

3.1 Problem

The WJ equation is formulated and its application to "skyddsfilter 90" is discussed. Ways of adapting the WJ equation to filter data is surveyed both for inorganic and organic compounds creating predictive models of the breakthrough times for each compound at varying concentrations only or varying flow rate and filter data. In order to estimate parameters a curve fitting tool is used using the WJ equation as a model and considering each compound at different concentrations.

3.2 Model

The WJ equation is an empirical equation that is derived by observing mass balance between the vapor entering the carbon filter and the sum of the vapor adsorbed and passed through the filter. This model assumes a perfect flow without any turbulence or radial diffusion. This is usually fulfilled for a cylindrical filter with a diameter larger than 2 cm[18]. The adsorption rate constant needs to be of first order with respect to C_{in} which is usually true for values of $C_{\text{out}}/C_{\text{in}} <$ 5-10%[18]. It was developed considering only physisorption onto micro pores. The WJ equation is well known to predict breakthrough times of organic vapor on activated carbon and has been proven valid in many studies. Recently research has shown that its use can be extended to some inorganic vapors[1][2][3].

The WJ equation is:

$$t_{\text{b}} = \frac{W_{\text{e}} W}{C_{\text{in}} Q} - \frac{W_e \rho_{\text{b}}}{k_{\text{v}} C_{\text{in}}} \ln \left[\frac{C_{\text{in}} - C_{\text{out}}}{C_{\text{out}}} \right] \tag{3.1}$$

where t_{b} is the breakthrough time (min), C_{in} is inlet concentration (g/cm^3), C_{out} is breakthrough concentration (g_{carbon}/cm^3), W is the weight of the carbon bed (g), W_{e} is the equilibrium adsorption capacity (g/g_{carbon}), Q is the volumetric flow rate (cm^3/min), ρ_{b} is the bulk density of the carbon bed (g_{carbon}/cm^3) and k_{v} is the overall adsorption rate (min^{-1}).

There are several ways of testing whether the WJ equation is applicable to model a certain compound. The method of choice here is plotting breakthrough time vs relative breakthrough concentration since inlet concentration is the variable. If the WJ equation is applicable this should result in a straight line for low output concentrations.

$$t_{\mathrm{b}} = \mathrm{A} - \mathrm{B}x \tag{3.2}$$

where A and B are constants and

$$x = \ln\left[\frac{C_{\mathrm{in}} - C_{\mathrm{out}}}{C_{\mathrm{out}}}\right] \tag{3.3}$$

This is the easiest method to use when considering one type of filter so that the filter data, height, depth and weight of the filter are held constant. According to Yoon and Nelson[15] the coefficient A = $\mathrm{t}_{0.50}$ which is the breakthrough time when the outlet concentration have reached 50% of the inlet concentration. Some studies have found the WJ equation to be applicable in the case of inorganic compounds such as ammonia[1], chlorine[2], cyanogen chloride, hydrogen sulfide, sulfur dioxide and phosgene[5]. Therefore some of the chemicals in Tab. 3.2 have penetration times that are already known to be predictable by the WJ equation.

The adsorption rate coefficient k_{v} and the equilibrium adsorption capacity W_{e} can be estimated according to existing models, regression calculations or curve fitting using experimental data. Since we are considering one type of filter all the parameters except those considering the kinetics of the flow are held constant. This opens up a possibility of further simplification of the WJ equation because as mentioned above the relationship between inlet concentration and breakthrough time if all other parameters are held constant should be linear for low output concentrations.

Taking a closer look at the existing ways of calculating the adsorption rate coefficient k_{v} and the equilibrium adsorption capacity W_{e} we find that k_{v} can be obtained from the same plot used to test the applicability of the WJ equation. k_{v} is then obtained by calculating the slope of the line[7].

Models to calculate k_{v} has been derived using this method. A model that takes into account the properties of the adsorbate is the following[4]:

$$k_{\mathrm{v}} = \left\{\left[\left(\frac{1}{v_{\mathrm{L}}}\right) + 0.027\right] \cdot \left[0.000825 + \frac{0.063 - 0.0058 \ln\left[\frac{C_{\mathrm{in}} - C_{\mathrm{out}}}{C_{\mathrm{out}}}\right]}{P_{\mathrm{e}}}\right]\right\}^{-1} \tag{3.4}$$

Here v_{L} is the linear velocity through the carbon filter (cm/s) and P_{e} is the molar polarization (cm^3/mol).

The adsorption capacity W_e can be calculated from the expression derived by Dubinin and Radushkevich also called the DR equation[8]. Consider a thermodynamic potential C expressed as:

$$C = RT \ln\left(\frac{P_\mathrm{s}}{P}\right) \tag{3.5}$$

where R is the universal gas constant, T is the absolute temperature, P_s is the saturated vapor pressure at temperature T and P is the partial pressure of the adsorbate. Dubinin hypothesized that the amount of vapor adsorbed is a function of this thermodynamic potential C. Empirical investigation using organic compounds yielded the conclusion that the function was a Gaussian of the form:

$$W_\mathrm{e} = W_0 \cdot \exp\left[-\left(\frac{C}{E_0\beta}\right)^2\right] \tag{3.6}$$

where W_0 is the maximum amount of vapor adsorbed and E_0 is the characteristic adsorption energy for a reference vapor and β is called the affinity coefficient and is the ratio of the characteristic free energies of adsorption for the reference vapors. Benzene is by convention used as a reference vapor for activated carbon filters and has the affinity coefficient $\beta = 1$ [4].

Because the parameters W_e and k_v are not known beforehand they need to be estimated by fitting the WJ equation to a linear equation of the form 3.2 using data from a breakthrough test where only the inlet concentration is varied. But equations 3.4 and 3.6 opens up the possibility to theoretically estimate these parameters for different compounds without experimental data needed. Values of β and P_e can be found in tables[9].

3.3 Analytical Calculations

The above formulas gives us the possibility to obtain estimates for the penetration times without making experimental measurements.

First method: An empirical way of estimating the parameters W_e and k_v is done by using data from a breakthrough test in this case the data given in Tab. 3.2 for "skyddsfilter 90". All of the filter parameters are held constant because we are considering one filter and one compound at a time at constant flow rate. This means that we can write the WJ equation as follows:

$$t_\mathrm{b} = \mathrm{A} - \mathrm{B}\ln\left[\frac{C_\mathrm{in} - C_\mathrm{out}}{C_\mathrm{out}}\right] \tag{3.7}$$

This means that we can estimate coefficients A and B by fitting Eq. 3.7 to the data using linear regression or curve fitting.

At low outlet concentrations it is now possible to calculate the parameters W_e and k_v from the fitted equation according to:

$$\mathrm{A} = \frac{W_\mathrm{e}W}{C_\mathrm{in}Q} \rightarrow W_\mathrm{e} = \frac{C_\mathrm{in}Q\mathrm{A}}{W} \tag{3.8}$$

and

$$\mathrm{B} = \frac{W_\mathrm{e}\rho_\mathrm{b}}{k_\mathrm{v}C_\mathrm{in}} \rightarrow k_\mathrm{v} = \frac{W_\mathrm{e}\rho_\mathrm{b}}{\mathrm{B}C_\mathrm{in}} \tag{3.9}$$

Equations 3.8 and 3.9 yields:

$$\mathrm{B} = \frac{C_\mathrm{in}Q\mathrm{A}\rho_\mathrm{b}}{k_\mathrm{v}C_\mathrm{in}W} = \frac{QA}{k_\mathrm{v}V} \rightarrow k_\mathrm{v} = \frac{Q\mathrm{A}}{\mathrm{B}V} \tag{3.10}$$

Second method: It is desirable to make W_e and k_v independent of C_in so that they take constant values and does not have to be recalculated for each inlet concentration. Another way of estimating these parameters is to plot $t_\mathrm{b} \cdot C_\mathrm{in}$ vs x according to:

$$t_\mathrm{b} \cdot C_\mathrm{in} = \mathrm{A} - \mathrm{B}\ln\left[\frac{C_\mathrm{in} - C_\mathrm{out}}{C_\mathrm{out}}\right] \tag{3.11}$$

$$x = \ln \left[\frac{C_{\text{in}} - C_{\text{out}}}{C_{\text{out}}} \right] \tag{3.12}$$

The parameters are then calculated according to the first method but without the dependence on inlet concentration.

Knowing that A $\approx$ $\mathrm{t}_{0.50}$ we may write the WJ equation on yet another form[30]:

$$\frac{t_{\text{b}}}{t_{0.50}} = 1 - \frac{Q}{k_{\text{v}}V} \ln \left[\frac{C_{\text{in}} - C_{\text{out}}}{C_{\text{out}}} \right] \tag{3.13}$$

but replacing t_{b} with $t_{0.05}$ in equation 3.13 which is the time when $C_{\text{out}} = 0.05C_{\text{in}}$ we obtain:

$$\frac{t_{0.05}}{t_{0.50}} = 1 - \frac{Q}{k_{\text{v}}V} \ln \left[\frac{C_{\text{in}} - 0.05C_{\text{in}}}{0.05C_{\text{in}}} \right] \approx 1 - 2.944\frac{Q}{k_{\text{v}}V} \tag{3.14}$$

and

$$\frac{t_{0.95}}{t_{0.50}} = 1 + \frac{Q}{k_{\text{v}}V} \ln \left[\frac{C_{\text{in}} - 0.05C_{\text{in}}}{0.05C_{\text{in}}} \right] \approx 1 + 2.944\frac{Q}{k_{\text{v}}V} \tag{3.15}$$

Solving for k_{v} we obtain:

$$k_{\text{v}} \approx \frac{2.944Q}{V\left[1 - \frac{t_{0.05}}{t_{0.50}}\right]} \tag{3.16}$$

and

$$k_{\text{v}} \approx \frac{2.944Q}{V\left[\frac{t_{0.95}}{t_{0.50}} - 1\right]} \tag{3.17}$$

Eqs. 3.16 and 3.10 yields:

$$\mathrm{B} = \frac{\mathrm{t}_{0.50} - \mathrm{t}_{0.05}}{2.944} \tag{3.18}$$

And Eqs. 3.17 and 3.10 yields:

$$\mathrm{B} = \frac{\mathrm{t}_{0.95} - \mathrm{t}_{0.50}}{2.944} \tag{3.19}$$

We collect the filter data weight, height and diameter from the FOI memo and some measurements shown in figure 3.1 and 3.2.

Table 3.1: Filter data from FOI and measurement.

weight incl. packaging(g)	height(cm)	diameter(cm)
106.2	1.9	10.5

Figure 3.1: Measurement of height of activated carbon part of Skyddsfilter 90.

Figure 3.2: Measurement of the diameter of skyddsfilter 90.

We calculate the value of ρ_b using this data:

$$\rho_\mathrm{b} = \frac{W}{V} = \frac{106.2}{V} \tag{3.20}$$

$$V = 1.9\pi\left(\frac{10.5}{2}\right)^2 = 164.5213 \tag{3.21}$$

Eqs. 3.20 and 3.21 yields:

$$\rho_\mathrm{b} = \frac{106.2}{164.5213} = 0.6455 \tag{3.22}$$

Varying concentration only

For the special case when the only variable is the concentration there is a simplified model we can use to predict the new penetration time for a certain compound knowing the former penetration time and the former inlet concentration[11]

$$t_2 = t_1\left(\frac{C_1}{C_2}\right)^n \tag{3.23}$$

where t_2 is the new penetration time, t_1 is the former penetration time,, C_2 is the new concentration, C_1 is the former concentration and n is a constant which is to be determined.

Using this we do not need more than two data points to determine n. Hence for cyclohexane the calculations yield (Tab. 3.2):

$$t_2 = t_1\left(\frac{C_1}{C_2}\right)^{0.7280} \tag{3.24}$$

Repeating the procedure for hydrogen cyanide Eq. 3.23 becomes:

$$t_2 = t_1 \left(\frac{C_1}{C_2} \right)^{2.1207} \tag{3.25}$$

and for sulfur dioxide Eq. 3.23 becomes:

$$t_2 = t_1 \left(\frac{C_1}{C_2} \right)^{0.9525} \tag{3.26}$$

3.4 Numerical Analysis

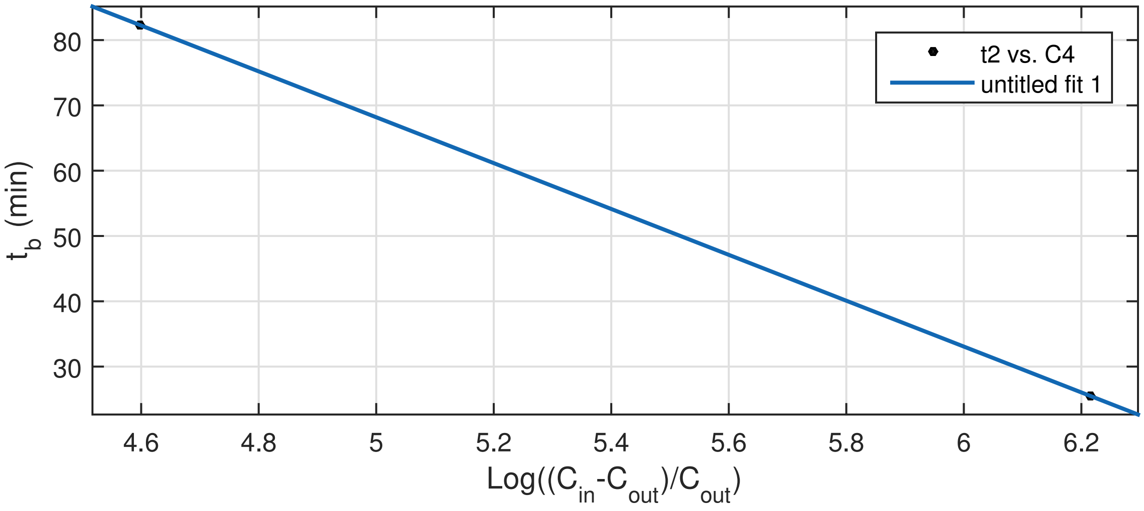
Tab. 3.2 shows the data provided by the Swedish defense forces and is taken directly from a report by FOI, Totalforsvarets forskningsinstitut[19]. The measurements have been carried out on 1-3 different filters for each chemical agent and each inlet concentration. Hence the penetration times presented in the table below is the average of the measured penetration times.

Table 3.2: Penetration times for different compounds at different concentrations and constant flow rate by FOI.

compound	Q (cm^3/min)	C_{in} (g/cm^3)	C_{out} (ppm)	C_{out}(g/cm^3)	t_{b} (min)
cyclohexane	$30 \cdot 10^3$	$3.5 \cdot 10^{-6}$	10	$3.49 \cdot 10^{-8}$	82.3
cyclohexane	$30 \cdot 10^3$	$17.5 \cdot 10^{-6}$	10	$3.49 \cdot 10^{-8}$	25.5
chlorine	$30 \cdot 10^3$	$3.0 \cdot 10^{-8}$	0.5	$1.47 \cdot 10^{-8}$	>60
chlorine	$30 \cdot 10^3$	$15.0 \cdot 10^{-6}$	0.5	$1.47 \cdot 10^{-8}$	12
hydrogen sulfide	$30 \cdot 10^3$	$1.4 \cdot 10^{-6}$	10	$1.41 \cdot 10^{-8}$	>90
hydrogen cyanide	$30 \cdot 10^3$	$5.6 \cdot 10^{-6}$	10	$1.12 \cdot 10^{-8}$	17.3
hydrogen cyanide	$30 \cdot 10^3$	$5.0 \cdot 10^{-6}$	10	$1.12 \cdot 10^{-8}$	22
sulfur dioxide	$30 \cdot 10^3$	$2.7 \cdot 10^{-6}$	5	$2.66 \cdot 10^{-8}$	48
sulfur dioxide	$30 \cdot 10^3$	$13.3 \cdot 10^{-6}$	5	$2.66 \cdot 10^{-8}$	9
ammonia	$30 \cdot 10^3$	$0.7 \cdot 10^{-6}$	25	$0.71 \cdot 10^{-8}$	7.7

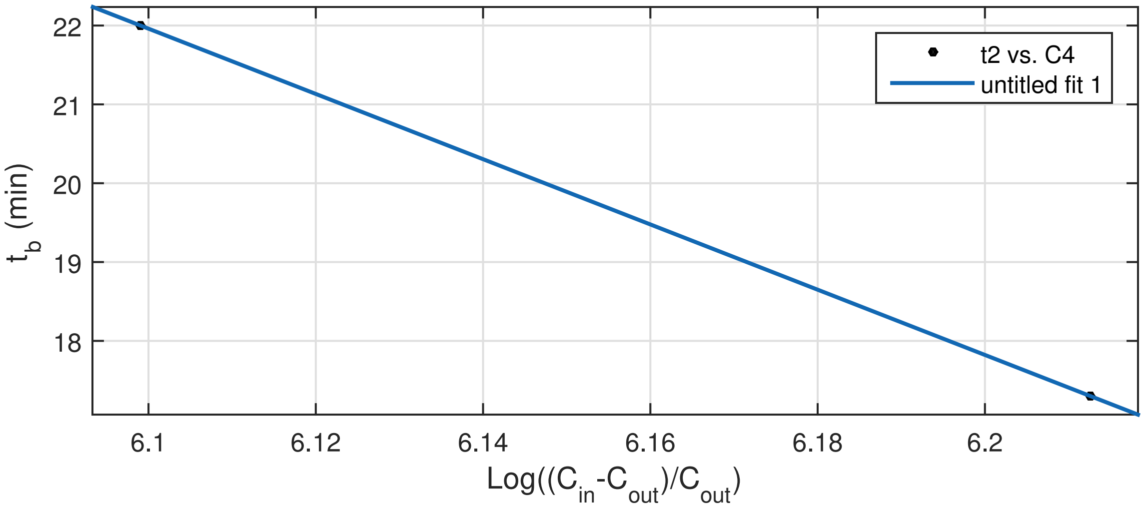
Using the first method figures 3.3, 3.4 and 3.5 shows the breakthrough time for varying inlet concentration. The data points are experimental values taken from Tab. 3.2. The line is a fit to Eq. 3.7 and was computed numerically using a curve fitting tool.

Figure 3.3: Fitted curve for cyclohexane.



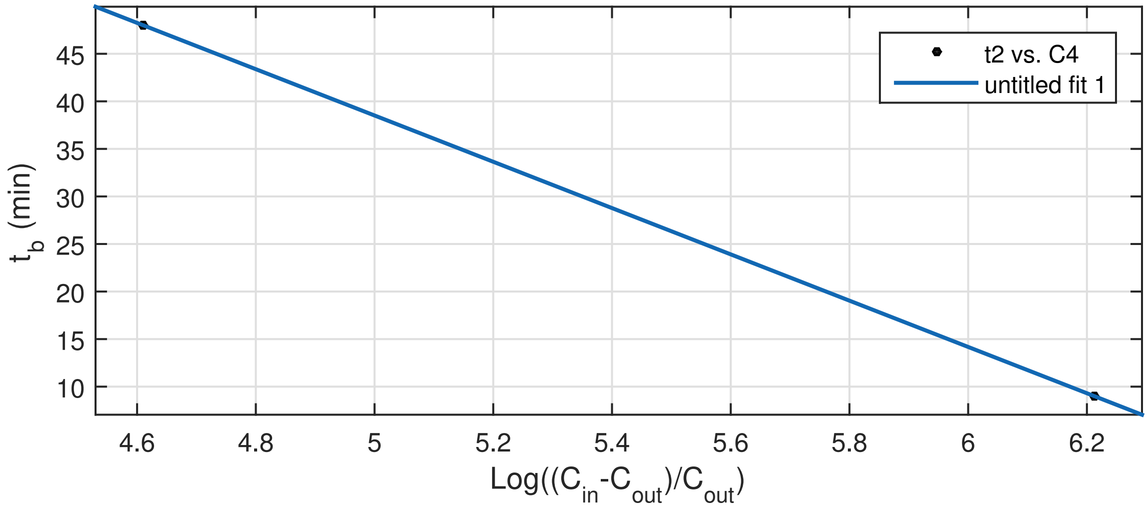
Linear model Poly1: f(x) = A - Bx Coefficients: B = 35.12 A = 243.8

Figure 3.4: Fitted curve for hydrogen cyanide.



Linear model Poly1: f(x) = A + Bx Coefficients: B = 41.38 A = 274.4

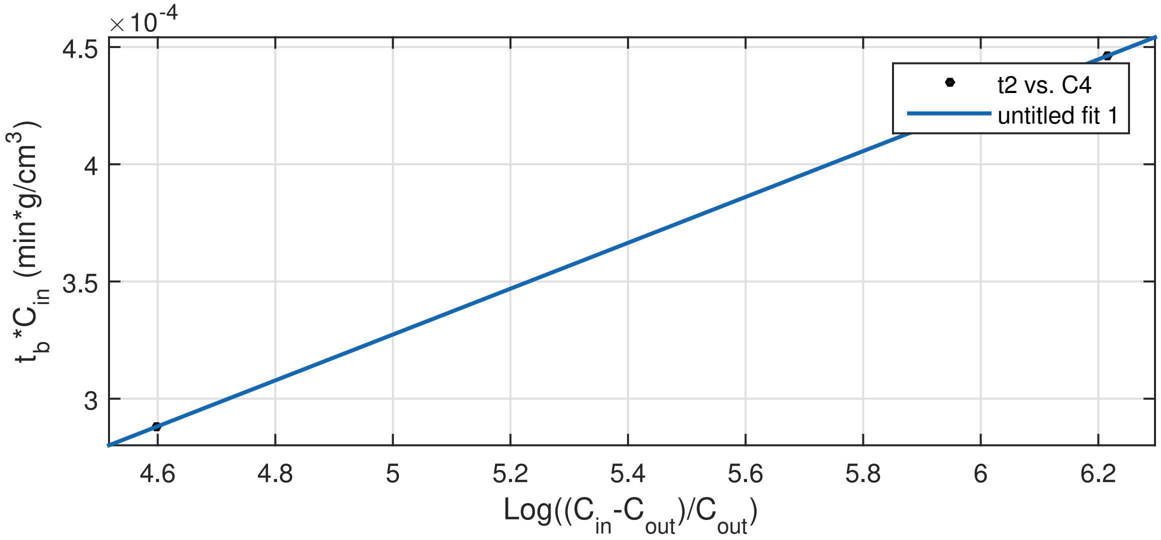
Figure 3.5: Fitted curve for sulfur dioxide.



Linear model Poly1: f(x) = A + Bx Coefficients: B = 24.34 A = 160.2

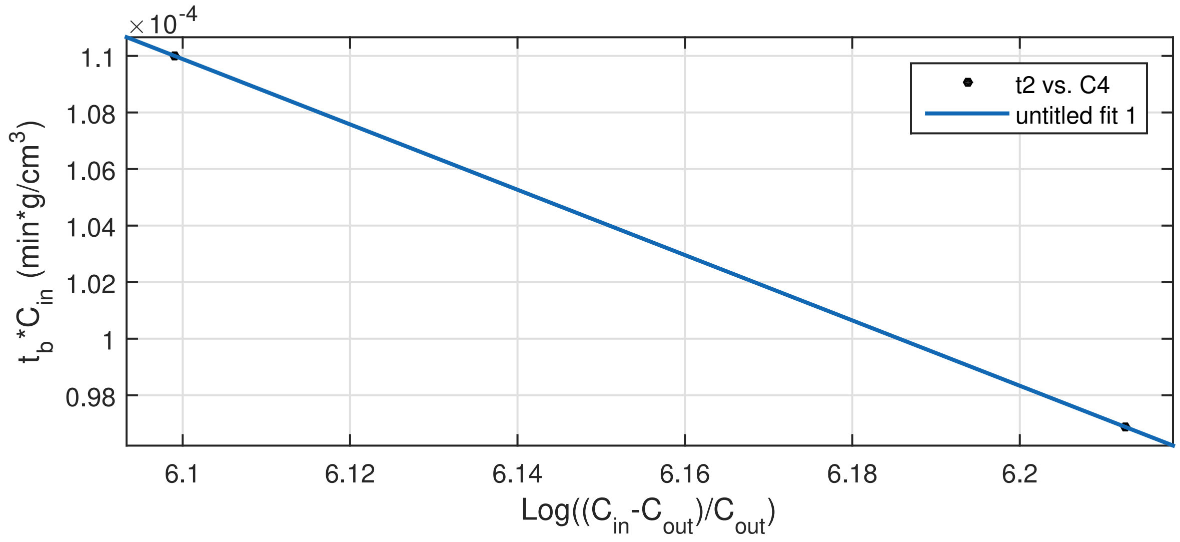
Using the second method figures 3.6, 3.7 and 3.8 shows the breakthrough time multiplied with the inlet concentration for varying inlet concentration. The data points are experimental values from table 3.2. The line is a fit to Eq. 3.11 and was computed numerically by using a curve fitting tool.

Figure 3.6: Fitted curve for cyclohexane.



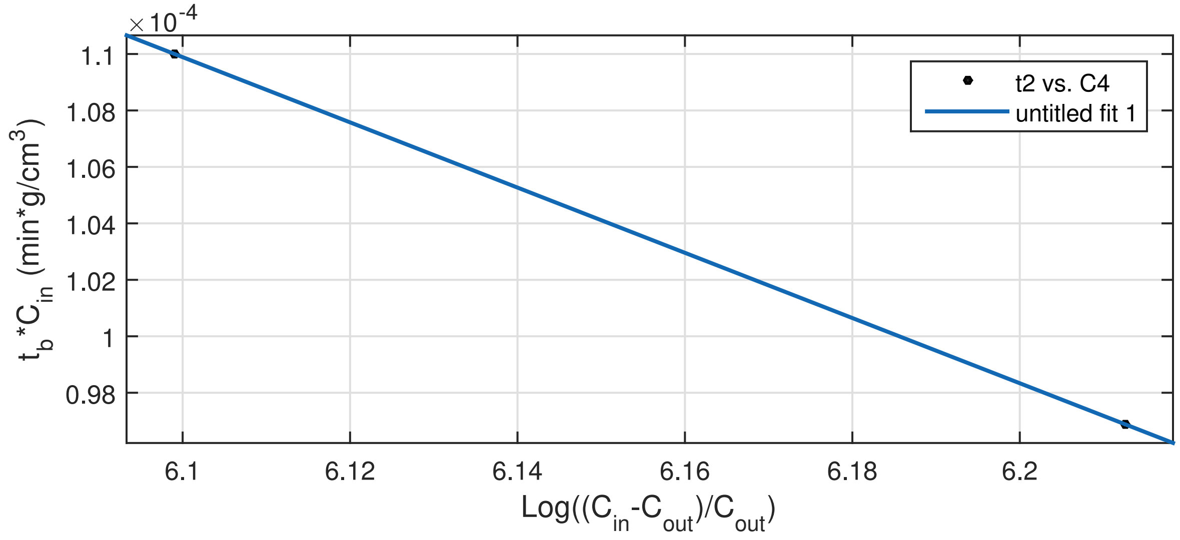
Linear model Poly1: f(x) = A - Bx Coefficients: B =$-9.781 \cdot 10^{-5}$, A = -0.0001617

Figure 3.7: Fitted curve for hydrogen cyanide.



Linear model Poly1: f(x) = A - Bx Coefficients: B = 0.0001155, A = 0.0008146

Figure 3.8: Fitted curve for sulfur dioxide.



Linear model Poly1: f(x) = A - Bx Coefficients: B = $6.178 \cdot 10^{-6}$, A = 0.0001581

3.5 Results

Tables 3.3 and 3.4 show the values of the parameters W_e and k_v obtained and breakthrough times calculated using the first method. Table 3.5 and 3.6 show the values of the parameters W_e and k_v obtained and breakthrough times calculated using the second method.

Table 3.3: Table of calculated values of W_e and k_v using the first method.

compound	W_e (g/g$_\mathrm{carbon}$)	k_v (min^{-1})	C_in (mg/l)
cyclohexane	0.2410	1265.8	3.5
hydrogen cyanide	0.3876	1209.2	5
sulfur dioxide	0.1222	1200.1	2.7

Table 3.4: Table of calculated values of W_e and k_v using the second method.

compound	W_e (g/g$_\mathrm{carbon}$)	k_v (min^{-1})
cyclohexane	-0.0457	301.6078
hydrogen cyanide	0.0447	$4.6703 \cdot 10^3$
sulfur dioxide	0.2301	$1.2857 \cdot 10^3$

Table 3.5: Table of calculated times using the WJ equation and the values of Tab. 3.3.

compound	t_b (min)	C_in (mg/l)	C_out (mg/l)
cyclohexane	82.3179	3.5	0.0349
hydrogen cyanide	22.0219	5	0.0112
sulfur dioxide	47.9879	2.7	0.0266

Table 3.6: Table of calculated times using the WJ equation and the values of Tab. 3.3.

compound	t_b (min)	C_in (mg/l)	C_out (mg/l)
cyclohexane	82.2684	3.5	0.0349
hydrogen cyanide	21.9996	5	0.0112
sulfur dioxide	48.0576	2.7	0.0266

The predictive equations for cyclohexane, hydrogen cyanide and sulfur dioxide that have been obtained under the premises that all variables except the inlet concentration are held constant are for each compound respectively:

Cyclohexane equation 3.24:

$$t_2 = t_1 \left(\frac{C_1}{C_2} \right)^{0.7280} \tag{3.27}$$

Figures 3.9, 3.10 and 3.11 shows the breakthrough time for varying inlet concentration. The data points are experimental values taken from Tab. 3.2. The line is a fit to Eq. 3.23 and was computed using a curve fitting tool and then plotted in a log plot to visualize the power law. Starting value 2 mg/l and end value 50 mg/l yields for cyclohexane, hydrogen cyanide and sulfur dioxide respectively:

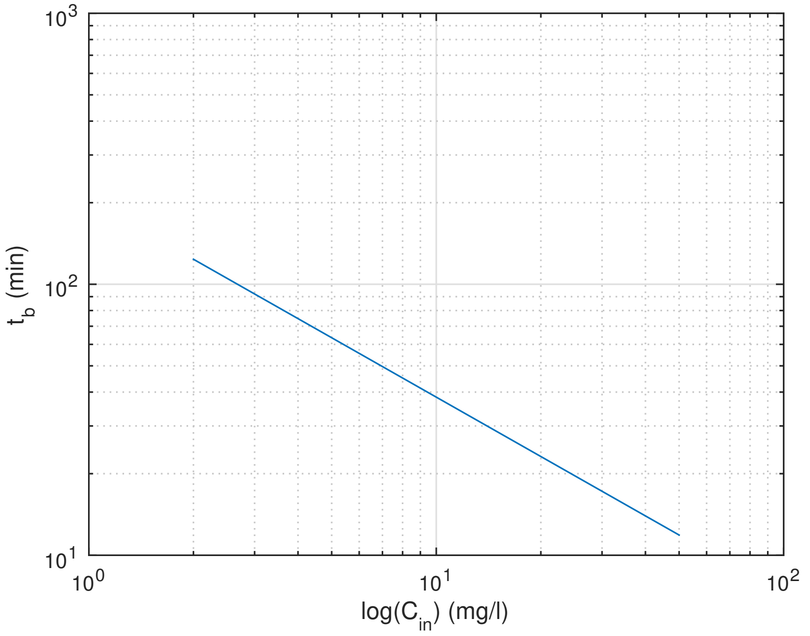


Figure 3.9: Log plot of penetration time for cyclohexane vs inlet concentration.

Hydrogen cyanide equation 3.25:

$$t_2 = t_1 \left(\frac{C_1}{C_2} \right)^{2.1207} \tag{3.28}$$

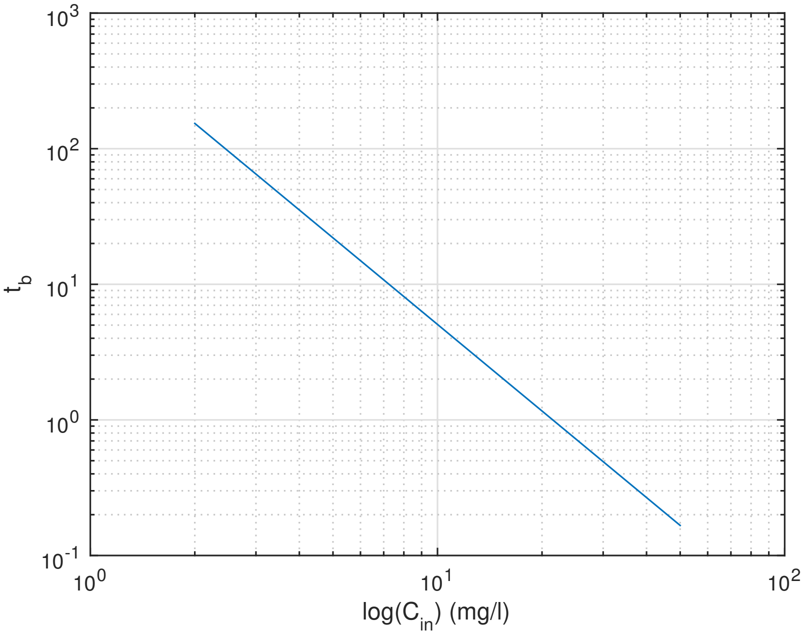


Figure 3.10: Log plot of penetration time for hydrogen cyanide vs inlet concentration.

For sulfur dioxide equation 3.26 becomes:

$$t_2 = t_1 \left(\frac{C_1}{C_2} \right)^{0.9525} \tag{3.29}$$

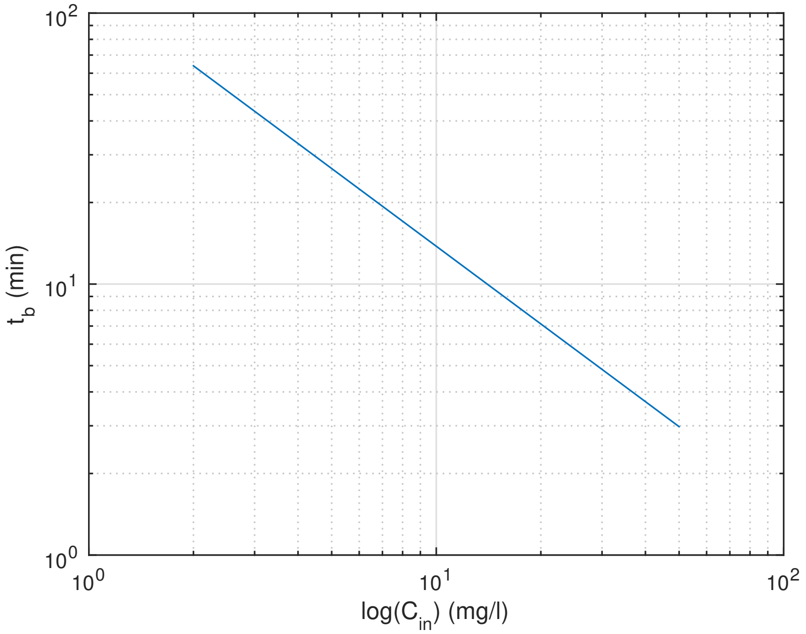


Figure 3.11: Log plot of penetration time for sulfur dioxide vs inlet concentration.

Using the parameters obtained with the second method Tab. 3.4 we may plot the WJ equation for varying inlet concentration. Figures 3.12, 3.13, 3.14 and 3.15 shows the breakthrough time for varying inlet concentration using the WJ equation and the Nelson-Harder expression overlapped.

Figure 3.12 shows the breakthrough time for varying inlet concentration where the red curve represents the Nelson-Harder expression Eq. 3.23 and the blue curve represents the WJ equation Eq. 3.1. The two equations are plotted over an interval of inlet concentrations between 0 and $5 \cdot 10^{-5}$ (g/cm^3). The fits was computed using a curve fitting tool.

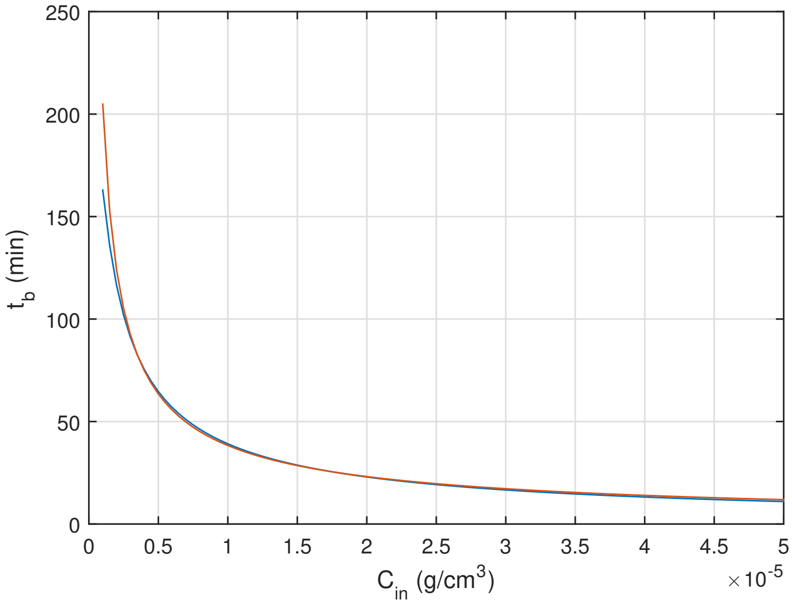


Figure 3.12: Plot of breakthrough time vs inlet concentration for cyclohexane.

Figure 3.13 shows the breakthrough time for varying inlet concentration where the red curve represents the Nelson-Harder expression Eq. 3.23 and the blue curve represents the WJ equation Eq. 3.1. The two equations are plotted over an interval of inlet concentrations between 0 and $5 \cdot 10^{-5}$ (g/cm^3). The fits was computed using a curve fitting tool.

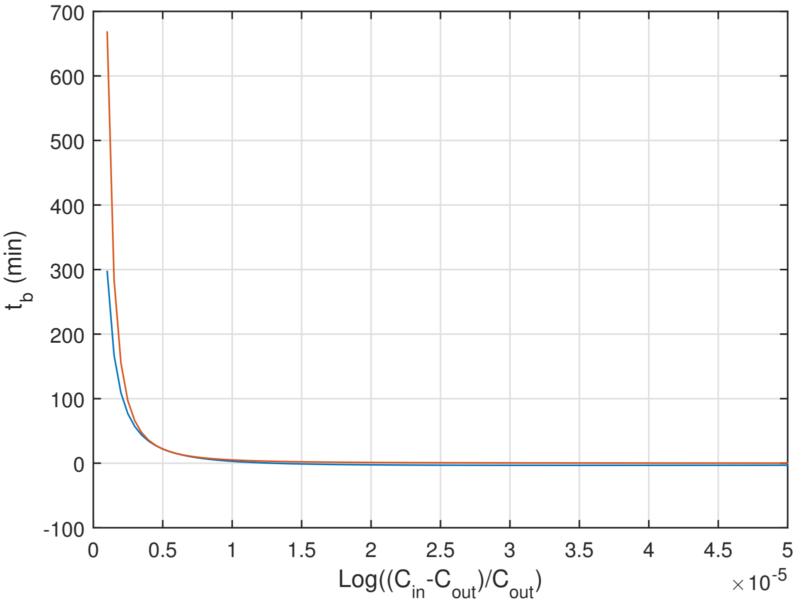


Figure 3.13: Plot of breakthrough time vs inlet concentration for hydrogen cyanide.

Figure 3.14 shows the breakthrough time for varying inlet concentration for the Nelson-Harder expression Eq. 3.23 and the WJ equation Eq. 3.1. It is impossible to tell which curve is which because they overlap well. The two equations are plotted over an interval of inlet concentrations between 0 and $5 \cdot 10^{-5}$ (g/cm^3). The fits was computed using a curve fitting tool.

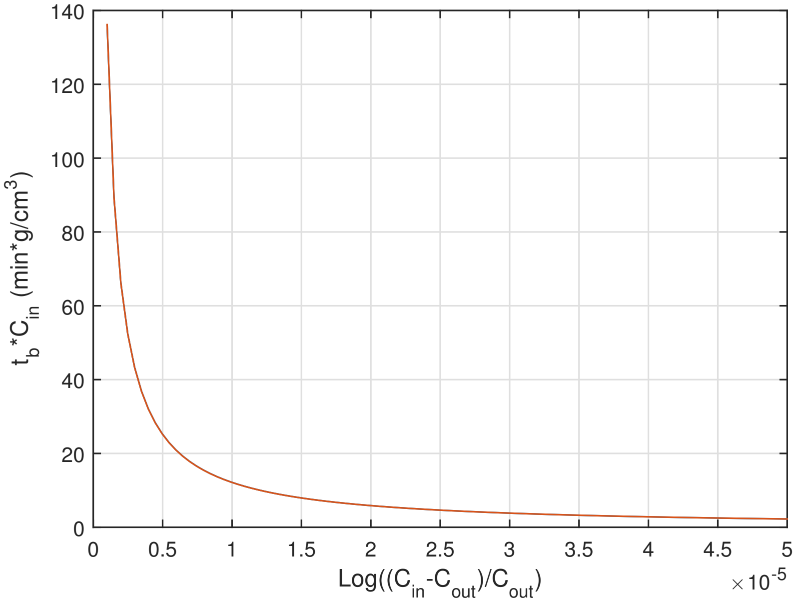


Figure 3.14: Plot of breakthrough time vs inlet concentration for sulfur dioxide.

Figure 3.15 shows a zoomed in visualization of the curves to demonstrate that they overlap.

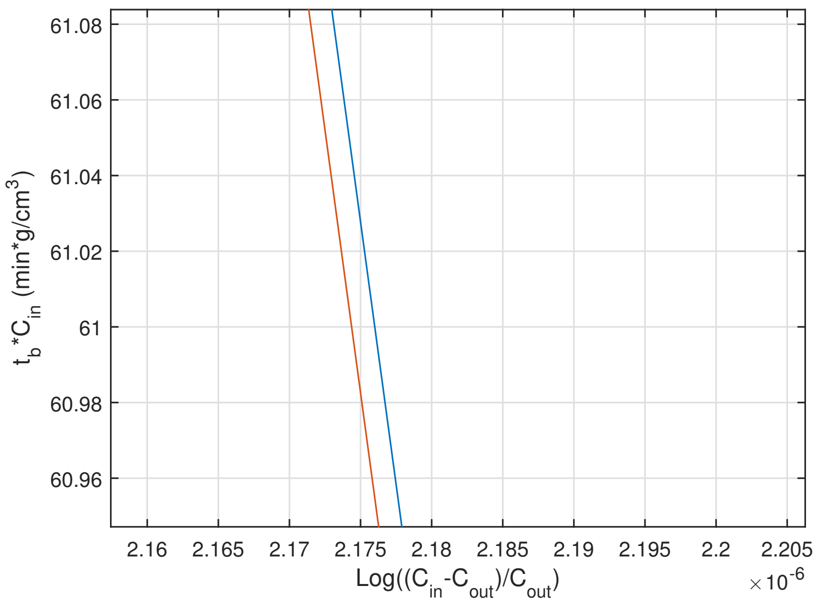


Figure 3.15: Plot of breakthrough time vs inlet concentration for sulfur dioxide.

A simple way of calculating k_v according to Eqs. 3.16 and 3.17.. And finally two ways of calculating the coefficient B according to 3.18 and 3.19 whence the coefficient A is already known to $= t_{0.50}$.

3.6 Discussion

We see from figures 3.12 to 3.15 that the WJ equation and the Nelson-Harder expression overlaps well which is what we expect in the case of varying inlet concentration only.

The two methods of empirically estimating the unknown parameters are equal in producing reliable values but there is a great advantage of not having to recalculate these values for each inlet concentration.

Since there is no clear definition of which are considered low output concentrations, figures 3.3, 3.4 and 3.5 should be used cautiously. The WJ equation might not at all be approximately linear in this interval. More data points are needed to conclude an interval for which the curve is approximately linear.

When calculating the values of the parameters W_e and k_v one has to remember that these depend on inlet concentration and has to be calculated for every inlet concentration.

From Tables 3.5 and 3.6 we see that times obtained with the WJ equation using the calculated values of the parameters are very accurate. The great advantage of having these parameters is the possibility of calculating new penetration times when varying for example air flow or filter parameters.

The exponent n of the Nelson-Harder expression has been suggested to equate to a value of 0.67 after investigating breakthrough data for nine different compounds. Values of n between 0.45 and 0.94 was obtained[12] in comparison to values obtained between 0.73 and 2.1 in this work. Taking the mean value of the exponents obtained in this work they equate to a value of approximately 1.276. The difference might be due to the type of compounds studied.

Eqs. 3.16, 3.17, 3.18 and 3.19 are derived theoretically and need to be tested with experiments. A way of calculating the coefficient B in terms of breakthrough times is desirable since it is known that A equates to $t_{0.50}$. Unfortunately knowledge of the very specific breakthrough times is needed.

The validity of Eqs. 3.15, 3.16, 3.17 and 3.18 comes from the fact that when the WJ equation is applicable the relationship between breakthrough time and concentration is linear when the rest of the parameters are held constant.

For the situation when air flow or filter parameters are varied we need to use the WJ equation and cannot use the simplified Eqs. 3.24, 3.25 or 3.26. The choice of method for estimating the parameters k_{v} and W_{e} is chosen based on available data. To use the theoretical approach i.e equations 3.4 and 3.6 values of the molar polarization P_{e} and affinity coefficient β is found in tables[9]. The other variables that need to be known for the theoretical approach are the saturated vapor pressure P_{s}, the partial pressure of the adsorbate P, the maximum amount of vapor adsorbed W_0 and the characteristic adsorption energy E_0 for a reference vapor.

Further on Eqs. 3.13, 3.14, 3.15,3.16,3.17, 3.18 and 3.19 have been derived according to[30] but with the assumption that the only variable is the concentration and observing only low output concentrations k_{v} should be constant as can be seen from equation 3.10. So equations 3.16 and 3.17 are equivalent and so are equations 3.18 and 3.19. This is supported by the claim that k_{v} varies with flow rate according to [30]

$$k_{\mathrm{v}} = 2.33Q^{0.755} \tag{3.30}$$

The value of the exponent may vary between compounds as is indicated by Eq. 3.4 where molar polarization is a variable. Also this is measured for varying air flow only because k_{v} also depends on inlet and outlet concentration.

That Eqs. 3.16 and 3.17 are equivalent can be shown directly under the assumption that the relationship between breakthrough time and inlet concentration is linear. Taken that $t_{0.50}$ is the breakthrough time at 50% of the inlet concentration then t_{100} is the breakthrough time at 100% of the inlet concentration. studying the quotient between equations 3.16 and 3.17 yields:

$$\frac{\frac{2.944Q}{V\left[1-\frac{t_{0.05}}{t_{0.50}}\right]}}{\frac{2.944Q}{V\left[\frac{t_{0.05}}{t_{0.50}}-1\right]}}=\frac{\left[\frac{t_{0.50}-t_{0.05}}{t_{0.50}}\right]}{\left[\frac{1-t_{0.50}-t_{0.05}}{t_{0.50}}\right]}=1$$

Chapter 4

Summary and Conclusions

It was found that the WJ equation has been researched many times in previous studies and that it is applicable in modeling adsorption of organic and some inorganic compounds through filters made from activated carbon especially "skyddsfilter 90". Modeling adsorption of organic compounds through activated carbon beds was the purpose of the WJ equation but it has since then been proven to be applicable also for non organic compounds which was desirable for the aim of this thesis.

When the applicability of the WJ equation is unknown there is an easy test to perform according to Eq. 3.2 with the help of a breakthrough test and plotting the measured breakthrough times vs inlet concentration. The model has limitations for example low output concentrations need to be studied in order to use Eq. 3.2. There is a condition on the inlet vs outlet concentration that needs to be fulfilled which is $C_{\text{out}}/C_{\text{in}} <$ 5-10%[18]. Fortunately in the use of respiratory filters this condition is often fulfilled. Also the condition of no radial diffusion is usually fulfilled for respiratory filters which are cylindrical shaped and have a radius larger than 2 cm.

Two empirical methods of estimating the unknown parameters was used and both produced reliable values when used in the WJ equation. Further on it was found that simplifications can be made when only varying the inlet concentration. The Nelson-Harder expression 3.22 can be used and the exponent value can be calculated using only two data points. If no data points are available it has been suggested that n equates to 0.67[12] but this should be used with caution because it might produce large errors since values of n can vary a lot. In this thesis the values lies between 0.47 and 2.1. It was found that the WJ equation and the Nelson-Harder expression overlap well in the case of varying inlet concentration only which is to be expected.

The model is applicable to filters of different sizes as long as these filters are made with activated carbon and have diameter larger than 2 cm. For filters made with different materials further research is needed. The equations describing the parameter k_{v}, the coefficient B and the breakthrough time at different breakthrough fractions are derived in a previous study[30]. However experimental validation of the equations have not been possible to conduct in this thesis do to lack of data. knowledge of specific breakthrough times are needed. Finally it is very important to know that this mathematical modeling offers only approximations of the breakthrough times and should be used with caution.

Chapter 5

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