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ABSTRACT

SENSITIVITY ANALYSIS AND DESIGN CALCULATIONS WITH BIOFILTRATION MODELS

by Michael Lawrence Cohen

Biofiltration is a new technology for biological treatment of volatile organic compounds present in airstreams. It is a complex process and thus, engineering models which attempt to describe it are by necessity very involved and contain a large number of parameters.

In this study, two models describing biofiltration of airstreams carrying a single pollutant (VOC) were used in detailed parameter-sensitivity studies. One model concerned biofiltration under steady-state conditions, while the second described the transient behavior of the process. The intent of the sensitivity studies was to determine which model parameters need to be known with accuracy in order to allow for a good prediction of the size of a biofilter needed to achieve a given VOC-control objective. Studies with the steady-state biofiltration model have shown that accurate knowledge of the values of two kinetic parameters and the specific area of biofilm (and therefore the packing configuration) are essential. Studies with the transient model have revealed that in regards to transient behavior, the mass transfer coefficient is the most important design parameter.

Design calculations were also performed in this study for an integrated process involving soil venting and biofiltration for cleaning a contaminated aquifer. Preliminary results (based on a number of simplifying assumptions) have shown that the proposed concept is plausible in the sense that a reasonable biofilter size is adequate for remediating a site in a relatively short period of time. It was also found that a given mass of contaminant can be treated more efficiently (shorter time, smaller biofilter volume) under constant venting rate if the volume of the aquifer is smaller (i.e., when the residence time of air in the aquifer is larger). This finding could be taken advantage of through faster remediation of a spill (before it spreads), or if seasonal variations affect the size of the aquifer.

SENSITIVITY ANALYSIS AND DESIGN CALCULATIONS WITH BIOFILTRATION MODELS

by Michael Lawrence Cohen

A Thesis

Submitted to the Faculty of New Jersey Institute of Technology in Partial Fulfillment of the Requirements for the Degree of Master of Science in Environmental Engineering

Department of Civil and Environmental Engineering

January 1996

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APPROVAL PAGE

SENSITIVITY ANALYSIS AND DESIGN CALCULATIONS WITH BIOFILTRATION MODELS

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This thesis is dedicated to Dr. Indira Nair without whom I would not have gotten this far.

ACKNOWLEDGMENT

The author would like to express his sincere gratitude to his thesis advisor, Dr. Basil C. Baltzis, for his encouragement and expert guidance throughout this research. The author would also like to express thanks to Dr. Hsin-Neng Hsieh and Dr. Gordon A. Lewandowski for serving as his committee members.

The author would also like to express thanks to Dr. Dimitrios Tsangaris, and especially to (soon to be Dr.) Steven Wojdyla for their excellent guidance and training.

The author appreciates the help, support and friendship of his fellow students and friends including: Huifang Fan, Jong-Wook Kim, Dilip Mandal, Christos Mpanias, Sachin Purekar, Dr. Kung-Wei Wang and Joshua Yi.

The author would like to sincerely express his appreciation to his family for their support and guidance: Mrs. Arlene Cohen and Dr. Irving Cohen, Mrs. Katherine Cohen and Mrs. Ruth Zamble, and of course, Dr. Jennifer Cohen.

Finally, the author would like to express his appreciation and love to Ms. Leah Carlberg for loving him.

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NOMENCLATURE

| A_S | : biolayer surface area per unit volume of biofilter (m ⁻¹) |
|------------------------|---|
| A_S^* | : total surface area available for biolayer formation and adsorption per unit volume of biofilter (m^{-1}) |
| c _G | : concentration of pollutant in air entering the extraction well (g/m^3) |
| c _j | : concentration of substance j in the air at a position h along the biofilter (g/m^3) |
| c_j^* | : equilibrium concentration of a pollutant j at the gas/solid interface (g/m^3) |
| c _{ji} | : value of c_j at $h = 0$ (g/m ³) |
| c _{jp} | : concentration of substance j on the solid particle (g of pollutant j-absorbed/g particle) |
| c_L | : concentration of pollutant in the contaminated aquifer (g/m^3) |
| c_{L0} | : concentration of pollutant in the contaminated aquifer at $t = 0 (g/m^3)$ |
| c _O | : oxygen concentration in the air at a position h along the biofilter (g/m^3) |
| c _{Oi} | : oxygen concentration in the air at the inlet of the biofilter (g/m^3) |
| \overline{c}_{j} | : dimensionless concentration of a compound j in the air ($\overline{c}_j = c_j/c_{ji}$) |
| $\overline{c}_{j,0}$ | : value of \overline{c}_j at t = 0 |
| \overline{c}_{jP} | : dimensionless concentration of substance j on the solid particle defined as $(1-\upsilon)\rho_P c_{jP}/\upsilon c_{ji}$ |
| $\widetilde{c}_{jP,0}$ | : value of \overline{c}_{jp} at $t = 0$ |
| \overline{c}_{O} | : dimensionless concentration of oxygen in the air ($\overline{c}_0 = c_0/c_{0i}$) |
| $\overline{c}_{O,0}$ | : value of \overline{c}_0 at t = 0 |
| D _{jw} | : diffusion coefficient of a compound j in water (m^2/h) |

NOMENCLATURE (Continued)

| D_{OW} | : diffusion coefficient of oxygen in water (m ² /h) | | | |
|-------------------------------------|--|--|--|--|
| e _j | : effectiveness factor based on a pollutant j | | | |
| e _O | : effectiveness factor based on oxygen | | | |
| F | : flow rate of airstream (m^3/h) | | | |
| $f(X_V)$ | : ratio of diffusivity of a compound in the biofilm to that in water | | | |
| $g(\overline{c}_j, \overline{c}_0)$ | $g(\overline{c}_j, \overline{c}_0)$: dimensionless version of $\mu_j(s_j, s_0)$ | | | |
| h | : position in the column (m); $h = 0$ at the entrance $h = H$ at the exit | | | |
| Н | : total height of the biofilter bed (m) | | | |
| k _a | : mass transfer coefficient between the gas and the solid surface (m/h) | | | |
| k _d | : Freundlich isotherm parameter | | | |
| К _ј | : constant in the specific growth rate expression of a culture growing on compound j (g-compound j/m^3) | | | |
| K _{1j} | : inhibition constant in the specific growth rate expression of a culture growing on compound j (g-compound j/m ³) | | | |
| Ko | : constant in the specific growth rate expression of a culture, expressing the effect of oxygen (g-oxygen/m ³) | | | |
| L | : rate of VOC-mass supply to the biofilter (g/h) | | | |
| m _j | : distribution coefficient for the substance j/water system | | | |
| m _O | : distribution coefficient for the oxygen-in-air/water system | | | |
| n | : Freundlich isotherm parameter | | | |
| Q_G | : flow rate of air entering the sparging point (m^3/h) | | | |

NOMENCLATURE (Continued)

- s_j : concentration of substance j at a position x in the biolayer at a point h along the column (g/m³)
- s_0 : oxygen concentration at a position x in the biolayer, at a point h along the column (g/m³)
- \bar{s}_i : dimensionless concentration of a compound j in the biolayer ($\bar{s}_j = s_j/K_j$)
- \bar{s}_0 : dimensionless oxygen concentration in the biolayer ($\bar{s}_0 = s_0/K_0$)
- t : time (h)
- u_g : superficial air velocity (m/h)
- V_L : volume of liquid in the contaminated aquifer (m³)
- V_P : volume of the biofilter bed (m³)
- X_V : biofilm density (kg/m³)
- x : position in the biolayer (m)
- Y_j : yield coefficient of a culture on compound j (g-biomass/g-compound j)
- Y_{Oj} : yield coefficient of a culture on oxygen (g-biomass/g-oxygen), when VOC j is the carbon source
- z : dimensionless position in the biofilter (z = h/H)

GREEK SYMBOLS

| α | : fraction of total surface area available for biofilm formation |
|-------------------|---|
| β_1 | : dimensionless parameter defined as $e_j \alpha \delta A_S^* X_V H \mu^* / Y_j u_g c_{ji} \upsilon$ |
| β_2 | : dimensionless parameter defined as $e_0 \alpha \delta A_S^* X_V H \mu^* / Y_0 u_g c_{0i} \upsilon$ |
| β ₃ | : dimensionless parameter defined as $k_a(1-\alpha)A_S^*H/u_g \upsilon$ |
| γ | : inverse dimensionless inhibition constant ($\gamma = K_j/K_{lj}$) |
| δ | : effective biolayer thickness (m) |
| ε ₁ | : dimensionless quantity defined as $c_{ji} / (K_j m_j)$ |
| ε2 | : dimensionless quantity defined as c_{Oi} / (K _O m _O) |
| ζ | : dimensionless time defined as t/τ |
| η | : dimensionless quantity defined as $A_S f(X_V) D_{jw} K_j \tau \ / \ (\delta c_{ji})$ |
| θ | : dimensionless position in the biolayer ($\theta = x/\delta$) |
| λ | : dimensionless quantity defined as $D_{jw}K_{j}Y_{j}$ / $(D_{Ow}K_{O}Y_{Oj})$ |
| $\mu_j(s_j, s_O)$ | : specific growth rate (h ⁻¹) |
| μ_j^* | : constant in the specific growth rate expression for substance j (h^{-1}) |
| ρ_P | : density of the solid particles (g/m^3) |
| τ | : space time defined as V / F |
| υ | : void fraction of the biofilter bed |
| ϕ^2 | : square of Thiele modulus based on compound j, defined as $\mu_j^*\delta^2 X_V/(f(X_V)D_{jw}K_jY_j)$ |
| ψ | : dimensionless quantity defined as $1/c_{ji}[\upsilon c_{ji}/(1-\upsilon)\rho_P k_d]^{1/n}$ |
| ω | : dimensionless quantity defined as $K_O D_{Ow} c_{ji} / (K_j D_{jw} c_{Oi})$ |

SPECIAL SUBSCRIPTS

- 0 : refers to conditions at t=0
- i : refers to conditions at h = 0, or z = 0
- j : compound j
- j = B : compound is butanol
- j = T : compound is toluene

CHAPTER 1

INTRODUCTION

Nature has the ability to decompose and recycle all substances produced by mankind. It can thus, treat all substances which are considered as wastes. However, environmental pollution is a serious problem. This arises from the fact that mankind produces wastes at rates much higher than those at which nature can decompose them. In addition, high levels of certain pollutants impact the health of humans and other living species while they destroy the natural ecosystem. Consequently, pollution control becomes an important issue and various laws regulate the presence of various pollutants in the air, water, and soil.

One of the most important groups of pollutants currently being regulated is that of Volatile Organic Compounds (VOCs). These compounds are among the major precursors, along with NO_x , of ground-level ozone. In an effort to reduce the occurrence of this ozone the Clean Air Act Amendments of 1990 (CAAA) have introduced restrictions on the amounts of VOCs that may be emitted. Presently, these restrictions are only on large-scale industrial operations. Eventually, these restrictions will be extended to include smaller scale contributors such as bakeries, dry cleaners, gasoline stations, and storage facilities [Baltzis and Wojdyla (1995a)].

In order to control VOC emissions many processes have been devised, including thermal and catalytic incineration, flares, condensers and adsorption [Moretti and Mukhopadhyay (1993)]. These processes are currently the most popular, but there are

1

several newer, possibly more effective and economical ones on the horizon. One of the more promising of these new technologies is biofiltration.

Biofiltration is a biological method for VOC treatment. It is based on the oxidation of VOCs by bacterial and fungal species which utilize the various compounds as a carbon or energy source. It can be argued that biofiltration is a naturally occurring process which is now used in a controlled manner as a specially designed technology. The first applications of biofiltration were in conjunction with wastewater [Fouhy and Grinthal (1994)], and later for odor control purposes. Presently biofilters are in use within many processes including aroma extraction, foundries, sewage (municipal and industrial), plastics processing, adhesives and rendering. They are used for the removal of many irritants and pollutants including odors, oxygen-, sulfur-, and nitrogencontaining organics and hydrogen sulfide [Fouhy, 1992]. In recent decades, there has arisen an interest in using biofiltration for dealing with emissions of hazardous and toxic substances.

There are a number of recent studies on biofiltration and they are reviewed in the next chapter of this thesis. Some of these studies have led to the development of mathematical models [e.g., Ottengraf and van den Oever (1983), Shareefdeen et al. (1993), Shareefdeen and Baltzis (1994)] with varying degrees of complexity. Models are very important for optimal engineering design of biofilters as well as for determining if biofiltration is an economically viable option for a given application.

Biofiltration models (both for steady-state and transient operation) involve a large number of parameters. Accurate knowledge of all these parameters requires extensive and expensive experimental work, something which is not practical when biofiltration is considered in preliminary decision making. It thus becomes important to know which parameters are most essential for a good estimation of the size of biofilters. This determination can be made through sensitivity studies with the models, and this was the main objective of the study presented in this thesis.

Biofiltration is a process which was originally conceived for treatment of air which is unintentionally polluted. Conceivably though, it could be also used for treating air which is intentionally contaminated in order to resolve other pollution problems. For example, if soil or an aquifer is contaminated with VOCs air can be used for decontaminating them. In this case the pollution problem is intentionally removed from one phase to another; more specifically it is transferred to the air. This contaminated air could be subsequently treated in a biofilter where the pollutants are destroyed. This idea of an integrated soil venting/biofiltration process was also considered as part of the present thesis. Clearly the idea of soil venting is not new. Actually, a number of studies on soil venting or air sparging exist in the literature and are reviewed in the next chapter of this thesis. With regard to the integrated process, some preliminary calculations were performed based on detailed biofiltration models, but simple models describing air sparging (vapor extraction).

CHAPTER 2

LITERATURE REVIEW

2.1 Biofiltration

In recent years biological processes have been shown to be effective in treating VOC contaminated airstreams. There are two major biological systems for treating these airstreams: classical biofilters and biotrickling filters. These processes can be effective _for a wide range of pollutants, are usually relatively inexpensive, produce _environmentally harmless emissions and can be easily maintained for a relatively long _period of time [Zilli et al. (1992)].

The classical biofilter (or simply biofilter) consists of a porous solid support placed either in an open or closed structure (reactor). Microorganisms having the ability to biodegrade volatile substances are immobilized on this solid support. The contaminated airstream passes through the classical biofilter, the contaminants enter the wet biofilm layer surrounding the particles, and are there degraded by the microorganisms. There is no liquid stream in a classical biofilter [Shareefdeen and Baltzis (1994), Hodge and Devinny (1994)]. The main factors affecting this process are the support (packing), the identity and properties of the contaminants, the microbial species and their characteristics, and the rates of VOC removal which can be achieved with a given unit.

The biotrickling filter is similar to the classical biofilter but it involves a recirculating liquid phase. This allows for continuous removal of chemicals such as

chlorinated compounds, which cause a change in the pH value. In these units pH-control is achieved by the addition of an acid or base when necessary. Biotrickling filters have also been shown to retain higher amounts of biomass in some instances, leading to higher degradation rates [Togna and Singh (1994)].

Due to the interest in biofiltration a lot of feasibility studies have been performed in the recent years. Detailed reviews of studies can be found in Shareefdeen (1994) and Androutsopoulou (1994). Removal rates vary with the compounds used, the size of biofilter, the concentration of pollutants in the airstream entering the biofilter, the packing material, etc. For example, Zilli et al. (1992) reported removal rates of phenol up to 124 $g/m^3/h$ with a packing material consisting of peat and glass beads in a 2:1 volume ratio. In their experiments they used *Pseudomonas* sp. Ottengraf and van den Oever (1983) studied the removal of mixtures (containing among others toluene and butanol) and reported maximum removal rates in the range of 20-40 $g/m^3/h$ depending on the identity of the pollutant. The packing material used was primarily a peat compost. Regarding ethanol, Baltzis and Androutsopoulou (1994) have reported removal rates up to 40 g/m³/h under steady-state conditions and much higher ones under transient conditions; they used a packing material consisting of peat and perlite (2:3 per volume). For the same substance (ethanol), Hodge and Devinny (1994) have reported removal rates ranging from 53 to 219 g/m³/h in biofilters packed with compost, or granular activated carbon (GAC), or a mixture of compost and diatomaceous earth. The foregoing review is not a complete account of existing studies, but it shows that various parameters affect the performance of biofilters.

Since the present thesis dealt with modeling of classical biofilters, following is a review of existing models.

The first model of biofiltration under steady-state conditions was published by Ottengraf and van den Oever (1983). Although the model was based on experiments with a mixture of VOCs, it essentially concerns removal of a single compound as it does not take into account potential interactions between pollutants. In addition, this model does not account for the potential impact of oxygen availability (although biofiltration is an aerobic process) and uses zero- or first-order kinetics with regard to the pollutant. Due to the extensive simplifying assumptions this model can be solved analytically, but is now considered as unrealistic.

The first detailed model describing steady-state biofiltration of a single VOC was published by Shareefdeen et al. (1993) and describes potential oxygen limitations of the process, while it accounts for more detailed (in fact complex) expressions for the degradation rate with regard to the VOC. Based on experiments with methanol, this model predicts that under most conditions oxygen is the limiting factor from the masstransfer view point while the carbon source (methanol) is limiting from the kinetics point of view. The same model was used by Androutsopoulou (1994) who experimentally studied the removal of ethanol and butanol in two separate units. She reached the same conclusions regarding oxygen and VOC limitation as those of Shareefdeen et al. (1993). The same model was used in describing biofiltration of benzene and toluene in two separate columns [Shareefdeen (1994)]. In this case, it was found that although oxygen affects the process to a certain extent, limitation both from kinetics and mass-transfer viewpoints is determined by the VOC. The conclusion from the foregoing studies is that although oxygen should be always considered it has to be definitely accounted for in cases where a hydrophilic compound is treated. This was not done by Hodge and Devinny (1994) who modeled ethanol biofiltration data along the lines of Ottengraf and van den Oever (1983). However, this new model incorporates rates of carbon dioxide evolution.

Models for steady-state biofiltration of VOC mixtures fall in two categories. Baltzis and Sharefdeen (1994) have proposed a model which accounts for competitive inhibition between pollutants and also accounts for oxygen effects. This model has been experimentally validated with mixtures of benzene and toluene. A model which accounts for competitive inhibition but neglects oxygen effects has been also used by Deshusses et al. (1995) based on experiments with MEK (methyl-ethyl-ketone) and MIBK (methylisobutyl-ketone). Recently, Baltzis and Wojdyla (1995b) have proposed a model which accounts for species differentiation in the biofilter bed. This model accounts for oxygen effects and assumes the formation of separate biofilm patches for each pollutant. This model has been used in explaining data of ethanol/butanol mixtures removal.

Transient biofiltration is a much more complex case since the process is complicated by the presence of adsorption/desorption effects. Shareefdeen and Baltzis (1994) were the first to propose a model for transient biofiltration of single VOCs. The model is an extension of the steady-state model proposed earlier by the same investigators [Shareefdeen et al. (1993)] and has been experimentally validated for the case of toluene removal under transient conditions. A transient model has also been proposed by Deshusses et al. (1995) and used for describing MEK or MIBK transient removal. This model does not account for oxygen limitations and instead of adsorption it uses absorption (dissolution) of the VOCs in the water retained within the pores of the packing material.

The present thesis dealt with single VOCs and used the models of Shareefdeen et al. (1993) and Shareefdeen and Baltzis (1994) in sensitivity and calculational studies. It should also be added that since this thesis dealt with classical biofilters, studies of biotrickling filters have not been reviewed. These studies are few in number and the only one on modeling has been published by Diks and Ottengraf (1991).

2.2 Soil Venting

Soils can become contaminated with VOCs in many ways. The main sources of contamination are intentional dumping, accidental spills and leaks in underground storage tanks. There are a number of current practices for removing these VOCs. They include excavation of the entire site followed by treatment of the soil, and flushing of the aquifer followed by treatment of the water [Hutzler et al. (1991)]. These methods are very expensive and time consuming, and for this reason new approaches and technologies are currently being investigated.

Soil venting (also known as soil vapor extraction or air sparging) is a new remediation technique which is both significantly cheaper and less time consuming than the current methods. In this process, VOCs are removed from the contaminated aquifer by forcing (sparging) air through the soil, and into the aquifer. The VOCs are volatized out of the water, and into the airstream. These VOCs are carried out of the ground, either into a vapor extraction system, or when permissible, into the atmosphere [Angell (1991)]. It has been found that soil venting can be effective in removing a wide range of VOCs, under numerous conditions [Hutzler et al. (1991)].

Wilson et al. (1987) have proposed a model for describing the removal of VOCs from the subsurface using forced venting. In this model a single component (gasoline) is forced upward through a uniform soil. Only diffusion through the soil is considered, with the only soil parameter used being porosity. This model was validated experimentally in the laboratory, and was found to need improvement.

Silka et al. (1991) proposed a simplistic mass balance model which assumed equilibrium between the liquid and gas. Transport through soil was described by a single variable, the effective diffusion coefficient (an overall coefficient accounting for partitioning, adsorption and tortuosity). This model has been found to have good qualitative agreement with data from vapor extraction of TCE.

Gierke et al. (1992) proposed a detailed model of vapor extraction. This model is more complex than previous ones, as it includes nonequilibrium effects and more soil parameters such as soil particle density, soil sorption capacity, aggregate radius and degree of saturation. These additional parameters make the model more realistic. Laboratory data on the extraction of toluene and methanol from Ottawa sand and an aggregated porous soil material were found to be in excellent agreement with the predictions of the model. Soil venting is a complex process which appears to need further detailed investigation both from the experimental and the modeling viewpoint. In the present thesis equilibrium between air and water (regarding the VOC) was assumed while soil parameters were not considered.

CHAPTER 3

OBJECTIVES

There were two main objectives in this study. The first was to perform detailed parameter-sensitivity studies with steady-state and transient biofiltration models. The second objective was to perform design calculations for an integrated process involving air stripping (soil venting) and biofiltration for treatment of a contaminated aquifer.

All studies were based on existing models and computer codes which are applicable for cases where the contaminated airstream contains a single pollutant.

The intent of the sensitivity studies was to determine which model parameters need to be accurately known so that the size a biofilter needed for meeting a given VOC-control objective can be safely predicted.

The intent of the design calculations for the integrated soil venting/biofiltration process was to obtain some preliminary knowledge regarding the size of the required biofilter and the time frame within which a contaminated aquifer could be remediated.

Sensitivity studies with the steady-state biofiltration model were extensions of similar studies by Shareefdeen (1994) and Androutsopoulou (1994). They were performed as follows. Two basic sets of model-parameters were first selected: one for toluene (a hydrophobic compound) and one for butanol (a hydrophilic compound). Each model parameter -one at a time- was varied within a range from 0.1 to 10 times its base value and the biofilter size required for performing a given duty was calculated. In most instances, the space (residence) time of the airstream in the biofilter rather than the

volume of the biofilter itself was calculated. This was done because the volume (V) is related to the space time (τ) through the relation $\tau = V/F$, where F is the volumetric flowrate of the airstream supplied to the biofilter, and the model gives the same results for a given value of τ regardless of the individual values of V and F. The results of these studies are presented in Chapter 4 of the thesis.

Sensitivity studies with the transient biofiltration model were performed with a single set of basic parameter values (toluene). Only parameters appearing in the transient but not in the steady-state model were examined. These parameters refer to adsorption equilibrium and mass transfer characteristics between VOC and packing material of the biofilter. The objective here was to investigate the effect of parameters on the time required to achieve steady-state and on the size of the biofilter. The size of a biofilter can be affected by transient behavior parameters due to potential concentration overshoots. Results from these studies are presented in Chapter 5.

For the integrated soil venting/biofiltration process, it was assumed that the aquifer was contaminated with toluene only. One set of biofiltration parameters was used, while it was also assumed that the air passed through the aquifer carries toluene at equilibrium concentrations at all times. The rate of soil venting was changed so that the biofilter operates under relatively constant toluene concentrations over different time segments. Various criteria, such as the threshold limit value (TLV) and acceptable source impact level (ASIL), for toluene were taken into account for the design calculations. Results from this part of the study are presented in Chapter 6 of the thesis.

CHAPTER 4

STEADY-STATE BIOFILTRATION OF SINGLE VOCs

The work presented in this chapter refers to biofiltration under steady-state conditions when the contaminated airstream contains a single VOC. The process had been earlier modeled by Shareefdeen et al. (1993). This model was also used in the studies reported here. The model, which is presented in the next section of this chapter, contains a large number of parameters. These parameters fall into two different categories: model parameters and operating parameters. Model parameters are those which are specific to a given system; i.e., the packing material (e.g., biofilm specific area), characteristics of the biofilm (e.g., density), etc. Operating parameters are those which can be varied through design and they involve the concentration of the VOC in the airstream supplied to the biofilter, the rate of either air supply (volumetric) or VOC supply (mass) to the filter-bed, etc.

The work presented here falls into two categories. The first category of studies involved sensitivity studies with regard to the model parameters. The intent of these studies was to examine the impact of potential uncertainties in the values of a given model parameter on the predicted required size for a biofilter. In these studies, the biofilter was assumed to be supplied with a given VOC concentration and required to achieve a given percent removal of the pollutant. Sensitivity studies were performed by changing the value of one model parameter at a time.

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As basis for the sensitivity studies, model parameter values from earlier studies were used. These studies concerned butanol which is a hydrophilic substance [Baltzis and Androutsopoulou (1994)], and toluene which is a hydrophobic substance [Shareefdeen and Baltzis (1994)]. The earlier reported/measured parameter values are referred to here as reference values.

The second category of studies reported here concern the operating parameters. Using the reference values of model parameters, the intent here was to find the required biofilter volume as a function of the inlet pollutant concentration for given values of rate of pollutant mass supply (load) to the biofilter bed. These studies are referred to as sizing calculations.

As mentioned earlier, two sets of reference parameter values were employed in the present study. The intent was to find if the same or different parameters are most important in the cases of hydrophilic and hydrophobic solvents. The use of parameters for butanol and toluene was due to the fact that these substances had been earlier used in detailed biofiltration experiments [Androutsopoulou (1994), Shareefdeen (1994)].

4.1 Model Equations and Numerical Methods

For airstreams carrying a single volatile organic compound (VOC) the biofiltration process in a classical biofilter can be described by the following mass balances, under steady-state conditions [Shareefdeen et al. (1993), Shareefdeen (1994)].
I. Mass balance for VOC j in the biolayer at a position h along the biofilter bed:

$$f(X_{v})D_{jw}\frac{d^{2}s_{j}}{dx^{2}} = \frac{X_{v}}{Y_{j}}\mu_{j}(s_{j},s_{0})$$
(4.1)

with boundary conditions,

$$s_j = \frac{c_j}{m_j} \qquad \text{at } x = 0 \qquad (4.2)$$

$$\frac{ds_j}{dx} = 0 \qquad \text{at} \quad x = \delta \tag{4.3}$$

Equation (4.1) implies that the rate of diffusion of VOC j in the biolayer is equal to the rate of its biodegradation.

II. Mass balance for oxygen in the biolayer at a position h along the biofilter bed:

$$f(X_{v})D_{Ow}\frac{d^{2}s_{O}}{dx^{2}} = \frac{X_{v}}{Y_{Oj}}\mu_{j}(s_{j},s_{O})$$
(4.4)

with boundary conditions,

$$s_0 = \frac{c_0}{m_0} \qquad \text{at } x = 0 \tag{4.5}$$

$$\frac{ds_0}{dx} = 0 \qquad \text{at} \quad x = \delta \tag{4.6}$$

Equation (4.4) implies that the rate of oxygen diffusion in the biolayer is equal to the rate of oxygen consumption in the biodegradation process.

III. Mass balance for VOC j in the airstream at a position h along the biofilter bed:

$$\frac{H}{\tau}\frac{dc_{j}}{dh} = A_{s}f(X_{v})D_{jw}\left[\frac{ds_{j}}{dx}\right]_{x=0}$$
(4.7)

with boundary condition,

$$c_j = c_{ji} \qquad \text{at} \quad h = 0 \qquad (4.8)$$

Equation (4.7) implies that the rate of loss of VOC j from the air along the biofilter is equal to the rate at which VOC j is transferred to the biolayer. This transfer is expressed as a flux.

IV. Mass balance for oxygen in the airstream at a position h along the biofilter bed:

$$\frac{H}{\tau} \frac{dc_0}{dh} = A_s f(X_v) D_{0w} \left[\frac{ds_0}{dx} \right]_{x=0}$$
(4.9)

with boundary condition,

$$c_{\rm O} = c_{\rm Oi} \qquad \text{at} \quad h = 0 \qquad (4.10)$$

The terms in equation (4.9) have the same meaning for oxygen as those in equation (4.7) have for VOC j.

Function $\mu(s_j, s_0)$ which appears in equations (4.1) and (4.4) assumes the following form,

$$\mu_{j}(s_{j}, s_{O}) = \frac{\mu_{j} s_{j} s_{O}}{\left(K_{j} + s_{j} + s_{j}^{2} / K_{Ij}\right)\left(K_{O} + s_{O}\right)}$$
(4.11)

when the degradation kinetics follow an Andrews expression with respect to the availability of the carbon source (VOC), and a Monod expression with respect to the availability of oxygen.

As has been shown by Shareefdeen et al. (1993) and Shareefdeen (1994) the model equations above can be brought in a dimensionless form once the following quantities are introduced,

$$\overline{s}_j = \frac{s_j}{K_j}, \qquad \overline{s}_O = \frac{s_O}{K_O}, \qquad \overline{c}_j = \frac{c_j}{c_{ji}}, \qquad \overline{c}_O = \frac{c_O}{c_{Oi}}, \qquad \gamma = \frac{K_j}{K_{lj}},$$

$$\lambda = \frac{D_{jw}K_{j}Y_{j}}{D_{ow}K_{o}Y_{oj}}, \qquad \phi^{2} = \frac{\mu_{j}\delta X_{v}}{f(X_{v})D_{jw}K_{j}Y_{j}}, \qquad \eta = \frac{A_{s}f(X_{v})D_{jw}K_{j}\tau}{\delta c_{ji}},$$
$$\omega = \frac{K_{0}D_{ow}c_{ji}}{K_{j}D_{jw}c_{oi}}, \qquad \varepsilon_{1} = \frac{c_{ji}}{K_{j}m_{j}}, \qquad \varepsilon_{2} = \frac{c_{oi}}{K_{0}m_{0}}, \qquad \theta = \frac{x}{\delta}, \qquad z = \frac{h}{H}$$

Equations (4.1)-(4.10), when expression (4.11) is also taken into account, take correspondingly the following form.

$$\frac{\mathrm{d}^2 \bar{\mathrm{s}}_j}{\mathrm{d}\theta^2} = \phi^2 \frac{\bar{\mathrm{s}}_j \bar{\mathrm{s}}_0}{\left(1 + \bar{\mathrm{s}}_j + \gamma \bar{\mathrm{s}}_j^2\right) \left(1 + \bar{\mathrm{s}}_0\right)} \tag{4.12}$$

$$\overline{s}_j = \varepsilon_1 \overline{c}_j$$
 at $\theta = 0$ (4.13)

$$\frac{d\bar{s}_j}{d\theta} = 0 \qquad \text{at } \theta = 1 \qquad (4.14)$$

$$\frac{d^2 \bar{s}_O}{d\theta^2} = \phi^2 \lambda \frac{\bar{s}_j \bar{s}_O}{\left(1 + \bar{s}_j + \gamma \bar{s}_j^2\right) \left(1 + \bar{s}_O\right)}$$
(4.15)

$$\bar{s}_0 = \epsilon_2 \bar{c}_0$$
 at $\theta = 0$ (4.16)

$$\frac{d\bar{s}_0}{d\theta} = 0 \qquad \text{at} \quad \theta = 1 \tag{4.17}$$

$$\frac{d\bar{c}_{j}}{dz} = \eta \left[\frac{d\bar{s}_{j}}{d\theta} \right]_{\theta=0}$$
(4.18)

$$\overline{c}_{j} = 1 \qquad \text{at} \quad z = 0 \qquad (4.19)$$

$$\frac{d\bar{c}_{0}}{dz} = \eta \omega \left[\frac{d\bar{s}_{0}}{d\theta} \right]_{\theta=0}$$
(4.20)

$$\bar{c}_0 = 1$$
 at $z = 0$ (4.21)

As has been shown by Shareefdeen et al. (1993), the four dependent variables $(\bar{s}_i, \bar{s}_0, \bar{c}_j, \bar{c}_0)$ are interrelated through the following two algebraic equations:

$$\overline{c}_{j} = \frac{\overline{c}_{0} - 1}{\lambda \omega} + 1 \tag{4.22}$$

$$\bar{s}_{j} = \frac{\bar{s}_{0}}{\lambda} - \varepsilon_{1} \left(\frac{1}{\lambda \omega} - 1 \right) - \frac{1}{\lambda} \left(\varepsilon_{2} - \frac{\varepsilon_{1}}{\omega} \right) \bar{c}_{0}$$
(4.23)

It is easy to show that equations (4.22) and (4.23) can be equivalently expressed as follows:

$$\bar{c}_{O} = \lambda \omega \left(\bar{c}_{j} - 1 \right) + 1 \tag{4.24}$$

$$\bar{s}_{O} = \lambda \bar{s}_{j} - \lambda (\varepsilon_{1} - \omega \varepsilon_{2}) \bar{c}_{j} - \varepsilon_{2} (\lambda \omega - 1)$$
(4.25)

Because of relations (4.22)-(4.25) one needs to solve two rather than four differential equations. There are two possible sets; set 1: equations (4.12)-(4.14), (4.18), (4.19), (4.24), and (4.25); set 2: equations (4.15)-(4.17), and (4.20)-(4.23). From the numerical point of view, one needs to keep differential equations referring to variables which exhibit the largest gradient. Hence, in cases where the VOC gets depleted faster than oxygen (in the biolayer) one needs to work with the equations of set 1, while in cases where oxygen is changing (in the biolayer) faster than the VOC one needs to work with the equations of set 2.

The volume (size) of a biofilter bed can be calculated via the following two formulas:

$$V = \tau F \tag{4.26}$$

$$V = \tau \frac{L}{c_{j_i}}$$
(4.27)

where L is the rate of VOC-mass supply to the biofilter (mass of VOC supplied to the biofilter per unit time). Although L is called load here, it is recognized that the usual definition of load is "amount of VOC supplied to the biofilter per unit time and per unit volume of packing material."

The model equations have been solved through the use of computer codes which are based on the use of the orthogonal collocation method for solving equation (4.12) [or (4.15)], and the Runge-Kutta method for solving equation (4.18) [or (4.20)]. In cases where both set 1 and set 2 of the model equations had to be used, due to changes in what compound is consumed first in the biolayer at different locations of the biofilter bed, the location of the change was first determined and each segment was solved as a separate biofilter. The codes used were primarily those developed earlier [Sharcefdeen et al. (1993); Shareefdeen (1994); Baltzis (1994)] while some parts were recently revised and/or refined by Tsangaris and Baltzis. These codes are given in Appendix C of this thesis.

4.2 Sensitivity Studies

As can be seen from equations (4.1)-(4.11) the model parameters are the following: kinetic parameters $[Y_{j}, Y_{0j}, and the four constants included in expression (4.11)];$ diffusion coefficients (D_{jw}, D_{0w}) of the VOC and oxygen in water; correction of diffusivities for biofilm $[f(X_V)]$; distribution coefficients or Henry's constants (m_j, m_0) for the VOC and oxygen; biofilm density (X_V) ; specific surface area of biofilm (A_S) . The thickness of the active biofilm (δ) is a model parameter but varies with the location in the biofilter bed. It is calculated through a trial and error procedure through the computer code [Shareefdeen et al. (1993)]. The correction factor for diffusivities $[f(X_V)]$ is a function of X_V as described by the correlation of Fan et al. (1990) and thus, it was not individually varied. With the exception of the yield coefficients, all other parameters were examined in sensitivity studies.

The results of the sensitivity studies are shown graphically in Figures A-1 through A-16. The x-axis in these graphs represents the relative value of the parameter studied. This relative value is defined as the ratio of the assumed value for that parameter to its reference one (reported in Table 4.1). The y-axis shows the residence (or space-) time required for achieving a given conversion of the pollutant. In all cases, two inlet concentrations of the pollutant (0.5 and 1.0 g/m³) were considered and for each concentration two levels of removal (95% and 99%) were examined. Since the residence time, τ , is defined as F/V, once the flowrate is specified the volume can be calculated, or for a biofilter of a given size the value of τ dictates the value of the flowrate of the polluted airstream which can be treated (to the conversion indicated) in the given unit.

| Parameter | Value | Units |
|--------------------------|------------------------|-------------------|
| A _s (butanol) | 38 | m |
| A _s (toluene) | 40 | m ⁻¹ |
| c _{Oi} | 275x10 ⁻³ | kg/m ³ |
| D_{BW} | 0.77×10^{-9} | m^2/s |
| D _{TW} | 1.03×10^{-9} | m^2/s |
| D _O | 2.41x10 ⁻⁹ | m ² /s |
| $f(X_V)$ | 0.195 | |
| μ _p | 0.579 | h^{-1} |
| μ* μ* | 1.50 | h ⁻¹ |
| K _B | 0.952 | kg/m ³ |
| K _T | 11.03×10^{-3} | kg/m ³ |
| K _{1B} | 0.857 | kg/m ³ |
| K _{IT} | 78.94×10^{-3} | kg/m ³ |
| Ko | 0.26×10^{-3} | kg/m ³ |
| m _B | 0.00036 | |
| m _T | 0.27 | |
| m _o | 34.4 | |
| Y _B | 0.458 | kg/kg |
| Y _T | 0.708 | kg/kg |
| Y _{OB} | 0.232 | kg/kg |
| Y _{OT} | 0.341 | kg/kg |
| Χ _ν | 100 | kg/m ³ |

Table 4.1 Base-values of model parameters for solving the steady-state equations^{*}

* Values taken from Androutsopoulou (1994) and Shareefdeen (1994)

During the studies reported here, the value of each parameter was changed (by one-tenth increments) from one-tenth to two times its reference value. For the sensitivity studies, and for the inlet concentration values considered, the calculations showed that for the case of butanol it is always oxygen which is depleted first in the biolayer. Hence, equations of set 2 (section 4.1) were used in the calculations. In the case of toluene the calculations showed that toluene rather than oxygen gets depleted first in the biolayer. For this reason, all calculations for the toluene case are based on the solution of equations of set 1 (section 4.1).

4.2.1 Kinetic Parameters

From expression (4.11) one can see that the kinetic expression involves four constants. The sensitivity of the model to the values of these constants can be judged from the results shown in Figures A.1 through A.8.

Figures A-1 and A-2 show the sensitivity of the model to the values of parameter μ_j^* . As can be seen from the graphs, for relative μ_j^* values larger than 1 the predicted τ values change slightly while for relative values less than 1 there is a very substantial effect on the predicted τ values. The conclusion here is that for both hydrophilic and hydrophobic compounds, accurate knowledge of the value of μ_j^* is important. It is also interesting to notice that the curves representing 95% and 99% conversion are very close to one another in both cases considered for butanol (Figure A-1) while they are far apart in the case of toluene (Figure A-2). Although there is not enough evidence to be sure about it, this difference may be due to the different actual values of μ_B^* and μ_T^* (observe that μ_T^* is almost 3 times the value of μ_B^*).

Figures A-3 and A-4 show the sensitivity of the model to the value of kinetic parameter K_j . In both cases, as the value of K_j increases the value of τ also increases. However, for the case of butanol the changes in τ are insignificant, while for the case of toluene they are quite substantial. This difference could be possibly attributed to the actual values of K_B and K_T which are different by almost two orders of magnitude. As in the case of μ_j^* one can observe that the 95 and 99% conversion curves are very close to one another in the case of butanol as opposed to the case of toluene. Figures A-5 and A-6 show the sensitivity of the model to the values of the inhibition constant K_{ij} . In the case of butanol (Figure A-5) the model is sensitive only when K_{IB} is underestimated (relative values less than 1). In the case of toluene (Figure A-6) the model is totally insensitive to the value of parameter K_{IT} . It should be observed that the reference values of K_{IB} and K_{IT} differ by one order of magnitude. One could possibly argue that the more inhibitory a compound is (K_{Ij} small) the less sensitive the model is to the K_{Ij} value. It should be also observed that the value (reference) of K_{Ij} for toluene is so small that it essentially remains the same when the relative value is varied from 0.1 to 2. This may explain the completely flat profiles of Figure A-6.

Figures A-7 and A-8 show the sensitivity of the model to the value of the kinetic constant which is related to oxygen (K_0). In all cases the model is insensitive to the actual K_0 value. This is an important result because the K_0 values spanned during this study cover essentially the entire spectrum of K_0 values which have been measured in various studies [Shareefdeen et al. (1993)].

If a general conclusion can be drawn from the sensitivity studies with the kinetic model parameters, it is the following. It appears that in all cases, two -not necessarily the same- kinetic parameters have to be known accurately or measured (μ_B^* and K_{IB} for butanol, μ_T^* and K_T for toluene). If two kinetic parameters are important, any effort to represent kinetics by a single parameter (zero- or first-order kinetics) is bound to lead to significant errors in sizing a biofilter unit.

4.2.2 Diffusion Coefficients

Figures A-9 and A-10 show the sensitivity of the model to the value of the diffusivity of the pollutant in water (or the biofilm since X_V is taken constant here). In the case of butanol the actual value of D_{BW} has absolutely no impact on the predicted value of τ , which is exactly the opposite to what happens in the case of toluene. It is worth observing from Figure A-10 that a serious mistake is made not only when D_{TW} is underestimated (relative value less than 1), but also when it is overestimated, as a slight overestimation leads to considerable underestimation of τ (observe that the τ values are large in the case of Figure A-10). This difference in behavior of butanol and toluene is hard to understand as the reference values of the two compounds are comparable. It may simply be the combined effect of the kinetics and mass transfer. This point needs further elaboration.

4.2.3 Distribution Coefficients

The sensitivity of the model to the value of Henry's constant, m_j , can be judged from the diagrams of Figures A-11 and A-12. For the case of toluene, m_T appears to be of considerable importance as there is an almost perfectly linear relation between the uncertainty in m_T and τ . In the case of butanol, for high inlet concentration values (Figure A-11b) severe underestimation of m_B creates problems. In all other cases the impact of m_B is minimal. It is interesting however to observe the shape of the constant conversion isoclines. They go through a minimum when the relative m_B value is about 0.7 in Figure A-11a and 1.4 in Figure A-11b. Although the existence of a minimum in

the case of Figure A-11b is not very clear from the graph, it does actually occur. It should be added here that since a lot of thermodynamic data are in fact available, it is unlikely that m_j is not known with certainty. What the graphs of Figures A-11 and A-12 actually (although indirectly) indicate, is the effect of uncertainty in the value of temperature which affects the m_j value.

4.2.4 Biofilm Density

Precise knowledge of the biofilm density, X_V , does not appear to affect biofilter size calculations unless the relative value is significantly less than 1. This can be seen from the diagrams of Figures A-13 and A-14. It should be also added that the reference (base) value for X_V is 100 kg/m³. As has been discussed by Shareefdeen et al. (1993) the reported X_V values are between 23 and 220 kg/m³. Hence, relative X_V values should be between 0.23 and 2.2. As can be seen from the graphs, the τ calculations are not sensitive to X_V for the aforementioned range of relative X_V values. A similar conclusion regarding toluene was reached by Shareefdeen and Baltzis (1994), who followed a different approach in sensitivity studies. It should be also mentioned here that since the correction for diffusivities $[f(X_V)]$ is a function of X_V , the results of Figures A-13 and A-14 were actually obtained by varying both X_V and $f(X_V)$. The dependence of $f(X_V)$ on X_V was taken to be that reported by Fan et al. (1990).

4.2.5 Specific Surface Area of Biofilm

The parameter to which the model appears to be most sensitive is A_S , the specific area of biofilm. This can be seen from the graphs of Figures A-15 and A-16. For relative values larger than 0.5 there is an almost linear relationship of slope -1. That is, if the surface area is doubled, the required residence time is halved. For very small relative values, the relation between A_S and τ is almost exponential. The fact that A_S has such a major impact on predicting τ is not surprising as it directly relates to the amount of biomass (catalyst) which is in direct contact with the pollutant. This finding implies that the packing configuration is very important.

4.2.6 Conclusions from Sensitivity Studies

Based on the results obtained in the sensitivity studies discussed in the preceding sections, the following conclusions can be reached.

In all cases, parameters μ_j^* and A_s are very important. Also in all cases, a second kinetic parameter is also important, but its identity depends on the compound. If the compound is highly inhibitory this second kinetic parameter is K_j , while for non-strong inhibitors K_{lj} is important. Finally, parameters m_j and D_{jw} appear to be significant only for highly volatile and inhibitory compounds.

4.3 Biofilter Sizing Calculations

As has been mentioned earlier, biofilter sizing calculations refer to studies with the operating parameters of the model. As can be seen from equations (4.1)-(4.11) these

parameters are the inlet concentrations of the VOC and oxygen (c_{ji}, c_{Oi}) , the biofilter height (H), and the residence time (τ) . Parameters H and τ always appear as a ratio (H/τ) and for this reason H was kept constant while τ was calculated. The inlet oxygen concentration was never varied since it was assumed that only atmospheric air is supplied to the biofilter. In these calculations the reference values of the model parameters were used (Table 4.1).

It should be mentioned here that for the case of butanol, as in the case of the sensitivity studies, it was found that oxygen is always depleted first. Thus, equations of set 2 were used (see preceding section). For the case of toluene, and for inlet concentration values exceeding 2.8 g/m^3 , it was found that in a segment of the biofilter bed close to the entrance oxygen is depleted first (hence, set 2 was used), but in the remaining part of the reactor (till a desired exit concentration level or conversion is achieved) toluene is depleted first in the biofilm (hence, equations of set 1 were used). This switching requires a considerable amount of additional calculations in order to determine the exact location of the changeover.

Figures A-17 and A-18 show the required residence time for two conversion levels as a function of the inlet concentration. These diagrams can be used in determining the required volume of a unit in two different cases: when the flowrate of the contaminated airstream is specified, or when the load (rate of mass supply) is dictated. The conversion of τ to volume can be easily made via equations (4.26) and (4.27). Once again, it is worth noticing that in the butanol case the additional τ for getting 99% rather than 95% conversion of the pollutant is not significant. However, for the case of toluene going from 95 to 99% conversion requires a significantly larger biofilter (Figure A-18).

Figures A-19 to A-22 show actual volume calculations when the load is specified. In this portion -for each value of load- four cases were considered: two based on conversion, and two based on exit concentrations. The most important feature of these diagrams is that there are cases (butanol, Figures A-19 and A-21) in which the isoclines go through a minimum. This is a finding originally reported by Baltzis (1994) for the case of ethanol. It suggests that if the inlet concentration is higher than that at which the minimum occurs one could -significantly- reduce the biofilter volume by diluting the contaminated airstream with pure air while keeping the load constant. The same is observed for the case of toluene, but it is only of mathematical/numerical importance as the minimum occurs at unrealistic concentration values in the order of 100 g/m³.

CHAPTER 5

TRANSIENT BIOFILTRATION OF SINGLE VOCs

In this chapter, results from sensitivity studies with a transient biofiltration model are presented. This model was originally developed by Shareefdeen and Baltzis (1994) and is given in the next section of this chapter.

There is a substantial difference between steady-state and transient biofiltration and this is what makes the results presented here particularly important. This difference is that, with the materials used for packing classical biofilters, transient operation involves an extra process. This is the adsorption of VOCs to the packing material, a process which does not affect steady-state behavior since at steady-state the adsorption process is at equilibrium.

In general, the questions pertaining to transient operation refer to the time required for the system to (practically) reach steady-state and the form of the response. The form of the response may be such that concentrations exhibit an overshoot which is potentially unacceptable. Hence, the intent of the sensitivity studies with the transient biofiltration model was to examine the impact of various parameters on the key features of the response of a biofilter during transients.

5.1 Model Equations and Numerical Methodology

The basic model equations describing transient biofiltration of airstreams carrying a single pollutant (VOC) are mass balances written for three phases: biofilm, air, and solids (packing material). These equations, taken from Shareefdeen and Baltzis (1994), are as follows:

I. Mass balance for VOC j and for oxygen in the biofilm:

$$\frac{\partial s_j}{\partial t} = f(X_v) D_{jw} \frac{\partial^2 s_j}{\partial x^2} - \frac{X_v}{Y_j} \mu_j(s_j, s_0)$$
(5.1)

$$\frac{\partial s_0}{\partial t} = f(X_v) D_{0w} \frac{\partial^2 s_0}{\partial x^2} - \frac{X_v}{Y_0} \mu_j(s_j, s_0)$$
(5.2)

II. Mass balances for VOC j and for oxygen in the gas phase:

$$\upsilon \frac{\partial c_{j}}{\partial t} = -u_{g} \frac{\partial c_{j}}{\partial h} + D_{jw} f(X_{v}) \alpha A_{s}^{*} \left(\frac{\partial s_{j}}{\partial x} \right)_{x=0} - k_{a} (1-\alpha) A_{s}^{*} (c_{j} - c_{j}^{*})$$
(5.3)

$$\upsilon \frac{\partial c_{O}}{\partial t} = -u_{g} \frac{\partial c_{O}}{\partial h} + D_{Ow} f(X_{V}) \alpha A_{s}^{*} \left(\frac{\partial s_{O}}{\partial x}\right)_{x=0}$$
(5.4)

III. Mass balance for VOC j in the solid phase (particles):

$$(1-\upsilon)\rho_{\rm P}\frac{\partial c_{\rm jp}}{\partial t} = k_{\rm a}(1-\alpha)A_{\rm s}^{*}(c_{\rm j}-c_{\rm j}^{*})$$
(5.5)

Equations (5.1) - (5.4) are the unsteady state versions of equations (4.1), (4.4), (4.7), and (4.9), respectively. The sole difference is the last term in equation (5.3) which stands for the rate of mass transfer of VOC j to the solid particles (excluding biolayer). Equation

(5.5) expresses that the rate of accumulation of VOC j in the solid particles is equal to the rate of mass transfer of VOC j to the particles. These equations are a set of partial differential equations, and their corresponding initial and boundary conditions can be found in Shareefdeen and Baltzis (1994) and Shareefdeen (1994).

Function $\mu_j(s_j,s_0)$ appearing in equations (5.1) and (5.2) expresses the kinetics of biodegradation and -as was also the case in Chapter 4- it is given by the following expression:

$$\mu_{j}(s_{j}, s_{0}) = \frac{\mu_{j}s_{j}}{K_{j} + s_{j} + \frac{s_{j}^{2}}{K_{1j}}} \frac{s_{0}}{K_{0j} + s_{0}}$$
(5.6)

The driving force for the mass transfer of the VOC from the air (gas phase) to the particles (solid phase) is $c_j - c_j^*$, as indicated in equations (5.3) and (5.5). Concentration c_j^* is related to the concentration of VOC in the solid phase through an adsorption isotherm. For the case of toluene, this isotherm was found [Shareefdeen (1994)] to follow the Freundlich equation. Hence, one can write

$$c_{jp} = k_d (c_j^*)^n \tag{5.7}$$

Equations (5.1) - (5.5) have not been exactly solved to date. They have been solved through an approximation which introduces the use of effectiveness factors defined as,

$$e_{j} = \frac{f(X_{v})D_{jw}\left(\frac{\partial s_{j}}{\partial x}\right)_{x=0}}{\delta \frac{X_{v}}{Y_{j}}[\mu_{j}(s_{j}, s_{0})]_{x=0}}$$
(5.8)
$$e_{0} = \frac{f(X_{v})D_{ow}\left(\frac{\partial s_{0}}{\partial x}\right)_{x=0}}{\delta \frac{X_{v}}{Y_{0}}[\mu_{j}(s_{j}, s_{0})]_{x=0}}$$
(5.9)

Actually it can be easily shown that $e_T = e_0$. The use of the effectiveness factor allows for omission of equations (5.1) and (5.2). Details of this approximation can be found in the original references [Shareefdeen and Baltzis (1994) and Shareefdeen (1994)], where it is also shown that the problem reduces to the following set of equations

$$\frac{\partial \overline{c}_{j}}{\partial \zeta} = -\frac{1}{\upsilon} \frac{\partial \overline{c}_{j}}{\partial z} - \beta_{1} g(\overline{c}_{j}, \overline{c}_{0}) - \beta_{3} (\overline{c}_{j} - \overline{c}_{j}^{*})$$
(5.10)

$$\frac{\partial \bar{c}_{0}}{\partial \zeta} = -\frac{1}{\upsilon} \frac{\partial \bar{c}_{0}}{\partial z} - \beta_{2} g(\bar{c}_{j}, \bar{c}_{0})$$
(5.11)

$$\frac{\partial \bar{c}_{j^{p}}}{\partial \zeta} = \beta_{3}(\bar{c}_{j} - \bar{c}_{j})$$
(5.12)

where

$$g(\bar{c}_{j}, \bar{c}_{0}) = \frac{\varepsilon_{1}\bar{c}_{j}}{(1 + \varepsilon_{1}\bar{c}_{j} + \varepsilon_{1}^{2}\gamma\bar{c}_{j}^{2})} \frac{\varepsilon_{2}\bar{c}_{0}}{(1 + \varepsilon_{2}\bar{c}_{0})}$$
(5.13)

and

$$\overline{c}_{j}^{*} = \psi(\overline{c}_{jP})^{\frac{1}{n}}$$
(5.14)

The initial and boundary conditions for equations (5.10) - (5.14) are,

$$\overline{c}_j = 1, \quad \overline{c}_0 = 1, \quad \overline{c}_{jP} = \overline{c}_{jP,0}(0) \quad \text{at } \zeta = 0 \text{ and } z = 0$$
 (5.15)

$$\overline{c}_{j} = \overline{c}_{j,0}(z), \quad \overline{c}_{0} = \overline{c}_{0,0}(z), \quad \overline{c}_{j\mu} = \overline{c}_{j\mu,0}(z) \quad \text{at } \zeta = 0 \text{ and } 0 < z \le 1$$
(5.16)

$$\tilde{c}_j = 1, \qquad \tilde{c}_0 = 1 \qquad \text{at } \zeta \ge 0 \text{ and } z = 0 \qquad (5.17)$$

Equations (5.10) - (5.12) are in dimensionless form, and the dimensionless quantities appearing in them are related to the dimensional quantities of the original equations through the following,

$$\overline{c}_{j} = \frac{c_{j}}{c_{ji}}, \qquad \overline{c}_{j} = \frac{c_{j}}{c_{ji}}, \qquad \overline{c}_{0} = \frac{c_{0}}{c_{0i}}, \qquad \overline{c}_{jp} = \frac{(1-\upsilon)\rho_{p}c_{jp}}{\upsilon c_{ji}},$$

$$z = \frac{h}{H}, \qquad \zeta = \frac{t}{\tau}, \qquad \varepsilon_{1} = \frac{c_{ji}}{m_{j}K_{j}}, \qquad \varepsilon_{2} = \frac{c_{0i}}{m_{0}K_{0}}, \qquad \gamma = \frac{K_{j}}{K_{lj}},$$

$$\beta_{1} = \frac{e_{j}\alpha\delta A_{s}^{*}X_{v}\mu^{*}\tau}{Y_{j}c_{ji}\upsilon}, \qquad \beta_{2} = \frac{e_{0}\alpha\delta A_{s}^{*}X_{v}\mu^{*}\tau}{Y_{0}c_{0i}\upsilon},$$

$$\beta_{3} = \frac{k_{a}(1-\alpha)A_{s}^{*}\tau}{\upsilon}, \qquad \psi = \frac{1}{c_{ji}} \left[\frac{\upsilon c_{ji}}{(1-\upsilon)\rho_{p}k_{d}}\right]^{\frac{1}{n}}$$

Equations (5.10) - (5.12) cannot be solved unless expressions for δ and e are available. For the case of toluene, and for relatively low toluene concentrations in an airstream fed to a biofilter such expressions were derived by Shareefdeen (1994), and they have been used in the present study. Solution of equations (5.10) - (5.12) was based on a computer code which employs the method of finite differences in the z-direction and integration of the resulting set of ordinary differential equations via the ODESSA algorithm. The basic code was that of Shareefdeen (1994), modified by Tsangaris and updated for the purposes of this study. The code is given in Appendix D of this thesis.

5.2 Results and Discussion

An example of concentration profiles at various locations in the biofilter bed is given in Figure 5.1. From this figure it is interesting to observe that the exit concentration (which is the most important concentration from the practical point of view) overshoots (albeit slightly) the eventual steady-state value. For this reason, it was decided to perform sensitivity studies with regard to the degree of overshoot and the time at which it occurs. Another parameter which was investigated was the time needed to achieve the steadystate level of operation. Mathematically, it takes an infinite amount of time to reach steady-state. Here, the time for reaching 50 and 90% of the steady-state level was investigated. The steady-state exit concentrations (from which the 50 and 90% values were calculated) were obtained by solving the transient model, and allowing the model to run until no further changes occurred in the exit concentration (usually several days). This was done only once for each set of studies as transient parameters do not affect steady state values. Although the steady-state model from the previous chapter could had been utilized, it was found that there were slight differences between the steady-state concentrations determined by these two models. This is due to the approximation required for the determination of the effectiveness factor.

As can be seen from the basic model equations (5.1) - (5.7) the model contains a number of various parameters. All parameters discussed in Chapter 4 are also present in the transient model. Although some of these parameters may be affecting transient behavior (e.g., overshoot of exit concentration), they were not examined during the course of the present work. They were kept constant at the values (measured or



Figure 5-1 Transient concentration profile in a biofilter bed at the exit, 2/3 height, and 1/3 height (curves 1, 2, and 3, respectively). The dashed line represents the steady-state exit concentrations

estimated) by Shareefdeen (1994) and reported in Table 5.1. The parameters which were examined here were those which appear in the transient, but not in the steady-state model. These are, the void fraction of the bed (υ), the density of the packing material (ρ_p), the fraction of the surface area covered by biofilm (α), the mass transfer coefficient (k_a), and the Freundlich constant (k_d). Base values for these parameters are also given in Table 5.1. Parameters which affect the transient behavior but were not studied here are, the second Freundlich constant (n) and the initial distributions of VOC concentration on the solids and in the air [$c_{jp}(h)$ and $c_j(h)$ at t = 0]. The latter appear in the boundary conditions of the model equations and for the purposes of the studies reported here it was always assumed that $c_{jp}(h) = c_j(h) = 0$ at t = 0. The implication is that the results are valid

| Parameter | Value | Units |
|----------------------------------|-------------------------|--------------------------|
| | 133.3 | m ⁻¹ |
| S | 275×10^{-3} | kg/m^3 |
| D | 2.41×10^{-9} | m^2/s |
| D | 1.03×10^{-9} | m^2/s |
| D_{TW} | 0.195 | |
| k _a | 6.04×10^{-3} | h ⁻¹ |
| k _a | 2.25×10^{-5} | kg/m ³ |
| K _{IT} | 78.94×10^{-3} | kg/m ³ |
| K ₀ | 0.26×10^{-3} | kg/m ³ |
| Kr | 11.03×10^{-3} | kg/m ³ |
| m _O | 34.4 | |
| m _T | 0.27 | |
| 11 | 1.04 | |
| τ | 3.09 | min |
| X _V | 100 | kg/m ³ |
| Y _{OT} | 0.341 | kg/kg |
| Y _T | 0.708 | kg/kg |
| α | 0.3 | |
| δ | 1.5c _j +33.4 | $\mu m (c_j in g/m^3)$ |
| e _T or e _O | $0.03c_{j}+0.2$ | $(c_j \text{ in g/m}^3)$ |
| υ | 0.3 | |
| ρ _p | 4.28x10 [°] | g/m ³ |
| μ _T * | 1.50 | h ⁻¹ |

 Table 5.1 Base-values of model parameters for the transient biofiltration studies*

* From Shareefdeen (1994)

under process start-up conditions, i.e., when a biofilter unit is first put into operation with new packing material.

As in the case of the studies reported in Chapter 4, only one parameter was changed at a time. Changes were made relative to the reference (or base) values given in Table 5.1. A relative value of 0.2 for a parameter, means (as in Chapter 4) that the actual value of that parameter used in the calculations is equal to 0.2 times the base value reported in Table 5.1.

Results from the studies with the transient biofiltration model are given in a graphical form in the figures of Appendix B of the thesis.

Figures B-1 through B-5 show the time needed for the exit VOC concentration to reach 50% and 90% of its steady-state value as a function of various parameters. Calculations were performed at two different VOC (toluene) concentrations in the air stream fed to the biofilter; namely, 0.5 and 2.0 g/m^3 .

Figure B-1 shows the effect of the void fraction of the biofilter bed (υ). Since this is a parameter that can be easily measured and varies from 0 to 1, actual rather than relative values of u were used and are shown in the x-axis of the two graphs. As can be seen from the graphs, it appears that there is a perfectly linear relationship between time and v. It also appears that for the two inlet concentrations tried, the time for reaching a given percentage of the steady-state level is essentially the same for a given value of u. Values of u very close to zero are meaningless because they imply that there is no room in the bed for the airstream to pass through. Values of u very close to unity are also meaningless since they imply that there is no packing -and thus, no process- in the (empty) structure. In this case, the time needed to reach steady-state is equal to the space time, if the air passes in plug flow through the vessel (structure). For realistic values of u, as u increases the adsorption process is faster (since there are less solids) but the reaction is slower in the sense that the material passes through the bed without enough time to react. The overall effect is that it takes longer to reach steady-state as u increases.

As Figure B-2 indicates, the value of the density of the packing (ρ_P) has no effect on the time needed to reach steady-state. Similar are the results with the Freundlich isotherm constant (k_d) as indicated by the graphs of Figure B-3.

The effect of parameter α (fraction of surface area covered with biofilm) on the time required to reach steady-state is shown in Figure B-4. As the graphs indicate, the effect of α is minimal. However, the following should be mentioned. The available correlations for the effectiveness factor and δ were for a value of $A_s = 40m^{-1}$. Since $A_s =$ αA_s^* , for the correlations to be valid the values of α and A_s^* were simultaneously changed so that their product remained constant. Thus, as α increases A_s^* decreases. This also implies that the area of solids available for adsorption, i.e., $(1 - \alpha)A_s^*$, also decreases. One would then expect that -if adsorption was the only process- it would take longer to reach steady-state as there is less area through which a constant amount of VOC needs to be adsorbed onto the solids. However, there is also reaction taking place. A slow-down of the adsorption leads (during transients) to higher VOC concentrations in the gas phase and this makes the reaction faster. Overall the effect is minimal, showing a slight decrease in the time needed to reach steady-state. If the explanation above is correct, one should observe an increase in the time needed to reach steady-state for higher inlet toluene concentrations. High concentration brings the kinetics into the inhibitory regime; hence, the reaction is slowed down. Since a decrease in A_s^* also slows down the adsorption process, one should observe an overall increase in time. This hypothesis was not tested during the course of this work.

Figure B-5 shows the effect of the mass transfer coefficient on the time needed to reach steady-state. Here the effect can be very substantial as the logarithmic scale of the y-axis indicates. It should be mentioned here that the curve showing the time for reaching 50% of the steady-state value at the exit exhibits the same behavior as the one indicating time for reaching 90% of the steady-state value (curve 2 in the graphs). However, for the case of curve 1 the substantial increase in time occurs at ka values which fall outside of the range of the graphs. The features of curve 2 could be potentially explained by the following arguments. At high values of k_a the pollutant is transferred fast to the solid packing and this leads to temporarily low VOC concentrations in the gas phase. This implies a lower VOC concentration in the biofilm and thus, a reduction in the reaction rate. The process is controlled by kinetics and thus the value of ka does not affect the time of response (upper plateau of curve 2). At low k_a values, the adsorption process is slow, but it leads to very fast kinetics due to the higher concentrations in the air and the biofilm. Hence, the process is again under kinetic limitation and this explains the lower plateau of curve 2. In the intermediate regime the process is under both mass transfer and kinetic control. It should be mentioned here that there is a lot of uncertainty in the values of ka since there are not experimental data for them. Further studies are needed here.

As was mentioned earlier, in conjunction with Figure 5.1, there are cases in which the exit biofilter concentration overshoots the steady-state exit concentration. Computer simulations have shown that almost invariably, the exit concentration exhibits a peak. However, with the reference values this peak does not exceed the steady-state value. In fact, a maximum (peak) is observed and then the concentration falls and subsequently rises and stabilizes at a level higher than the peak. In such cases, the existence of the concentration peak is unimportant from the practical point of view. This was the case for the studies performed with low inlet concentrations (2.0 g/m³) and shown in the graphs of Figures B-6 through B-8. The only parameters found to affect the concentration at the peak are α and k_a (Figures B-7a and B-8). Observe that for very high α -values or very low values of k_a the peak concentration is a real overshoot; that is, it exceeds the steadystate value. This becomes an important factor (at realistic α and k_a values) when the inlet VOC concentration increases. The time at which the peak concentration occurs is only affected by the void fraction of the bed, as Figure B-9 indicates. A comparison of Figures B-1 and B-9 shows that as υ increases the extent of the transient period of the process increases from every point of view.

A small effort was made in examining whether the inlet concentration value of the VOC affects the extent of the transients of the process. An example is shown in Figure B-10. The effect of inlet concentration appears to be minimal. However these results should be considered with extreme caution as they were obtained based on correlations for δ and e (Table 5.1) which were originally derived for a range of inlet concentrations much narrower than the one used in Figure B-10.

The conclusion which can be drawn from the results of the studies presented in this chapter is that the transients of the biofiltration process are primarily affected by the mass transfer coefficient and the void fraction (porosity) of the biofilter bed.

CHAPTER 6

CONCEPTUAL DESIGN FOR REMEDIATION OF A CONTAMINATED AQUIFER THROUGH THE USE OF BIOFILTRATION

In this chapter results from some preliminary work performed on the conceptual design of an integrated soil venting/biofiltration process are presented. This integrated process is proposed as an alternative method for treating a contaminated aquifer. A schematic of this integrated process is shown in Figure 6.1.



Figure 6-1 Schematic of the integrated soil venting/biofiltration process.

The ideas incorporated in the schematic of Figure 6.1 are the following. Air is passed through the aquifer via multiple sparging wells. The air forces the volatile contaminants into the gas phase (air) which is then collected through vapor extraction wells. If the air exiting the soil (aquifer) contains VOCs at high concentrations which are not appropriate to be supplied to the biofilter, it is diluted with clean air. The clean air is first humidified in order to ensure that the biofilter bed will not get dry. After mixing of the two airstreams, the combined stream is passed through a biofilter. The inlet to the biofilter is at the top of the biofilter bed so that if humidification of the airstream is not 100% and thus, there is the potential of drying part of the biofilter bed, this part is at the top and can be easily brought to the correct conditions of water content by supplying water at this location. The airstream exiting the biofilter bed meets the appropriate environmental standards. Looking at the process as a whole, the inlet consists of clean air (to the sparging wells and humidification tower) and the exit (from the biofilter) also consists of clean air.

6.1 Basic Assumptions

The work presented in this chapter is based on the following assumptions.

- 1. Contamination is uniform throughout the liquid (water) contained in the aquifer. The volume of the water is constant.
- 2. There are no contaminants adsorbed on the soil.
- 3. Air sparging is uniform throughout the aquifer.
- 4. All air supplied to the soil at sparging points is recovered at the extraction wells.

- 5. There is a single contaminant (toluene was assumed) in the aquifer.
- 6. The contaminant in the liquid phase (aquifer) and the gas phase (air) is in equilibrium at all times. The equilibrium distribution is dictated by Henry's law.

Based on the foregoing assumptions, one can write the following equations,

$$V_{L}\frac{dc_{L}}{dt} = -Q_{G}c_{G}$$
(6.1)

$$\mathbf{c}_{\mathrm{G}} = \mathbf{m}_{\mathrm{j}} \mathbf{c}_{\mathrm{L}} \tag{6.2}$$

Combining equations (6.1) and (6.2) and integrating the resulting equation leads to the following expression,

$$c_{L} = c_{Lo} e^{-\frac{Q_{G}m_{j}t}{V_{L}}}$$
(6.3)

Combining expression (6.3) with (6.2) leads to the following expression,

$$c_{G} = mc_{Lo} e^{-\frac{Q_{G}m_{j}t}{V_{L}}}$$
(6.4)

6.2 Objectives of the Design

The objectives set for the design of the integrated process were the following.

- 1. The concentration of toluene in the aquifer at the end of the remediation operation should be at or below the toluene Action Level in Groundwater as per existing regulations (see Table 6.1).
- 2. The concentration of toluene in the air exiting the extraction wells should be very close to the Threshold Limit Value (TLV) as per existing regulations (see Table 6.1).

| Parameter | Value | Units |
|---|--------------|------------------|
| Threshold Limit Value (TLV) ^a | 86.69 | g/m ³ |
| Acceptable Source Impact Level (ASIL) ^b | 0.2817 | g/m ³ |
| Action Level in Groundwater ^c | 1.0 | g/m ³ |
| ^a TIV actablished in the Federal Dec | iston(1002a) | |

 Table 6.1 Regulations for control of toluene levels

^a TLV established in the Federal Register (1993a).
 ^b ASIL established by the Washington State Department of Ecology (1994).

^c Action Level established in the Federal Register (1993b).

The TLV is the maximum concentration of a pollutant to which human exposure is allowed for short time periods. It usually relates to people in the immediate vicinity of the source (e.g. workers). For example, if there was a leak from or a rupture of the pipe carrying the air from the extraction wells people in the immediate vicinity of the accident would be exposed to the toluene concentration in the air exiting the aquifer.

- 3. The concentration of toluene at the exit of the biofilter should meet the Acceptable Source Impact Level (ASIL) as per existing regulations (see Table 6.1).
- 4. The biofilter should be exposed to relatively constant toluene concentration over the majority of the remediation operation. The maximum toluene concentration in air supplied to the biofilter should be at values for which there is experimental evidence that the process works (i.e., this concentration should not be too high). Finally the required volume of the biofilter bed should have a reasonable value.

6.3 Methodology for Calculations

The methodology followed in the calculations was as follows.

The values of various parameters for toluene (given in Chapter 4 as base-values) were used in calculations with the steady-state biofiltration model. In these calculations, the value of the toluene concentration in the air entering the biofilter was set at different levels and the required space (residence) time was calculated so that the exit toluene concentration met ASIL requirements. It was finally decided to use an inlet concentration of 9.2 g/m³ as biofiltration experiments had been performed at values close to that and showed that the process works [Shareefdeen (1994)]. Clearly, this represents the "worst case scenario" since this is the maximum value of toluene concentration that the biofilter would be faced with.

Having the space time from the calculations above (a value of $\tau = 22$ min was determined) and since $\tau = V_P/F$, a value of $F = 0.85 \text{ m}^3/\text{min}$ (30 cfm) was selected so that the volume of the biofilter bed comes to a very reasonable value of 18.70 m³.

The volumetric flowrate of the air supplied to the biofilter was kept constant at all times, and the next objective was to determine what should be the flowrate of the air sparged through the aquifer, so that the concentration profile of the toluene concentration at the inlet of the biofilter was maintained relatively constant over substantial time periods. In order to meet objective 4 (see preceding section) a trial and error approach, using expressions (6.3) and (6.4) and accounting for appropriate dilution with clean air was used. This led to the concentration profile shown in Figure 6.2. Based on this profile and taking into consideration the value of the action level for toluene in groundwater, it was determined that the remediation would take 51 days. It should be mentioned here that the minimum value for Q_G in formula (6.4) was 3 cfm, implying that



Figure 6.2 Toluene concentration profile in the air supplied to the biofilter.



Figure 6.3 Toluene concentration profile in the air exiting the biofilter.

during the first period of time shown in Figure 6.2 the air from the extraction wells is diluted with clean air at a 1:10 ratio. The value of Q_G , and that of dilution, were varied in each segment of the profile of Figure 6.2.

Once the toluene concentration prome in the air supplied to the pioniter was determined, the transient biofiltration model (discussed in Chapter 5) was used in order to determine the profile of the toluene concentration at the exit of the biofilter. This required some modifications in the computer code given in Appendix D of the thesis. This code solves the transient biofiltration problem for a single value of the inlet pollutant concentration. However here the inlet toluene concentration varies continuously as per the profile of Figure 6.2. The modifications of the code are given in Appendix E of the thesis. The results are shown in the concentration profile of Figure 6.3. The reason for performing these calculations was the following. Although the space time was originally calculated for the maximum value of inlet toluene concentration in ways that ensure exit concentration below ASIL values, this was done under steady-state conditions. However, the biofilter here works always under transient conditions. The variations in the inlet concentration imply that adsorption and desorption phenomena are also occurring during the periods of inlet concentration increase and decrease, respectively. It was thus necessary to ensure that desorption phenomena during the operation will never lead to exit concentration values exceeding ASIL. This is in fact the case, as can be seen from Table 6.2 where all parameter values (other than those mentioned for toluene in Chapters 4 and 5) and results are listed. It is worth noticing that the maximum toluene concentration at the exit of the biofilter is in fact higher than the corresponding value

| Parameter | Value | Units |
|---|--------|---------------------|
| Volume of Aquifer (V_L) | 1000 | m ³ |
| Initial Toluene Concentration in Aquifer $(c_{1,0})$ | 340 | g/m ³ |
| Volume of Biofilter (V _P) | 18.70 | m ³ |
| Flowrate of Air Supplied to Biofilter (F) | 0.85 | m ³ /min |
| Residence Time in Biofilter (τ) | 22 | min |
| Maximum Toluene Concentration at Biofilter Exit (actual) | 0.0700 | g/m ³ |
| Maximum Toluene Concentration at Biofilter Exit (steady-state model prediction) | 0.0585 | g/m ³ |
| Final Toluene Concentration in Aquifer | 0.4967 | g/m ³ |
| Time for Remediation of Aquifer | 51 | days |

Table 6.2 Parameters for the design of the integrated soil venting/biofiltration process.

determined from the steady-state biofiltration model. Thus, desorption effects need to be considered in the calculations.

6.4 Discussion of Results and Other Calculations

As the numbers in Table 6.2 indicate, with the design calculations discussed in the previous section the final toluene concentration in the aquifer is 50% of the value of the action level in groundwater while the exit concentrations from the biofilter are always substantially lower than the ASIL value. These levels were chosen as a "safety factor"

and do not add more than 4-5 days to the time needed for remediation based on values conforming exactly to the regulations. A possibly substantial reduction in remediation time could be obtained if the flowrate of the air supplied to the biofilter is increased at about the 25th day. As can be seen from Figure 6.3, after the 25th day the exit concentrations drop substantially. A decrease in space time (i.e., an increase in air flowrate) would keep the toluene concentration exiting the biofilter relatively constant. This should be investigated in the future.

Keeping most of the parameters the same as in the case of calculations discussed in the preceding section (i.e., V_P , τ , F) the values of the volume of the aquifer (V_L) and the initial concentration of toluene in the aquifer (c_{L0}) were varied and calculations were performed regarding the time needed for remediation. Essentially, these studies were based on inlet concentration profile determination (as in the case of Figure 6.2) and the intent was to get a profile with a maximum value of 9 g/m³ (for toluene at the inlet of the biofilter) which remains practically constant over most of the remediation time.

For a constant value of c_{L0} equal to 100 g/m³, Figure 6.4 shows the days required for remediation as a function of the volume of the aquifer. Similarly, for an aquifer of a constant volume of 1,000 m³ the initial (maximum) toluene concentration in the aquifer was varied and the time required for remediation was determined; these results are shown in Figure 6.5. For both cases, six calculations were performed and the results were found to fall on the straight lines shown in Figures 6.5 and 6.6.

In another set of calculations both V_L and c_{L0} were varied so that their product remained constant. As the results shown in Figure 6.6 indicate the time drops as the



Figure 6.4 Remediation time as a function of the volume of the aquifer when $c_{L0} = 100 \text{ g/m}^3$.



Figure 6.5 Remediation time as a function of the maximum toluene concentration in an aquifer of volume $1,000 \text{ m}^3$.


Figure 6.6 Remediation time as a function of c_{L0} for constant original amounts ($V_L c_{L0}$) of toluene in the aquifer. $V_L c_{L0} = 100$ kg in (a) and 10 kg in (b).

value of c_{L0} increases (which implies that the value of V_L decreases). It appears that some type of a minimum is reached. The results suggest that in a case where there is a spill, the faster it is decided to remediate it (before it spreads; spreading implies larger volume and lower concentration) the shorter is the time for that remediation. On the other hand, if the volume of the aquifer decreases due to seasonal variations in the water level and if the entire amount of the pollutant stays in the water, the results of Figure 6.6 suggest that it is better to select as the date of remediation that season which results in the lowest volume (V_L).

6.5 Conclusions

The results presented here are only from a preliminary effort to perform design calculations for an integrated soil venting/biofiltration process. The only conclusion that can be drawn is that these calculations (based on worst case scenaria in most instances) do indicate that remediation appears to be feasible in reasonable time-frames and with reasonable biofilter sizes.

Extensive studies need to be performed for this process in the future. The exit (from the biofilter) concentration profiles (e.g. Figure 6.3) need to be optimized so that concentration values do not fall far below ASIL values. This will require the use of a variable flowrate value (F). The assumption of equilibrium between aquifer and air is probably incorrect. More realistic expressions (discussed in Chapter 2 of this thesis) need to be used. It appears that future efforts need to concentrate on the air sparging portion of the process while this thesis primarily dealt with biofiltration.

CHAPTER 7

CONCLUSIONS AND RECOMMENDATIONS

The main conclusion from the sensitivity studies performed during the course of this thesis is that despite the fact that biofiltration models contain a large number of parameters, few of them need to be accurately known for safely predicting the size of a biofilter.

The parameters which mostly affect the size of biofilters are: two kinetic constants, the mass transfer coefficient, and the specific area of biofilm. Although few in number, the important parameters fall in three different categories: kinetics, flow characteristics (mass transfer), and type of packing/microbiology (the latter affect/ determine the biofilm surface area). Hence, there is no single aspect of the biofiltration process which is more important than others when it comes to design.

The fact that two kinetic parameters are important implies that efforts to model the process with one kinetic parameter (zero- or first-order kinetics) are bound to lead to inaccurate designs for biofilter units. A detailed kinetics study appears to be needed for each application. However, these studies are not too difficult or expensive to perform. The high importance of kinetic constants also implies that the selection of microorganisms for the biofilter unit is very important as kinetics depend not only on the identity of the VOC, but also on that of the bacteria (catalysts of the reaction). Determination of the mass transfer coefficient is also important. This relates to the selection of the packing material and knowledge of the air flow characteristics through the bed.

The biofilm surface area has been found to be very important. As could be anticipated, the larger the area of the biofilm the smaller is the required biofilter volume. This implies that optimal biofilter design depends on the selection of packing material which allows for complete (if possible) coverage of the surface with bacterial films. Unfortunately, experimental determination of the biofilm surface area is not easy, if at all possible. New techniques need to be developed before this parameter can be accurately determined.

Another interesting finding from this study is that in some cases the size of the biofilter has a complex dependence on the inlet concentration. The existence of a minimum volume under constant load for the case of butanol suggests (as originally reported by Baltzis (1994) for the case of ethanol) that one could substantially reduce the required biofilter volume by mere dilution of the contaminated airstream with clean air.

Following are some recommendations for further sensitivity studies. With steadystate biofiltration models studies are needed for cases where the airstreams carry mixtures of pollutants. Regarding transient behavior, studies are needed in a number of areas. In the present study characteristic values for a hydrophobic compound were used. For the case of hydrophilic compounds other parameters (such as adsorption isotherm constants) may be important. In addition, during the present study variations in the inlet concentration of VOC were not studied regarding changes from one steady-state to another. Consequently, desorption effects which are known to occur upon a decrease in the inlet VOC concentration were not considered and need to be studied in the future. Furthermore, in this study it was assumed that the value of the mass transfer coefficient is constant at all values of air flowrates. Recent studies [Wojdyla (1996)] have developed correlations between the mass transfer coefficient and the air flowrate, and they need to be used in future sensitivity studies with the transient model. Finally, modeling and sensitivity studies are needed for the transient biofiltration of VOC mixtures.

The results from the design calculations for the integrated soil venting/ biofiltration process can only be viewed as preliminary. The air was assumed to be uniformly passing through the aquifer and always carrying toluene (the VOC) at concentrations in equilibrium with those in the aquifer. The presence of the VOC on the soil per se was not considered. Future studies need to relax the foregoing assumptions and also consider factors such as the radius of influence for the air forced into the soil and minimum (and/or maximum) air flowrates which are realistically permissible. However, the results of the first attempt to study (from the design perspective) this integrated process have shown that the process seems feasible with very reasonable biofilter volumes, the time of remediation is relatively short, and the concentration at the inlet of the biofilter can be kept relatively constant over considerable time periods. Two interesting findings were the following; in cases where there is a spill, the faster it is decided to remediate it the shorter is the time for that remediation, and that a nonspreading aquifer (or plume) can be treated faster during periods in which -due to weather changes- its volume is at a minimum level. It is believed that the work performed here

paved the path for future detailed studies on the design of the integrated soil venting/biofiltration process.

APPENDIX A

BIOFILTRATION OF SINGLE VOCs UNDER STEADY-STATE CONDITIONS: RESULTS (IN GRAPHICAL FORM) OF SENSITIVITY AND BIOFILTER SIZING STUDIES



Figure A-1 Sensitivity of the model to the value of μ_j^* for the case of butanol. Curve 1: 99% conversion; Curve 2: 95% conversion



Figure A-2 Sensitivity of the model to the value of μ_j^* for the case of toluene. Curve 1: 99% conversion; Curve 2: 95% conversion



Figure A-3 Sensitivity of the model to the value of K_j for the case of butanol. Curve 1: 99% conversion; Curve 2: 95% conversion



Figure A-4 Sensitivity of the model to the value of K_j for the case of toluene. Curve 1: 99% conversion; Curve 2: 95% conversion



Figure A-5 Sensitivity of the model to the value of K_{lj} for the case of butanol. Curve 1: 99% conversion; Curve 2: 95% conversion



Figure A-6 Sensitivity of the model to the value of K_{Ij} for the case of toluene. Curve 1: 99% conversion; Curve 2: 95% conversion



Figure A-7 Sensitivity of the model to the value of K_0 for the case of butanol. Curve 1: 99% conversion; Curve 2: 95% conversion



Figure A-8 Sensitivity of the model to the value of K_0 for the case of toluene. Curve 1: 99% conversion; Curve 2: 95% conversion



Figure A-9 Sensitivity of the model to the value of D_{jw} for the case of butanol. Curve 1: 99% conversion; Curve 2: 95% conversion



Figure A-10 Sensitivity of the model to the value of D_{jw} for the case of toluene. Curve 1: 99% conversion; Curve 2: 95% conversion



Figure A-11 Sensitivity of the model to the value of m_j for the case of butanol. Curve 1: 99% conversion; Curve 2: 95% conversion



Figure A-12 Sensitivity of the model to the value of m_j for the case of toluene. Curve 1: 99% conversion; Curve 2: 95% conversion



Figure A-13 Sensitivity of the model to the value of X_V for the case of butanol. Curve 1: 99% conversion; Curve 2: 95% conversion



Figure A-14 Sensitivity of the model to the value of X_V for the case of toluene. Curve 1: 99% conversion; Curve 2: 95% conversion



Figure A-15 Sensitivity of the model to the value of A_S for the case of butanol. Curve 1: 99% conversion; Curve 2: 95% conversion



Figure A-16 Sensitivity of the model to the value of A_S for the case of toluene. Curve 1: 99% conversion; Curve 2: 95% conversion



Figure A-17 Required residence time in a biofilter removing butanol as a function of inlet butanol concentration.

Curve 1: 99% conversion; Curve 2: 95% conversion



Figure A-18 Required residence time in a biofilter removing toluene as a function of inlet toluene concentration.

Curve 1: 99% conversion; Curve 2: 95% conversion



Figure A-19 Required biofilter volume as a function of inlet concentration for a butanol load of 2.0 kg/h.

Curve 1: 99% conversion; Curve 2: 95% conversion; Curve 3: $C_{ex}=0.01 \text{ g/m}^3$; Curve 4: Cex=0.1 g/m³



Figure A-20 Required biofilter volume as a function of inlet concentration for a toluene load of 2.0 kg/h.

Curve 1: 99% conversion; Curve 2: 95% Conversion Curve 3: $C_{ex}=0.01 \text{ g/m}^3$; Curve 4: $C_{ex}=0.1 \text{ g/m}^3$



Figure A-21 Required biofilter volume as a function of inlet concentration for a butanol load of 0.5 kg/h.

Curve 1: 99% conversion; Curve 2: 95% conversion Curve 3: $C_{ex}=0.01 \text{ g/m}^3$; Curve 4: $C_{ex}=0.1 \text{ g/m}^3$



Figure A-22 Required biofilter volume as a function of inlet concentration for a toluene load of 0.5 kg/h.

Curve 1: 99% conversion; Curve 2: 95% conversion Curve 3: $C_{ex}=0.01 \text{ g/m}^3$; Curve 4: $C_{ex}=0.1 \text{ g/m}^3$

APPENDIX B

RESULTS FROM STUDIES WITH THE TRANSIENT BIOFILTRATION MODEL



Figure B-1 Time for reaching 50% (curve 1) and 90% (curve 2) of the steady state level as a function of void fraction (υ).



Figure B-2 Time for reaching 50% (curve 1) and 90% (curve 2) of the steady state level as a function of the density of packing (ρ_p).



Figure B-3 Time for reaching 50% (curve 1) and 90% (curve 2) of the steady state level as a function of the Freundlich adsorption constant (k_d) .



Figure B-4 Time for reaching 50% (curve 1) and 90% (curve 2) of the steady state level as a function of surface biofilm coverage (α).



Figure B-5 Time for reaching 50% (curve 1) and 90% (curve 2) of the steady state level as a function of the mass transfer coefficient (k_a) .



Figure B-6 Peak-VOC concentration in exiting exiting air stream as a function of υ (a) and $\rho_{\rm p}$ (b). Dashed lines represent steady state exit concentrations.


Figure B-7 Peak-VOC concentration in exiting exiting air stream as a function of α (a) and k_d (b). Dashed lines represent steady state exit concentrations.



Figure B-8 Peak-VOC concentration in exiting exiting air stream as a function of k_a . Dashed lines represent steady state exit concentrations.



Figure B-9 Time at which the VOC-peak concentration occurs as a function of υ (a) and α , k_a , k_d and ρ_p (b).



Figure B-10 Time for reaching 50% (curve 1) and 90% (curve 2) of the steady state level of operation as a function of the VOC concentration in the inlet airstream.

APPENDIX C

COMPUTER CODE FOR SOLVING THE STEADY-STATE BIOFILTRATION MODEL FOR A SINGLE VOC

main.f

c** ******* c Purpose : "Solution Of The Steady-State Biofiltration С Model For Single VOCs" С С Orthogonal Collocation Method : С C Language : FORTRAN с C Dimitrios Tsangaris, Newark, NJ on January 26,1995 С Written By : с Updated By : Michael Cohen, Newark, NJ in May 1995 с C implicit none include "Include/parameters.h" real*8 height(ng+1),gasB(ng+1), gasO(ng+1) real*8 solcol(2*n),xdat(n+2),Bdat(n+2),Odat(n+2) real*8 delz,z real*8 deriB, deriO, one, deltainit real*8 resinit, foo, step, relative, mBin character outfile*80 integer outrep, rep, maxrep integer igas,k integer status, iconv include "Include/operating.h" include "Include/collocation.h" include "Include/liquid.h" include "Include/gas.h" include "Include/interface.h" include "Include/system.h" include "Include/volumetric.h" include "Include/kinetic.h" real*8 fcNew external fcNew * open(6,file='btcolw.out',status='new') * Read the program parameters one = 1* This controls which area is examined during the * sensitivity analysis step = 0.02open (unit=4,file='in', status='old') read (4,*) foo read (4,*) resinit close (4) * This gives the initial value of the parameter ¥ to be studied, it will be then multiplied by * different relative values (usually 0.1-2.0) mBin=0.27 maxrep = 2000do outrep=2,20

```
relative=outrep/10.0
                  rep = 1
                  do while (rep.lt.maxrep)
                           restime=resinit+step*(rep-1)
                  mB=mBin*relative
                           if (restime.lt.10) then
                                   write(outfile,'(f4.2,1x,f3.1)') restime, relative
                           else
                                   write(outfile,'(f5.2,1x,f3.1)') restime, relative
                           endif
                           open (unit=6,file=outfile,status='unknown')
                          call input()
                          call Update()
                          call output()
                          call PrintDim()
                          deltainit = delta
         Initialize the orthogonal collocation routines
с
         call InitCollocation()
         status=TRUE
         status=DEBUG
         CALL today
         WRITE (6,101) n
 101
         Format(' Solution of the Model using Orthogonal Collocation'
                    with [',i3,'] col. points',/)
   &
         ,/,'
c gas
         delz
                  = 1./float(ng)
                  = 0.0
         Z
         height(1) = z
         gasB(1) = cgasB
         gasO(1) = cgasO
*START THE LOOP OVER Z AXIS
         do 100 igas=2,ng+1
                 iconv = FALSE
         write(6,123)
         write(6,102)z+delz
                 format(' Height =',5x, f14.3)
102
                 delta = deltainit
         call Update()
6
                 if (status.eq.DEBUG) call PrintDim()
                 call InitProfile(solcol)
                 CALCULATE LIQUID PHASE CONCENTRATION
С
                 call newton(status, solcol)
                 if (status.eq.DEBUG) call PrintSolution(solcol,root)
                 call interpolate(status, solcol, nt, root, dif1, xdat, Bdat, Odat)
                 call CheckConvergance(iconv,Bdat,Odat)
                 if (iconv.eq.TRUE) then
                 call interpolate(THETACONV, solcol, nt, root, dif1,
                                   xdat,Bdat,Odat)
   &
                          CALCULATE GAS PHASE CONCENTRATION
с
                 call deri (solcol, deriB, deriO)
                          CALL RK4(eta,one,deriB,delz,cgasB)
                          z = z + delz
                          height(igas) = z
                          cgasO = fcNew(cgasB)
```

```
gasB(igas) = cgasB
                      gasO(igas) = cgasO
                      write(6, *)
                      write(6,'(a)')' Gas phase concentration so far'
                      do k=1,igas
                              write(6,'(4(f12.6,3x))')
  &
                              height(k),gasB(k),gasO(k)
                      enddo
               else
                      goto 6
               endif
100
       continue
*END OF LOOP OVER Z AXIS
       call Results(height,gasB,gasO)
       close(6)
123
       if (gasB(ng+1).gt.(0.30)) then
               rep=rep+19
       else
               if (gasB(ng+1).ge.(0.10)) rep=rep+9
               if (gasB(ng+1).ge.(0.070).and.gasB(ng+1).lt.(0.10)) rep=rep+4
       endif
       if (gasB(ng+1).ge.(0.020).and.gasB(ng+1).lt.(0.049)) rep=rep+9
       if (gasB(ng+1).ge.(0.015).and.gasB(ng+1).lt.(0.020)) rep=rep+4
       rep=rep+1
       if (gasB(ng+1).le.(.01)) rep=2001
               end do
       end do
       stop
       end
```

```
io.f
```

include "Include/interface.h" include "Include/jas.h" include "Include/gas.h" include "Include/collocation.h" include "Include/operating.h" include "Include/volumetric.h" include "Include/kinetic.h" include "Include/system.h"

character filename*80 real*8 foo integer status, unfn unfn=7 *ResTime must be entered in Minutes *cgB00 must be entered in g/m3 open (unit=5,file='in',status='old') read(5,*) cgb00,foo read(5,'(a)')filename close (5) open (unit=unfn,file=filename,status='old') read(unfn,*) read(unfn,*) foo read(unfn,*) read(unfn,*) foo read(unfn,*) read(unfn,*) delta read(unfn,*) foo read(unfn,*) Now read from the standard input the operating conditions System parameters itmax = 100iprnewton = TRUEiprnewton = FALSE eps1 = 1.e-9eps2 = 1.e-9Collocation parameters n0:1 if 0 is included in the collocation interval n1 :1 if 1 is included in the collocation interval alpha and beta are the parameters for the Gauss Trial functions n0 = 1nl = 1nt = n0 + n1 + nalpha = 0.beta = 0. Biofilm parameter (in kg/m3) read(unfn,*)b0 Kinetic constants for Ethanol and Butanol read(unfn,*) miouB miouB = miouB/3600read(unfn,*) KB read(unfn,*) KBI read(unfn,*) KO Diffucivities read(unfn,*) DBW read(unfn,*) DOW Yield coefficients read(unfn,*) YB read(unfn,*) YOB Henry's constants

- * This parameter (mB) is not read in
- * here, as it is the one being tested
- read(unfn,*) mB С
- read(unfn,*) foo

¥

*

*

*

*

*

*

*

*

- read(unfn,*) mO
- * Entrance concentrations cgB00 = cgB00 * 1.e-3 read(unfn,*) cgo00
 - cg000 = cg000 * 1.e-3
- * Volumetric properties
- * Delta belongs here but it is more convenient to put it at the top
- * of the input file since it is Inlet conditions dependent
 - read(unfn,*) As
 - read(unfn,*) Volume
 read(unfn,*) Surface
 - restime = restime*60
 - Testine restine o
- * Initialize the concentrations of B,E,O at zero theta
 - cgasB = 1.0
 - cgasO = 1.0
- * Now calculate the delta dependent values: eta,phiB2,phiE2 rewind(unfn)
- c This Update is now called in the main program
- c call Update() return end

- * This subroutine calculates some dimensionless units that depend on
- * the parameter 'delta'. Delta, is the depth of the biofilm
- ************************

```
subroutine Update()
implicit none
include "Include/parameters.h"
include "Include/volumetric.h"
include "Include/volumetric.h"
include "Include/kinetic.h"
include "Include/operating.h"
include "Include/operating.h"
include "Include/jgas.h"
include "Include/jgas.h"
include "Include/liquid.h"
real*8 xv,fd
real*8 deltaMt
```

* Now calculate some Dimensionless quantities using the above values

```
* This section (10 lines) was in Input, but has been moved to Update
lamdaB = DBW*KB*YB/(DOW*Ko*YOB)
gamaB = KB/KBI
omegaB = (DOW*KO*cgB00)/(DBW*KB*cgO00)
epsilnB = cgB00/(mB*KB)
epsilnO = cgO00/(mO*KO)
deltaMt = delta*1.e-6
xv = b0
fd = 1-0.43*xv**0.92/(11.19+0.27*xv**0.99)
eta = As*DBW*fd*restime*KB/(deltaMt*cgB00)
phiB2 = xv*deltaMt*deltaMt*miouB/(fd*DBW*KB*YB)
return
end
```

************ This subroutine Prints out the Updated values of the dimensionless units that depend on delta ****** subroutine PrintDim() implicit none include "Include/liquid.h" include "Include/interface.h" include "Include/gas.h" include "Include/operating.h" WRITE(6,123) WRITE(6,1)FORMAT (' ', ' Dimensionless Parameters :', /) 1 write(6,52)delta,eta 52 format (3x, 'delta = ', f12.3,& 3x,'eta =', f12.3) WRITE(6,2) phiB2,lamdaB 2 FORMAT $(3x, phiB^2) = 12.6$, 3x,'lamda B = ',e12.6)& write(6, *)WRITE(6,3) epsilnB,epsilnO 3 FORMAT (3x, Epsilon B = , f12.6,& 3x, 'Epsilon O = ', f12.6) write(6, *)WRITE(6,5) omegaB,gamaB FORMAT (3x, 'omega B = ', e12.6,5 3x,'gamma B = ',e12.6) & write(6, *)write(6, *)123 format(' ',/) return end C***** Print the variables subroutine output () implicit none include "Include/parameters.h" include "Include/liquid.h" include "Include/gas.h" include "Include/interface.h" include "Include/operating.h" include "Include/kinetic.h" include "Include/volumetric.h" С write(6,123) WRITE(6,1) FORMAT (' ',//, ' VARIABLES IN THE MODEL',//) 1 WRITE(6,2)

2 FORMAT (3x,'1 - Butanol',/,3x,'2 - Ethanol',/,3x,'3 - Oxygen',/)

| | WRITE(6,19) restime/60 | |
|-----------------|---|--------------|
| 19 | format (' ', 'Residence Time (min) = ', f12.3) | |
| | WRITE(6.3) volume*1e6 | |
| 3 | FORMAT(', ', 'Volume of the column(cm2) = (fl2 2) | |
| 5 | $VDTE(6.4) \land c$ | |
| 4 | $\mathbb{P}(\mathcal{P}(\mathcal{P}), \mathcal{P}) = \mathbb{P}(\mathcal{P}(\mathcal{P}), \mathcal{P}) = \mathbb{P}(\mathcal{P}(\mathcal{P}), \mathcal{P})$ | |
| 4 | FORMAT ($^{\circ}$, Biolayer Sur.Area($m2/m3$) = $^{\circ}$, f12.3) | |
| | write(6,44) b0 | |
| 44 | format (' ', 'Biomass Conc. ($kg/m3$) = ', f12.3) | |
| | WRITE(6,5) delta*1e-3 | |
| 5 | FORMAT (' ', 'Film thickness (mm) $=$ ', f12.3) | |
| | WRITE(6,18) CGB00*1000. | |
| | WRITE(6,22) CGO00*1000. | |
| 18 | FORMAT (' ', 'Inlet conc. $(g/m3 \text{ of air})(B) = ', f12,3$) | |
| 22 | FORMAT (' ', 'Inlet conc. $(g/m_3 \text{ of air})(O) = ', f12.3$) | |
| | write(6.31) YB | |
| 31 | format (' ' 'Yield Coefficient (B) = ' $f(2,3)$ | |
| | write(6 34) YOB | |
| 34 | format (' ' 'Vield Coefficient (OB) = ' f12.3) | |
| J- 1 | WRITE(6.51) DRW*1 = 49 | |
| | WRITE($(0,51)$ DBW 1.c+9 | |
| 51 | $W KITE(0, 33) DOW^{-1} RETY$ | |
| 51 | format(-, Diff. Coeff. (B) + 1e9(m2/s) = -, f12.3) | |
| 22 | format(-, Diff. Coeff. (0) + 1e9(m2/s) = -, 112.3) | |
| | WRI1E(6,565) mB | |
| 565 | FORMAT (' ', 'Dist. Coeff. (B) $=$ ', e12.3) | |
| | WRITE(6,567) mO | |
| 567 | FORMAT (' ', 'Dist. Coeff. (O) = ', $e12.3$) | |
| | write(6,123) | |
| | write(6,*) ' Andrews and other Parameters' | |
| | WRITE(6,6) | |
| & | miouB*3600,KB*1000,KBI*1000,Ko*1000 | |
| 6 | format (' ',/, | |
| & | miou B(1/hr) = ', f12.3, /, | |
| & | 'KB (g/m3) = ',f12.3,/, | |
| & | 'KBI $(g/m3) = ',f12.3/,$ | |
| & | 'KO (g/m3) = '.f12.3) | |
| 123 | FORMAT(' | <u>(</u> \.' |
| | return | ,,, |
| | end | |
| * * * * * | ·************************************* | ***** |
| * | | |
| | subrouting today | |
| * | EXTERNAL TDATE | |
| * | CALL TDATE (IDAY MONTH IVEAD) | |
| | CALL IDATE (IDAT, MONTH, ITEAK) | |
| | WD(TE(6,125)) | |
| ~ ~ | WKITE $(0,00)$ month, iday, iyear | |
| 00 | Format($3x$, $Date : 1,2,7,12,7,14,7,$ | |
| & | Model Predictions for Ethanol-Butanol Mixture', | |
| & | by Orthogonal Collocation Method ',/, | |
| & | written by Dimitrios I sangaris ',/, | 1.10 |
| & | | ====' //) |
| 123 | FORMAT(' | ;/) |
| | return | |
| | end | |

| | subroutine Results(height,gasB,gasO) | |
|---------|--|------|
| | implicit none | |
| | include "Include/parameters.h" | |
| | include "Include/Irquid.h" | |
| | include "Include/operating.h" | |
| | include "Include/volumetric.h" | |
| | real*8 height(1),gasB(1),gasE(1),gasO(1) | |
| | real*8 removal(2) | |
| | integer igas | |
| | write(6,123) | |
| | WRITE(6,22) | |
| 22 | format(//,5x,' Gas Phase Concentration Profile',//) | |
| | WRITE(6,13) | |
| 13 | FORMAT (' ',12x, 'Height',10x,'Cg(B)',10x,'Cg(O)',10x,'1-Cg(B)'/) | |
| | do 44 $igas=1,ng+1$ | |
| | write(6,33) height(igas), gasB(igas), gasO(igas),1 gasB(igas) | |
| 44 | continue | |
| 33 | format(4x,F14.6,2x,F14.6,1x,f14.6,1x,f14.6,1x,f14.6) | |
| | WRITE(6,25) | |
| 25 | format(//,5x,' Gas Phase Concentration Profile[g/m3]',//) | |
| | WRITE(6,15) | |
| 15 | FORMAT (' ',12x, 'Height',10x,'Cg(B)',10x,'Cg(O)',10x,'Cg(-)') | |
| | d0 45 igas = 1, ng + 1 | |
| | write($(0, 34)$ neight(igas), | |
| -1- | gasB(1gas) * cgB00 * 1000., | |
| + 15 | gasO(Igas)*cgO00*1000. | |
| 43 | $\operatorname{continue}_{\operatorname{removal}(1) = (2600/\operatorname{regrisso}) * (\operatorname{acc} B(1) - \operatorname{acc} B(n(n+1)) * (\operatorname{co} B(0) * 1000)$ | |
| | removal(2) = (3600/restime) * (gasO(1) - gasO(ng+1)) * (cgB00 + 1000) + removal(2) = (3600/restime) * (gasO(1) - gasO(ng+1)) * (cgB00 + 1000) | |
| | write(6.99) removal(1) removal(2) | |
| 99 | format(/ ' Removal rates for Butanol[ø/m3*hr] ' f12.4 / | |
| 8 | $\frac{1}{2} - \frac{1}{2} - \frac{1}$ | |
| 34 | format(4x E) = 6.7x E) = 6.1x E = 6.1 | |
| - • | write(6,123) | |
| 123 | FORMAT(' | ',/) |
| | return | |
| | end | |

init.f

subroutine InitCollocation()

implicit none include "Include/parameters.h" include "Include/system.h" include "Include/collocation.h" integer i,j

c ----calculate the collocation point----

```
call jcobi(nt,n,n0,n1,alpha,beta,dif1,dif2,dif3,root)
c ----calculate the discretization matrices a & b----
        do i=1,nt
                 call dfopr(nt,n,n0,n1,i,1,dif1,dif2,dif3,root,v)
                 do j=1,nt
                         a(i-1,j-1)=v(j)
                 enddo
                 call dfopr(nt,n,n0,n1,i,2,dif1,dif2,dif3,root,v)
                 do j=1,nt
                        b(i-1,j-1)=v(j)
                 enddo
        enddo
        return
        end
****
                                       ******
*
        subroutine InitProfile(xold)
        implicit none
        include "Include/parameters.h"
        real*8 xold(1)
        integer i,nlocal
        nlocal = n
        do i=1,nlocal
                xold(i) = .1
        enddo
        return
        end
```

newton.f

| C**** | *************************************** |
|--------------|---|
| c purpe C | ose : NEWTON RAPHSON to solve the system of non-linear algebraic equations There are nsize equations, where nsize is 2*n |
| C C | because every concentration has it unknowns-equations |
| C****** | · · · · · · · · · · · · · · · · · · · |
| | subroutine newton(status,xold) |
| | implicit none |
| | include "Include/parameters.h" |
| | real*8 xold(1) |
| | include "Include/collocation.h" |
| | include "Include/system.h" |
| | include "Include/operating.h" |
| * | |
| * | Define new nmatrices for the Newton method |
| | real*8 xinc(2*n),jac(2*n,2*n+1) |
| | integer iter,n2,indic,i,itcon,status |
| | real*8 deter |
| | real*8 simul1 |
| | external simull |

n2 = n

| | if ((status.eq.DEBUG).or.(status.eq.TRUE)) then |
|-------------|---|
| | write(6,123) |
| 123 | FORMAT('NEWTON ITERATION,/) |
| | if(iprnewton eq.TRUE) then |
| | write(6.202) iter.deter.n2.(xold(i),i=1,n2) |
| | endif |
| | do 9 iter=1,itmax |
| | call Model(xold,jac,n2) |
| с | call PrintA(jac,n) |
| С | Simul computes the Jacobian and the Correction DX in xinc indic = 1 |
| | deter = simul1 (n2,jac,xinc,eps1,indic,n2+1) |
| | if (deter.eq.0.0) then |
| | write(6,201) |
| | return |
| | endif |
| с | check for convergence and update xold value |
| | $\frac{1100}{100} = 1 \text{ KUE}$ |
| | $if(dahs(xinc(i)) \text{ ot ens}^2) \text{ it con=FALSE}$ |
| | $xold(i) \approx xold(i) + xinc(i)$ |
| 5 | continue |
| | if(iprnewton.eq.TRUE) then |
| | write(6,202) iter,deter,n2,(xold(i),i=1,n2) |
| | endif |
| | if (itcon.ne.FALSE) then |
| | if ((status.eq.TRUE).or.(status.eq.DEBUG)) then write(6,203)iter,delta |
| | endif |
| | return |
| 0 | endif |
| 9 | continue |
| | return |
| С | formats for input and output statements |
| 200 | format(' itmax = ',i8/' iprint = ',i8/' n = ',i8/ |
| &' e | eps1 = ',1pe14.1/' eps2 = ',1pe14.1/10x,'xold(1)xold(', |
| & i | 2,')'//(1h,1p4e16.6)) |
| 201 | format(38h0matrix is ill-conditioned or singular) |
| 202 | format(' iter =', $i8/10h$ deter = , $e18.5/$ |
| \$ 2 202 | 26h xold(1)xold(,12,1h) / (1h,1p4e16.6)) |
| ∠Uغ ₽. | Iormai(Successiul convergence: Iteration=',15, |
| يم 204 | format(' no convergence') |
| 204 | end |
| | |

interpolate.f

| | | interpointery |
|--------------|--|--|
| ** | ***** | **** |
| ** * * * * * | purpose : | interpolating the results that you get from newton raphson subroutine The xold contains the solution of sB,sO at positions between 1>n>2n. Those values are unpacked to Bsol,Osol and later used to obtain the values at xdat->Bdat,Odat |
| * * | ***** | *********** |
| | subrouti | ne interpolate(iflag,xold,nt,root, dif1,xdat,Bdat,Odat) |
| | implicit integer i include real*8 x real*8 x real*8 s integer i include real*8 s real*8 s real*8 s | none flag "Include/parameters.h" old(1),root(1),dif1(1) dat(1),Bdat(1),Odat(1) intp(n+2),Bsol(n+2),Osol(n+2) o,sb,dist i,j,nt "Include/operating.h" "Include/operating.h" "Include/interface.h" b0,so0 sNew I fsNew |
| | if ((iflag write(6, 12 FORM/ & '`,10 WRITE 13 FORM/ & | g.eq.DEBUG).or.(iflag.eq.THETACONV)) then 123) WRITE(6,12) AT (x, 'Concentration Profiles in the Biofilm ', /) 5(6,13) AT (5x,' x ',6x,'s(B)',10x,'s(O)',10x,'s(E)'/) |
| | endif sb0 = e Bsol(1) do i=1, enddo Bsol(n+ do 20 i | <pre>epsilnB*cgasB =sb0 n Bsol(i+1)=xold(i) +2)=Bsol(n+1) =1,n+1 dist = float(i-1)/n call intrp(nt,nt,dist,root,dif1,xintp) sb=0.0</pre> |
| | 30 | do 30 j=1,n+2 sb = sb+xintp(j)*Bsol(j) continue so = fsNew(sb) if ((iflag.eq.DEBUG).or.(iflag.eq.THETACONV)) then write(6,40) dist,sb,so endif xdat(i)=dist |

```
Bdat(i)=sb
              Odat(i)=so
20
       continue
40
       format(2x, f7.2, 2x,
       f12.6,2x,f12.6,2x,f12.6,2x,
  &
  &
       f14.6,2x,f12.6)
123
       return
       end
C*****
                  *****
С
\mathbf{C}
   Subroutine for evaluating the derivative
   necessary for gas phase profiles
С
с
subroutine deri (xold, deriB, deriO)
       implicit none
       include "Include/parameters.h"
       include "Include/liquid.h"
       include "Include/interface.h"
       include "Include/gas.h"
       include "Include/collocation.h"
       include "Include/operating.h"
       real*8 deriB, deriO, sb0, so0, sb, so
       real*8 xold(1)
       real*8 sum1,sum2
       integer j
       sum 1 = 0.0
       sum2 = 0.0
       do 10 j = 1, n
              sb = xold(j)
              sum l = sum l + (a(0,j)-a(0,n+1)*a(n+1,j)/a(n+1,n+1))*sb
  10
       continue
       sb0 = epsilnB*cgasB
       deriB = sum1 + (a(0,0)-a(0,n+1)*a(n+1,0)/a(n+1,n+1))*sb0
       return
       end
 C*****
                         *******
 с
       for gas phase
 c
       using the fourth order runge kutta method
 CC******
        SUBROUTINE RK4(eta,omega,deri,H,cg)
        implicit none
        real*8 eta,omega,deri,cg,H,FUN
        external FUN
        cg= cg+H*FUN(eta,omega,deri)
        RETURN
        END
                       *****
                                                  *****
 C****
               give the function for RK method, in the gas phase
 c purpose :
               balance
 С
                           *****
 C**
```

real*8 FUNCTION Fun(eta,omega,deri) implicit none real*8 eta,omega,deri Fun = eta*omega*deri RETURN END

check.f

subroutine CheckConvergance(status,Bdat,Odat)

implicit none include "Include/parameters.h" include "Include/interface.h" include "Include/operating.h" integer status real*8 Bdat(1),Odat(1) real*8 uplmB,uplmO real*8 sbf,sof real*8 fsnew external fsnew

* *** calculate the concentrations at the end of the biofilm (theta=1)

```
sBf = Bdat(n+1)
     sOf = Odat(n+1)
     sof = fsNew(sbf)
     if (sof.ne.Odat(n+1)) then
     print*, 'Warning: Odat contains different value for SB then SO predicts'
     print*,sof,odat(n+1)
     endif
     uplmB = epsilnB*cgasB*PERCENTAGE
     upImO = epsilnO*cgasO*PERCENTAGE
     if (sof.gt.0.0.and.sof.le.uplmO)then
              status = TRUE
     elseif ((sbf.gt.0.0.and.sbf.le. uplmB).or.
     (sof.gt.0.0.and.sof.le. uplmO)) then
&
              status = TRUE
     elseif(delta.lt.300)then
              delta = delta + 2.0
              status = FALSE
     elseif(delta.ge.300)then
     delta = 300
              status = FALSE
     endif
     return
     end
```

printsol.f

```
subroutine PrintSolution(xold,root)
```

```
implicit none
include "Include/parameters.h"
real*8 xold(1),root(1)
integer i
write(6,'(3a12)')' theta',' S (B)',' S (O)'
do i=1, n+1
         write(6,'(3f14.8)') root(i+1),xold(i)
enddo
return
end
subroutine PrintA(a,m)
implicit none
real*8 a(20,1)
integer m,i,j
do i=1,m
do j=1,m
         if (a(i,j).nc.0.0) then
         write(*,'(2i5,f14.8)') i,j,a(i,j)
         endif
enddo
enddo
do i=1,m
         write(*,'(2i5,f14.8)') i,0,a(i,m+1)
enddo
return
end
```

model.f

```
c purpose :
              construct the jacobian matrix and on the last
С
              column vector -f
              df contains the jacobian at (nsize,nsize)
С
              and the -F vector at (nsize,nsize+1)
С
С
              notice that nsize = n
C********
                          *****
       subroutine Model(x,df,nsize)
       implicit none
       include "Include/parameters.h"
       real*8 x(nsize),df(nsize,n+1)
       integer nsize
       include "Include/liquid.h"
       include "Include/interface.h"
       include "Include/collocation.h"
       include "Include/operating.h"
       real*8 sB,sO,sB0,so0
       real*8 kinetic10,kinetic11
       real*8 fk1
```

```
real*8 sum,q1,q2,q3
       real*8 fsNew
       external fsNew
       integer i,j,m
*Reset The jacobian matrix
       do i=1,nsize
               do j=1,nsize+1
                       df(i,j)=0.0
               enddo
       enddo
*Those are the concentrations at theta=0
       sb0= epsilnB*cgasB
       so0=epsilnO*cgasO
       m = nsize
       do 10 i=1,m
                sum = 0.
                do 20 j=1,m
                        sB = x(i)
                        sO = fsNew(sb)
                        df(i,j) = b(i,j)-b(i,m+1)/a(m+1,m+1)*a(m+1,j)
                        if (i.eq.j) then
                               q1 = 1. + sB + gamaB*sB*sB
                               q_2 = 1. + sO
                                q3 = 1. - gamaB*sB*sB
                                kinetic10 = phiB2*sO/q2*sB/q1
                                kinetic11 = phiB2*((1/q_2/q_2)*(sb/q_1)*lamdaB+(sO/q_2)*(q_3/q_1/q_1))
                                df(i,j) = df(i,j) - kineticll
                        endif
                        sum = sum + (b(i,j)-b(i,m+1)/a(m+1,m+1)*a(m+1,j))*sb
 20
                continue
*
                This is the value of F\{k\}
                fk = (b(i,0) - b(i,m+1)*a(m+1,0)/a(m+1,m+1))*sb0
                df(i,(nsize+1))=-(fk1 + sum - kinetic10)
  10
        continue
        return
        end
                    ******
c*
С
        Those subroutines calculate the concentration of fsE,fcE
        given the concentrations of the other components
С
real*8 function fsNew(sb)
        implicit none
        include "Include/parameters.h"
        include "Include/liquid.h"
        include "Include/gas.h"
        include "Include/interface.h"
        include "Include/operating.h"
        real*8 sb
        real*8 cO,cB
        cO = cgasO
        cB = cgasB
 *Now solve for SB given CO,CB and SO
```

```
fsNew = epsilnO*Co + lamdaB*(sb-epsilnB*Cb)
return
end
real*8 function fcNew(cb)
implicit none
include "Include/parameters.h"
include "Include/liquid.h"
include "Include/liquid.h"
include "Include/interface.h"
real*8 sb,so
real*8 cb
*Now solve for SB given CO,CB and SO
fcNew = (cb-1.)*lamdaB*omegaB + 1.
return
end
```

in

1.65 7.7 Toluene.in

```
Toluene.in
```

***** 0.00 Toluene concentration (g/m3) ***** 0.00 0 Residence time (in min) or Flowrate (m3/h) ******* 30 This is used by the old version 1 Initial guess for delta (in micrometers) ***** 100 B0 [Kg] 1.50 Miou i [1/h]11.03e-3 Ki [Kg/m3] 78.94e-3 Kil [Kg/m3] 0.26e-3 KO [Kg/m3]

| 1.03e-9 | DiW | [m2/s] |
|----------|---------|---------|
| 2.41e-9 | DOW | [m2/s] |
| 0.708 | Yi | [Kg/Kg] |
| 0.341 | YOi | [Kg/Kg] |
| 0.27 | mi | [-] |
| 34.4 | mО | [-] |
| 275 | C[o] | [g/m3] |
| 40 | As | [m-1] |
| 15291e-0 | 5 Volum | e [m3] |
| 1.82e-2 | Surface | [m^2] |
| | | |

Include

parameters.h

integer n,ng,ndata parameter (n=20,ng=20,ndata=20) real*8 PERCENTAGE parameter (PERCENTAGE=0.01) integer TRUE,FALSE parameter (TRUE=1,FALSE=0) integer RESITENCE parameter (RESITENCE = 10) integer LASTZ,MIDDLEZ parameter (LASTZ = 20,MIDDLEZ=30) integer THETACONV parameter (THETACONV = 10) integer DEBUG parameter (DEBUG = 100)

operating.h

real*8 cgB00,cgo00 common /cgas/cgB00,cgo00 real*8 delta common/del/delta real*8 cgasB,cgasO common /cgas/cgasB,cgasO

collocation.h

real*8 a(0:n+1,0:n+1),b(0:n+1,0:n+1) common /colloc/ a,b real*8 root(n+2) real*8 dif1(n+2),dif2(n+2),dif3(n+2) real*8 v(n+2) common /colloc1/ root,dif1,dif2,dif3,v

liquid.h

real*8 lamdaB real*8 gamaB common /lamda/lamdaB common /gama/gamaB real*8 phiB2 common /phi/phiB2 real*8 sigmaB common /sigma/sigmaB

gas.h

real*8 omegaB,eta common /omega/eta,omegaB

interface.h

real*8 epsilnB,epsilnO common /epsiln/epsilnB,epsilnO

system.h

real*8 eps1,eps2 common/sysm/eps1,eps2 integer itmax,iprnewton common/flowcontrol/itmax,iprnewton integer n0,n1,nt real*8 alpha,beta common/initll/n0,n1,nt common/expon/alpha,beta

volumetric.h

real*8 volume,surface,volrate,restime real*8 as common/volumetric/volume,surface,volrate,restime common/volumetric1/as

kinetic.h

real*8 KB,KBI,KO,miouB real*8 DOW,DBW real*8 YB,YOB real*8 b0 common/kinetic1/KB,KBI,KO,miouB common/kinetic2/DOW,DBW common/kinetic3/YB,YOB common/kinetic4/b0 real*8 mB,mO common/henry/mB,mO

APPENDIX D

COMPUTER CODE FOR SOLVING THE TRANSIENT BIOFILTRATION MODEL FOR A SINGLE VOC

main.f

| ******* | | |
|------------------|--------------|---|
| с с с | Purpose : | "Solution Of The Transient Biofiltration Model For A Single VOC" |
| с с с с | Method : | ODESSA-Ordinary Differential Equation Solver With Explicit Sensitivity Analysis; Stiff Mode When User Supplied Jacobian Option Is Used |
| c c c | Language : | FORTRAN |
| c c | Written By : | Dimitrios Tsangaris, Newark, NJ on March 28,1995 |
| с с с* | Updated By : | Michael Cohen, Newark, NJ in August 1995 |
| - | | |

implicit none include "Include/parameters.h" external fun,dfun,jfun include "Include/odessa.h" real*8 cg(0:nhmax,0:ntmax) real*8 co(0:nhmax,0:ntmax) real*8 cp(0:nhmax,0:ntmax) real*8 time(0:ntmax), ht(0:nhmax) include "Include/operation.h" include "Include/dimensional.h" include "Include/dimensional.h" include "Include/dimensionless.h" real*8 dt,t,tout,err,tau,avcgb integer istate,istatus,i integer ndim,npar,nt,nh,it,ih,tlast integer sens Read the system parameters, and initi

*

4

- Read the system parameters, and initialize the concentrations do sens=1,10
 call Reset(rwork,iwork,itask,istate,iopt,mf)
 - call today()
- * This gives the original value of the parameter to be
- * examined, and then checks its relative values
 - (usually 0.1 to 10.0)
 - kapaA=6.04e-3
 - kapaA=kapaA*sens
 - call ReadParam(istatus,ndim,npar,nh,nt,dt,err,tau)
 - call InitConditions(istatus,nh,nt,cg,co,cp,ht,dt,time,y)
 - call InitOdessa(neq,ndim,npar,
 - iopt,itask,lrw,liw,mf,itol,rtol,atol,err)
 - call PrintDimensional()
 - call PrintDimensionless()
 - call PrintOne(cg,co,cp,time,ht,nh,zero)
 - call C2Y(cg,co,cp,y,zero,nh)
 - do it = 1,ntmax

```
T = time(it-1)
                tout = time(it)
       Find the average concentration for this time instance
                avcgb = cg(nh/2,it-1)*cgB00
                if (it.eq.1) avcgb=0.0
                call Update(avcgB)
                if (it.gl.(ntmax-5)) call PrintDimensionless()
                call Pack(par)
                istate = TRUE
                CALL ODESSA(fun,dfun,NEQ,Y,PAR,T,TOUT,ITOL,RTOL,ATOL,
  &
                   ITASK, ISTATE, IOPT, RWORK, LRW, IWORK, LIW, jfun, MF)
                if(istate.LT.0) then
                         write(6,*) ' istate= ',istate
                          stop
                 endif
                 call Y2C(cg,co,cp,y,it,nh)
                 if (it.gt.(ntmax-5)) call PrintOne(cg,co,cp,time,ht,nh,it)
                 call CheckSteadyState(istatus,cg,co,cp,nh,it,nt,tau,tout)
                 if (istatus.eq.TRUE) then
                          t last = it
                          goto 10
                 endif
        enddo
        Output your results
10
        continue
        call PrintSum(cg,co,cp,time,ht,nh,tlast,tau)
        enddo
```

```
stop
end
```

С

init.f

subroutine InitConditions(istatus,nh,nt,cg,co,cp,ht,dt,time,y)

```
implicit none
include "Include/parameters.h"
include "Include/dimensionless.h"
include "Include/operation.h"
integer istatus,nh,nt
real*8 cg(0:nhmax,0:ntmax)
real*8 co(0:nhmax,0:ntmax)
real*8 cp(0:nhmax,0:ntmax)
real*8 time(0:ntmax),ht(0:nhmax)
real*8 y(negmax,nparmax+1)
real*8 dt
character*80 filename
integer ih, it
```

* Initial profile along the z axis (t=0)

```
if (colstatus.eq.OLD) then
         open(unit=9,file=fileprev,status='old')
         read(9,*)
```

```
read (9,*) ht(ih),cg(ih,0),co(ih,0),cp(ih,0)
                  cg(ih,0) = cg(ih,0)/cgB00/1000
                  co(ih,0) = co(ih,0)/cgO00/1000
         cp(0,0) = (cg(0,0)/psi)^{**}(1./an)
elseif(colstatus.eq.FRESH) then
```

```
cp(0,0) = (cg(0,0)/psi)**(1./an)
       else
       write(6,'(a)')'Error in Initial Status selection'
       stop
       endif
       do ih = 0, nh
       cp(ih,0) = cg(ih,0)/psi
       enddo
Initial conditions (t=0) at the entrance of the column
       do it =1,nt
                cg(0,it) = cg(0,0)
                co(0,it) = co(0,0)
                cp(0,it) = cp(0,0)
       enddo
       do it =0,nt
                 time(it) = float(it)*dt
       enddo
       if (istatus.ne.OLD) then
                 do ih=0,nh
                          ht(ih) = float(ih)*dz
                 enddo
       endif
       return
       end
```

do ih = 0, nh

enddo cg(0,0) = 1.0co(0,0) = 1.0

close(9)

cg(ih,0) = 1.0e-4co(ih,0) = 1.0e-4

do ih = 0, nh

cg(0,0) = 1.0co(0,0) = 1.0

enddo

```
***********
```

```
subroutine InitOdessa(neq.ndim.npar.iopt.itask.lrw.liw.mf.itol.rtol.atol.err)
```

```
implicit none
include "Include/parameters.h"
real*8 atol(neqmax,nparmax+1),rtol(neqmax,nparmax+1)
integer mf,itask,lrw,liw,itol
integer neq(2),iopt(3)
integer ndim,npar
integer nsv
real*8 err
integer i,j
neq(1)≈ndim
neq(2)=npar
```

```
nsv=nparmax+1
itol=4
do i=1,ndim
         do j=1,nsv
                  rtol(i,j)=err
                  atol(i,j)=err
         enddo
enddo
itask=1
iopt(1)=0
iopt(2)=0
iopt(3)=0
Irw=Irwmax
liw=liwmax
mf=22
return
end
subroutine Reset(rwork, iwork, itask, istate, iopt, mf)
implicit none
include "Include/parameters.h"
real*8 rwork(lrwmax)
integer iwork(liwmax)
integer itask, istate, iopt(3), mf, i
istate = 0
itask = 0
mf = 0
iopt(1) = 0
iopt(2) = 0
iopt(3) = 0
do i=1,lrwmax
         rwork(i) = 0.
enddo
do i=1,liwmax
         iwork(i) = 0
enddo
return
```

```
end
```

print.f

| | real*8 time(0:ntmax),ht(0:nhmax) integer nt,nh,it,ih |
|--------|---|
| | |
| 84 | write (6,84) format(//.5x.'Solution of the Transient Model'.//) |
| 0. | do it = 0, nt |
| | write (6,86) time(it) |
| 86 | format (/, $10x$, 'At Time = ', $f14.3$,/) |
| 89 | write $(0,89)$ format(// 8x 'h/H' 9x 'cg' 13x 'cg' 13x 'cg' /) |
| 0,7 | do ih = 0, nh |
| | write (6,96) ht(ih), cg(ih,it), co(ih,it), cp(ih,it) |
| 96 | format (5x, f7.3,3x,f10.4,5x,f10.4,5x,f10.4) |
| | enddo |
| | return |
| | end |
| ***** | ************* |
| * | The subroutine Prints out the Updated values of the dimensionless units |
| ***** | ************************************** |
| | |
| | subroutine PrintDimensionless() |
| | include "Include/dimensionless h" |
| | nende mende dimensioness.it |
| | WRITE(6,123) |
| , | WRITE(6,1) |
| ļ | FORMAT (* ', ' Dimensionless Parameters :', /) |
| | WRITE(6.5) betaB.betaO |
| 5 | FORMAT $(2x, Beta [B] = , f14.8,$ |
| & | 2x, Beta [O] = 1, 14.8 |
| 6 | WRITE(6,6) effectB, effectO |
| e e | PORMAT(2x, Effectv[D] = ,114.8, 2x 'Effectv[O] = ' f14.8) |
| | WRITE(6,3) epsilnB,epsilnO |
| 3 | FORMAT $(2x, Epsilon[B] = , f14.8,$ |
| & | 2x, 'Epsilon[O] = ', f14.8) |
| | WR(0, 7) WR[TE(6, 8)] gamaB |
| 8 | FORMAT (2x, gamaB = ', f14.8) |
| | write(6,*) |
| | write(6,52) psi,beta |
| 52 | format $(2x, p_{5} = f 4.8,$ |
| æ | 2x, deta $=$, 114.6) WRITE(6.2) porosity delta |
| 2 | FORMAT (2x, porosity = $, f14.8,$ |
| & | 2x, delta = ', f14.8 |
| - | WRITE(6,7) 1./an,dz |
| / | $f \cup KMA + (2x, n) = -, 114.8,$ $2x \cdot dz = - + f + 4.8,$ |
| CC. | write(6,*) |
| | write(6,*) |
| | |

| 123 | format(' '/) |
|--------|--|
| | return |
| | end |
| C**** | ************ |
| * | Print the variables |
| C***** | ************** |
| | subroutine Printdimensional () |
| | implicit none |
| | include "Include/parameters h" |
| | include "Include/dimensional.h" |
| | include "Include/operation.h" |
| | include "Include/dimensionless.h" |
| | write(6,123) |
| | WRITE(6,1) |
| 1 | FORMAT ('_',//, ' VARIABLES IN THE MODEL',//) |
| | WRITE(6,11) |
| 11 | FORMAT (5x,/, 'Input data for Transient Biofilter Model'./) |
| | WRITE(6,2) |
| 2 | FORMAT $(2x, 1 - Toluene', 2x, 2 - Oxygen',)$ |
| | WRITE(6,19) restime/60 |
| 19 | format (' ', 'Resitance Time (min) = ', f12.5) |
| | WRITE(6,3) volume*1e6 |
| 3 | FORMAT (' ', 'Volume of the column(cm3) = ', $f12.5$) |
| | WRITE(6,4) As |
| 4 | FORMAT (' ', 'Biolayer Sur Area($m2/m3$) = ', f12.5) |
| | WRITE(6,41) alpha |
| 41 | FORMAT (' ', '% area covered by biomass $=$ ', f12.5) |
| | write(6,44) b0 |
| 44 | format (' ', 'Biomass Conc. $(kg/m3) = ', f12.5$) |
| _ | WRITE(6,5) delta*1e-3 |
| 5 | FORMAT (',','Film thickness (mm) $=$ ', f12.5) |
| 60 | WKI $E(6,59)$ porosity |
| 39 | FORMAT(, POPOSity = , 112.5) |
| | $WR(TE(0,18) COB00^{+}1000.$ |
| 10 | $\mathbb{E}(\mathbf{P}(\mathbf{A}, \mathbf{Z})) = \mathbb{E}(\mathbf{Q}(\mathbf{A}, \mathbf{Z})) = \mathbb{E}(\mathbf{Q}(\mathbf{A}, \mathbf{Z})) = \mathbb{E}(\mathbf{Q}(\mathbf{A}, \mathbf{Z})) = \mathbb{E}(\mathbf{Q}(\mathbf{A}, \mathbf{Z}))$ |
| 10 | FORMAT ($(, \text{ inter conc. } (g/m3 \text{ of air})(\Omega) = (12.5)$ |
| | $\frac{1}{100} = \frac{1}{112.5}$ |
| 31 | format (' ' 'Vield Coefficient (B) $=$ ' fl2 5) |
| 51 | write(6.34) VOB |
| 34 | format (' ' 'Vield Coefficient (OB) = ' $f12.5$) |
| 24 | WRITE(6.51) DBW*1 $e+9$ |
| | WRITE(6,55) DOW*1 e+9 |
| 51 | format (' ' 'Diff_Coeff_(B)*1e9(m2/s) = ', f12.5) |
| 55 | format (' ' 'Diff. Coeff. (O)*1e9(m2/s) = ', f12.5) |
| | WRITE(6.565) mB |
| 565 | FORMAT (', 'Dist. Coeff. (B) = ', $e12.5$) |
| | WRITE(6,567) mO |
| 567 | FORMAT (' ', 'Dist. Coeff. (O) = ', $e12.5$) |
| | WRITE(6,566) Kapaa*3600. |
| 566 | FORMAT (' ', 'Mass Trans. Coef. Ka [m/h]≈ ', e12.5) |
| - | WRITE(6,568) Kapad |
| 568 | FORMAT (' ', 'Adsorption Parameter Kd [g/g]= ', e12.5) |
| | WRITE(6,569) rho |

569 FORMAT (' ', 'Particle Density [kg/m3]= ', e12.5) write(6,123) write(6,*) ' Andrews and other Parameters' WRITE(6,6)miouB*3600,KB*1000,KBI*1000,Ko*1000 & 6 format (' ',/, ' miou B(1/hr) = ',f12.3,/,& ' KB (g/m3) = ',f12.3,/, 81 ' KBI (g/m3) = ',f12.3,/, & & ' KO (g/m3) = ',f12.3) write(6,123) ',/) 123 FORMAT(' return end ***** subroutine today() × EXTERNAL TDATE * CALL TDATE (IDAY, MONTH, IYEAR) write(6,123) WRITE (6,66) month, iday, iyear 66 Format(2x, ' Date : ',i2,'/',i2,'/',I4,//, Model Predictions for Toluene System ',/, Ľ . written by Dimitrios Tsangaris ',/, & , & 123 FORMAT('_____ `,/) return end C print concentration changes along the column time subroutine PrintOne(cg,co,cp,time,ht,nh,it) implicit none include "Include/parameters.h" include "Include/operation.h" real*8 cg(0:nhmax,0:ntmax),co(0:nhmax,0:ntmax) real*8 cp(0:nhmax,0:ntmax) real*8 time(0:ntmax),ht(0:nhmax) integer nh,it,ih write (6,84) 84 format(//,5x,'Solution of the Transient Model',//) write (6,86) time(it) 86 format (/, 10x, 'At Time = ', f14.3,/) write (6,89) 89 format(//,8x,'h/H',9x,'cg',13x,'co',13x,'cp',//) do ih = 0, nhс write (6,96) ht(ih), cg(ih,it), co(ih,it), cp(ih,it) write (6,96) ht(ih), cg(ih,it)*cgB00*1000, co(ih,it)*cgo00*1000, cp(ih,it) & 96 format (5x, f7.3,3x,f10.4,5x,f10.4,5x,f10.4) enddo return end

```
subroutine PrintSum(cg,co,cp,time,ht,nh,nt,tau)

implicit none

include "Include/parameters.h"

include "Include/dimensional.h"

include "Include/dimensional.h"

real*8 cg(0:nhmax,0:ntmax),co(0:nhmax,0:ntmax)

real*8 cp(0:nhmax,0:ntmax)

real*8 time(0:ntmax),ht(0:nhmax),tau

integer nh,it,ih,nt
```

```
write (6,84)
format(//,5x,'Summary Results for the Transient Model',//)
write (6,89)
```

```
96 format (5x, f8.3,3x,f10.4,5x,f10.4,5x,f10.4)
enddo
write(6,*)
return
end
```

readparam.f

subroutine ReadParam(istatus,ndim,npar,nh,nt,dt,err,tau) implicit none include "Include/parameters.h" include "Include/operation.h" include "Include/dimensional.h" include "Include/dimensionless.h" include "Include/dimensionless.h" include "Include/system.h" integer istatus,nh,nt,ndim,npar,column real*8 dt,err,tau,flowrate real*8 foo character filename*80

integer unfn unfn=7 filename = 'Toluene.in'

- ResTime must be entered in Minutes
- cgB00 must be entered in g/m3
- read(5,*) cgb00,restime
- * read(5,'(a)')filename
 - open (unit=unfn,file=filename,status='old') read(unfn,*) flowrate

```
read(unfn,*) cgb00
```

```
read(unfn,*)
```

- Now read from the standard input the operating conditions
- * * System parameters iprnewton = TRUE iprnewton = FALSE **ODESSA** parameters ndim = neqmaxnpar= nparmax nt = ntmaxnh = nhmax* Biofilm parameter (in kg/m3) read(unfn,*)b0 Kinetic constants for Ethanol and Butanol read(unfn,*) miouB miouB = miouB/3600read(unfn,*) KB read(unfn,*) KBI read(unfn,*) KO * Diffucivities read(unfn,*) DBW read(unfn,*) DOW * Yield coefficients read(unfn,*) YB read(unfn,*) YOB * Henry's constants read(unfn,*) mB read(unfn,*) mO Entrance concentrations cgB00 = cgB00 * 1.e-3read(unfn,*) cgo00 cgo00 = cgO00 * 1.e-3* Volumetric properties read(unfn,*) Volume read(unfn,*) Surface flowrate = flowrate/3600restime = volume/flowrate velocity = 1./restime = restime/24.0/3600 tau * Adsorption parameters read(unfn,*) read(unfn,*) As read(unfn,*) alpha read(unfn,*) foo с read(unfn,*) kapaA read(unfn,*) kapad read(unfn,*) porosity read(unfn,*) rho read(unfn,*) an kapaa= kapaa/3600. ý.
- Numerical parameters colstatus= FRESH read(unfn,*) column if (column.eq.(20.0)) colstatus = OLD read(unfn,'(a)') fileprev read(unfn,*) err

```
* Now calculate some Dimensionless quantities using the above values
         gamaB = KB/KBI
         epsilnB = cgB00/(mB*KB)
         epsilnO = cgO00/(mO*KO)
* Now calculate some Dimensionless quantities using the above values
         istatus= FRESH
         dt = 0.01
с
         read(unfn,*) dt
         dz = 1.0/float(nh)
         call Update(zero)
         close (unfn)
         return
         end
         The subroutine calculates some dimensionless units that depend on
*
         the parameter 'delta'. Delta, is the depth of the biofilm
         subroutine Update(cgasB)
          implicit none
          include "Include/parameters.h"
          include "Include/operation.h"
          include "Include/dimensional.h"
          include "Include/dimensionless.h"
          real*8 xv,cgasB
         real*8 deltaMt,const
          call FindDelta(cgasB,delta,effectB,effectO)
*A correction is needed because the empirical formula Cjp = Kd (Cj*)^n holds
          only when cj is in [g j / m3 air]. Then, const= g/m3->Kgr/m3.
          After this correction, cstar_reduced = psi*Cjp_reduced
          const = 1.e-3
          deltaMt = delta*1.e-6
          xv = b0
          betaB=effectB*(alpha*As)*deltaMt*xv*restime*miouB/(YB *cgB00*porosity)
          betaO=effectO*(alpha*As)*deltaMt*xv*restime*miouB/(YOB*cgO00*porosity)
          beta = kapaa*(1-alpha)*As*restime/porosity
```

```
psi = (const/cgB00)*(porosity*cgB00/((1-porosity)*rho*Kapad))**an
return
end
```

```
util.f
```

```
subroutine C2Y(cg,co,cp,y,it,nh)
implicit none
include "Include/parameters.h"
real*8 y(neqmax,nparmax+1)
real*8 cg(0:nhmax,0:ntmax), co(0:nhmax,0:ntmax),cp(0:nhmax,0:ntmax)
integer ih,it,nh
```

```
do ih = 1, nh
y(ih, 1) = cg(ih, it)
```

```
y(ih+nh,1) = co(ih,it)
                y(ih+2*nh, 1) = cp(ih, it)
       enddo
       return
       end
       subroutine Y2C(cg,co,cp,y,it,nh)
        implicit none
        include "Include/parameters.h"
       real*8 y(neqmax,nparmax+1)
       real*8 cg(0:nhmax,0:ntmax), co(0:nhmax,0:ntmax),cp(0:nhmax,0:ntmax)
        integer ih, it, nh
        do ih = 1, nh
                cg(ih,it) = y(ih,1)
                co(ih,it) = y(ih+nh,1)
                cp(ih,it) = y(ih+2*nh,1)
        enddo
        return
        end
****
        subroutine pack(par)
        implicit none
        include "Include/parameters.h"
        include "Include/dimensionless.h"
        real*8 par(1)
        par(1) = epsilnB
        par(2) = epsilnO
        par(3) = gamaB
        par(4) = betaB
        par(5) = betaO
        par(6) = beta
        par(7) = psi
        par(8) = porosity
        par(9) = dz
        par(10) = an
        return
        end
*****
                                                                *****
        subroutine CheckSteadyState(istatus,cg,co,cp,nh,it,nt,tau,tout)
        implicit none
        include "Include/parameters.h"
        real*8 cg(0:nhmax,0:ntmax), co(0:nhmax,0:ntmax),cp(0:nhmax,0:ntmax)
        real*8 d1,d2,d3,tau,tout
        integer it, nh, istatus, nt
        dl = abs (cg(nh,it) - cg(nh,it-1))
        d2 = abs (co(nh,it) - co(nh,it-1))
        d3 = abs (cp(nh,it) - cp(nh,it-1))
        if(d1.le.TOLERR.and.d2.le.TOLERR.and.d3.le.TOLERR) then
        As this program is checking sensitivity it goes until done,
```

с *

121

and does not use the steady state checker
if(it.ge.ntmax-5) then
istatus = TRUE
write(6,47) tout*tau, it, nt
else
istatus = FALSE
endif
format(//,5x,'Steady state was reached in',f10.3, ' days',
& /,5x,'Iterations = ',i10,
& /,5x,'Maximum Iterations = ',i10,//)

```
return
end
```

```
model.f
```

c this subroutine computes the vectorfield C******* subroutine fun(ndim,t,y,par,ydot) implicit none include "Include/parameters.h" real*8 y(neqmax), ydot(neqmax), par(nparmax), t integer ndim real*8 y1,y2,y3,fun1,fun2,y4 real*8 cbpr,copr,cb,co,cp real*8 der1.der2 real*8 cstar integer i,offset,nh include "Include/UNFOLD.h" write(6, (5f10.4))(par(i), i=1, 10)* write(6, (10f8.4))(y(i), i=1, ndim) nh = ndim/3* print*,nh do i = 1, nhcb = y(i)cbpr = 0.if (i.ge.2) cbpr = y(i-1)co = y(i+nh)cp = y(i+2*nh)cstar= psi*(cp**an) y1 = epsilnB*cb $y_2 = epsilnO*co$ $y_3 = 1. + y_1 + gamaB*y_1*y_1$ y4 = 1. + y2 $fun1 = (y1/y3)^*(y2/y4)$ fun2 = cb-cstarif (i.eq.1)then der1 = (cb-1.)/dzelse der 1 = (cb-cbpr)/dzendif
```
ydot(i)= -der1/porosity-betaB*fun1-beta*fun2
      enddo
      offset = nh
      do i = 1, nh
             cb = y(i)
             co = y(i+nh)
             copr = 0.
             if (i.ge.2) copr = y(i+nh-1)
             yl = epsilnB*cb
             y^2 = epsilnO*co
             y_3 = 1.+y_1 + gamaB^*y_1^*y_1
             y4 = 1.+y2
             funl = (y1/y3)^*(y2/y4)
             if (i.eq.1)then
                    der2 = (co-1)/dz
             else
                    der2 = (co-copr)/dz
             endif
             ydot(i+offset)= -der2/porosity-betaO*fun1
      enddo
*
      Equations for Solid adsorption
      offset = 2*nh
      do i = 1, nh
             cb = y(i)
             cp = y(i+2*nh)
             cstar= psi*(cp**an)
             fun2 = cb-cstar
             ydot(i+offset) = beta*fun2
      enddo
      write(6, (10(f8.4))))(ydot(i), i=1, ndim)
      return
      end
                                    *****
              ******
      subroutine dfun(ndim,t,y,par,dfdp,jpar)
partial derivatives wrt. parameters of interest
С
      implicit none
      real*8 y(ndim),par(1),dfdp(1),t
      integer ndim, jpar
      return
       end
c this subroutine computes the jacobian
c of the vectorfield
subroutine jfun(ndim,t,y,par,ml,mu,pd,nrpd)
       implicit none
       include "Include/parameters.h"
       integer ndim,ml,mu,nrpd
       real*8 y(neqmax),pd(neqmax,neqmax),par(nparmax),t
       real*8 y1,y2,y3,y4,y5
       real*8 co,cb,cp,dfyi,dfyn
```

integer offset, nh, i, j

```
include "Include/UNFOLD.h"
        nh = ndim/3
c jacobian of the vectorfield
         do i=1,ndim
                 do j=1,ndim
                          pd(i,j)=0.
                  enddo
         enddo
         dCB partial derivatives
         do i = 1, nh
                  cb = y(i)
                  co = y(i+nh)
                  cp = y(i+2*nh)
                  yl = epsilnB*cb
                  y^2 = epsilnO*co
                  y_3 = 1. + y_1 + gamaB^*y_1^*y_1
                  y4 = 1. + y2
                  y5 = epsilnB^*(1.-gamaB^*y1^*y1)
                  dfyi = (y5/y3/y3)^*(y2/y4)
                  dfyn = (y1/y3)^*(epsilnO/y4/y4)
                  if (i.gt. 1) pd(i,i-1) = 1/porosity/dz
                  pd(i,i) = -1/porosity/dz-betaB*dfyi-beta
                  pd(i, nh+i) = -betaB*dfyn
                  pd(i,2*nh+i) = beta *psi*an*(cp**(an-1))
         enddo
         dCO partial derivatives
         offset = nh
         do i = 1, nh
                  cb \approx y(i)
                  co = y(i+nh)
                  cp = y(i+2*nh)
                  y1 = epsilnB*cb
                  y_2 = epsilnO*co
                  y_3 = 1. + y_1 + gamaB^*y_1^*y_1
                  y4 = 1. + y2
                  y_5 = epsilnB^*(1.-gamaB^*y_1^*y_1)
                  dfyi = (y5/y3/y3)^*(y2/y4)
                  dfyn = (y1/y3)^*(epsilnO/y4/y4)
                  pd(offset+i,i) = -betaO*dfyi
                  pd(offset+i, offset+i) = -1/porosity/dz-betaO*dfyn
                  if (i.gt.1) pd(offset+i,offset+i-1) = 1/porosity/dz
         enddo
 ¥
         dCp partial derivatives
         offset = 2*nh
         do i = 1, nh
                  cb = y(i)
                  pd (offset+i,i)
                                    = beta
                  pd (offset+i,offset+i)
                                             = -beta*psi*an*(cb**(an-1))
         enddo
         return
         end
```

finddelta.f

```
subroutine FindDelta(avcg,delta,effectB,effectO)

implicit none

real*8 avcg,delta,effectB,effectO

delta = 1.513*avcg*1e3+33.35

effectB= 0.031*avcg*1e3+ 0.19

if (avcg.eq.0) then

delta = 20

effectB = 0.2

else

delta = 23.3061*(avcg**0.436968)

effectB = 0.43163*(avcg**(-1.87141))

endif

effectO = effectB

return

end
```

Makefile.f

rm -f *.o

*

*

*

*

*

*

*

Toluene.in

| 0.1 | Flowrate | |
|----------|---------------|---------|
| 5.0 | cg | |
| ****** | *Toluene***** | ***** |
| 100 | B0 | [Kg] |
| 1.50 | Miou i | [1/h] |
| 11.03e-3 | Ki | [Kg/m3] |
| 78.94e-3 | Kil | [Kg/m3] |
| 0.26e-3 | КО | [Kg/m3] |
| 1.03e-9 | DiW | [m2/s] |
| 2.41e-9 | DOW | [m2/s] |
| 0.708 | Yi | [Kg/Kg] |
| 0.341 | YOi | [Kg/Kg] |
| 0.27 | mi | [-] |

| 34.4 275 5.15e-3 1.82e-2 | mO C[o] Volume Surface | [-] [g/m3] [m3] [m^2] |
|-----------------------------------|---------------------------------|--------------------------------|
| 133.33 | As | [m-1] |
| 0.3 | Alpha | [-] |
| 6.04e-3 | Ka | [m/h] |
| 2.254e-5 | Kd | [g/g] |
| 0.3 | Porosity [-] | |
| 428 | RhoP | [kg/m3] |
| 0.96 | 1/n | [This is 1/n] |
| 10 | if 20 then use OLD initial | profile below |
| 0.625.las | st | - |
| 1e-6 | Error for ODESSA | |
| 0.01 | dt | |
| | | |

Include

parameters.h

integer nhmax,ntmax parameter(ntmax=100) parameter(nhmax=20) integer neqmax,nparmax,liwmax,lrwmax,colstatus character *80 fileprev parameter(neqmax=3*nhmax,nparmax=20,lrwmax=5000,liwmax=100) integer FRESH,OLD parameter (FRESH=10,OLD=20) real*8 TOLERR parameter (TOLERR=1.e-4) integer TRUE, FALSE parameter (TRUE=1,FALSE=0) real*8 zero parameter (zero=0.0) common/colstatus/colstatus common/fileprev/fileprev

odessa.h

real*8 par(nparmax),y(neqmax,nparmax+1)
real*8 atol(neqmax,nparmax+1),rtol(neqmax,nparmax+1)
real*8 rwork(lrwmax)
integer iwork(liwmax)
integer neq(2),iopt(3)
integer mf,itask,lrw,liw,itol

operation.h

* Concentrations real*8 cgB00,cgo00 common/concen/cgB00,cgo00

dimensional.h

* Kinetic Parameters

real*8 KB,KBI,KO,miouB real*8 DOW,DBW real*8 YB,YOB real*8 b0 common/kinetic1/KB,KBI,KO,miouB common/kinetic2/DOW,DBW common/kinetic3/YB,YOB common/kinetic4/b0

* Henry's Parameters

real*8 mB,mO common/henry/mB,mO

* Volumetric Parameters

real*8 volume, surface, volrate, restime, As, velocity common/volumetric/volume, surface, volrate, restime, As, velocity

*Adsorption

real*8 kapaa,kapad,alpha,rho common/adsorp/kapaa,kapad,alpha,rho

dimensionless.h

real*8 epsilnB,epsilnO real*8 betaB,betaO real*8 psi,gamaB,porosity,beta real*8 dz,an common/dim1/epsilnB,epsilnO,betaB,betaO common/dim2/beta,gamaB,psi,porosity,dz,an real*8 effectB,effectO,delta common/aux/effectB,effectO,delta

system.h

integer iprnewton common/flowcontrol/iprnewton

unfold.h

real*8 epsilnB,epsilnO,gamaB,betaB,betaO,beta,psi,porosity,dz,an

| ł, | · . | | |
|----|----------|----|---------|
| | epsilnB | = | par(1) |
| | epsilnO | = | par(2) |
| | gamaB | = | par(3) |
| | betaB | = | par(4) |
| | betaO | = | par(5) |
| | beta | = | par(6) |
| | psi | = | par(7) |
| | porosity | = | par(8) |
| | dz | == | par(9) |
| | an | = | par(10) |
| | | | |

APPENDIX E

COMPUTER CODE FOR SOLVING THE TRANSIENT BIOFILTRATION MODEL FOR A SINGLE VOC WITH A VARYING INLET CONCENTRATION (only portions differing from Appendix D shown)

main.f

**** ***** c Purpose : "Solution Of The Transient Biofiltration с Model For A Single VOC, С With A Varying Inlet Concentration." С c Method : **ODESSA-Ordinary Differential Equation** Solver With Explicit Sensitivity Analysis; С Stiff Mode When User Supplied Jacobian С Option Is Used с С с Language : FORTRAN С с Written By : Dimitrios Tsangaris, Newark, NJ on March 28,1995 с Updated By: Michael Cohen, Newark, NJ in August 1995 С implicit none include "Include/parameters.h" external fun,dfun,jfun include "Include/odessa.h" · real*8 cg(0:nhmax,0:ntmax) real*8 co(0:nhmax,0:ntmax) real*8 cp(0:nhmax,0:ntmax) real*8 time(0:ntmax), ht(0:nhmax) include "Include/operation.h" include "Include/dimensional.h" real*8 dt,t,tout,err,tau,avcgb integer istate, istatus, i integer ndim, npar, nt, nh, it, ih, tlast * * Read the system parameters, and initialize the concentrations call Reset(rwork, iwork, itask, istate, iopt, mf) call today() call ReadParam(istatus,ndim,npar,nh,nt,dt,err,tau)

call InitConditions(istatus,nh,nt,cg,co,cp,ht,dt,time,y)

call InitOdessa(neq,ndim,npar,

iopt,itask,lrw,liw,mf,itol,rtol,atol,err)

call PrintDimensional()

call PrintDimensionless()

call PrintOne(cg,co,cp,time,ht,nh,zero)

- call C2Y(cg,co,cp,y,zero,nh)
- do it = 1,ntmax

+

T = time(it-1)

* Find the average concentration for this time instance

c The formula used is cgB00=mB*Clo*exp(-Qg*mB*time)/VL)

- c to get time from time(it) it is necessary to divide
- c by restime, so replace Qg with volume (and divide
- c by dilution, as only Qg, not flowrate is leaving soil)

| & | cgB00 = mB*Clo*exp(-(volume/dilution) |
|-----|---|
| 000 | call PrintDimensionless() |
| 000 | call Pack(nor) |
| | istate = TRUF |
| | CALL ODESSA(fun,dfun,NEO,Y,PAR,T,TOUT,ITOL,RTOL,ATOL, |
| & | ITASK,ISTATE, IOPT,RWORK,LRW,IWORK,LIW,jfun,MF) |
| | if(istate.LT.0) then |
| | write(6,*)' istate= ',istate |
| | stop |
| | endif |
| | call Y2C(cg,co,cp,y,it,nh) |
| | If (II.II.(ntmax-20)) goto 999 |
| 000 | continue |
| /// | call CheckSteadyState(istatus on color nh it nt tau tout) |
| | if (istatus eq TRUF) then |
| | t last = it |
| | goto 10 |
| | endif |
| | enddo |
| с | Output your results |
| 10 | continue |
| | call PrintSum(cg,co,cp,time,ht,nh,tlast,tau) |
| | stop end |

print.f (partial)

| 86 | format (/, 10x, 'At Time = ', $f14.3, 3x, Cg = 'f10.3, /$) |
|---------|---|
| | write (6,89) |
| 89 | format(//,8x,'h/H',9x,'cg',13x,'co',13x,'cp',//) |
| | do $ih = 0$, nh |
| | write (6,96) ht(ih), cg(ih,it)*cgB00*1000, |
| & | co(ih,it)*cgo00*1000, cp(ih,it) |
| 96 | format (5x, f7.3,3x,f10.4,5x,f10.4,5x,f10.4) |
| | enddo |
| | return |
| | end |
| C**** | ************ |
| C print | concentration changes along the column time |
| ~ | |

subroutine PrintSum(cg,co,cp,time,ht,nh,nt,tau) implicit none include "Include/parameters.h" include "Include/operation.h" real*8 cg(0:nhmax,0:ntmax),co(0:nhmax,0:ntmax) real*8 cp(0:nhmax,0:ntmax) real*8 time(0:ntmax),ht(0:nhmax),tau integer nh,it,ih,nt

write (6,84)

*

| 84 | format(//,5x,'Summary Results for the Transient Model',//) write (6,89) |
|----|---|
| 89 | format(//,8x,'time(h)',6x,'cgin',9x,'cg (1/3)',9x,'cg',//) |
| | do it = 0, ntmax |
| | write (6,96) time(it)*tau*24, in let(it), |
| & | cg(nh/3,it)*inlet(it),cg(nh,it)*inlet(it) |
| 96 | format (5x,f8.3,3x,f10.4,5x,f10.4,5x,f10.4) |
| | enddo |
| | write(6,*) |
| | return |
| | end |

readparam.f

**

subroutine ReadParam(istatus,ndim,npar,nh,nt,dt,err,tau) implicit none include "Include/parameters.h" include "Include/operation.h" include "Include/dimensional.h" include "Include/dimensionless.h" include "Include/dimensionless.h" include "Include/system.h" integer istatus,nh,nt,ndim,npar,column real*8 dt,err,tau,flowrate character *80 filename integer unfn unfn=7 filename = 'Toluene.in' ResTime must be entered in Minutes

- * cgB00 must be entered in g/m3
- * read(5,*) cgb00,restime
- * read(5,'(a)')filename
 open (unit=unfn,file=filename,status='old')
 read(unfn,*) flowrate
 read(unfn,*) Clo
 read(unfn,*) Vplume
 read(unfn,*) dilution
 read(unfn,*)
- *
- Now read from the standard input the operating conditions
 System parameters
 - System parameters
 - iprnewton = TRUE
- iprnewton = FALSE
 - ODESSA parameters
 - ndim = neqmax
 - npar= nparmax
 - nt = ntmax
 - nh = nhmax
- * Biofilm parameter (in kg/m3) read(unfn,*)b0
- Kinetic constants for Ethanol and Butanol read(unfn,*) miouB miouB = miouB/3600 read(unfn,*) KB read(unfn,*) KBI
 - read(unfn,*) KO
- Diffucivities
 read(unfn,*) DBW
 read(unfn,*) DOW
- * Yield coefficients read(unfn,*) YB read(unfn,*) YOB
- * Henry's constants read(unfn,*) mB
- read(unfn,*) mD
- * Entrance concentrations
 cgB00 = mB*Clo
 cgB00 = cgB00/dilution
 inlet(0) = cgB00
 cgB00 = cgB00 * 1.e-3
 read(unfn,*) cg000
 cg000 = cgO00 * 1.e-3
- Volumetric properties read(unfn,*) Volume read(unfn,*) Surface flowrate = flowrate/3600 restime = volume/flowrate velocity = 1./restime tau = restime/24.0/3600
 Adsorption parameters
- read(unfn,*)
 read(unfn,*) As
 read(unfn,*) alpha

```
read(unfn,*) kapaA
        read(unfn,*) kapad
        read(unfn,*) porosity
        read(unfn,*) rho
        read(unfn,*) an
        kapaa= kapaa/3600.
     Numerical parameters
        colstatus= FRESH
        read(unfn,*) column
        if (column.eq.20) colstatus = OLD
        read(unfn,'(a)') fileprev
        read(unfn,*) err
* Now calculate some Dimensionless quantities using the above values
        gamaB = KB/KBI
        epsilnB = cgB00/(mB*KB)
        epsilnO = cgO00/(mO*KO)
* Now calculate some Dimensionless quantities using the above values
        istatus= FRESH
        dt = 0.01
        dz = 1.0/float(nh)
        call Update(zero)
        close (unfn)
        return
        end
        The subroutine calculates some dimensionless units that depend on
        the parameter 'delta'. Delta, is the depth of the biofilm
*****
                                    *********
        subroutine Update(cgasB)
        implicit none
        include "Include/parameters.h"
         include "Include/operation.h"
         include "Include/dimensional.h"
        include "Include/dimensionless.h"
         real*8 xv,cgasB
         real*8 deltaMt,const
* Now recalculate some Dimensionless quantities using the new values
* of cgB00
         epsilnB = cgB00/(mB*KB)
         epsilnO = cgO00/(mO*KO)
         call FindDelta(cgasB,delta,effectB,effectO)
*A correction is needed because the empirical formula Cjp = Kd (Cj^*)^n holds
*
         only when cj is in [g_j / m_3 air]. Then, const= g/m<sub>3</sub>->Kgr/m<sub>3</sub>.
         After this correction, cstar_reduced = psi*Cjp_reduced
         const = 1.e-3
         deltaMt = delta*1.e-6
         xv = b0
         betaB=effectB*(alpha*As)*deltaMt*xv*restime*miouB/(YB *cgB00*porosity)
         betaO=effectO*(alpha*As)*deltaMt*xv*restime*miouB/(YOB*cgO00*porosity)
         beta = kapaa*(1-alpha)*As*restime/porosity
         psi = (const/cgB00)*(porosity*cgB00/((1-porosity)*rho*Kapad))**an
         return
         end
```

| 14 | • | | | | • |
|----|---|-----|-----|----|-----|
| | n | 111 | 011 | a | 134 |
| | v | ш | cu | c. | uu |
| | | | | | |

| 51 | Flowrate | | | |
|----------|---------------|-------------------------------------|--|--|
| 100 | Clo | Clo | | |
| 1000 | Volume of Pl | Volume of Plume | | |
| 3 | dilution | | | |
| ***** | *Toluene***** | ***** | | |
| 100 | B0 | [Kg] | | |
| 1.50 | Miou i | [1/h] | | |
| 11.03e-3 | Ki | [Kg/m3] | | |
| 78.94e-3 | Kil | [Kg/m3] | | |
| 0.26e-3 | KO | [Kg/m3] | | |
| 1.03e-9 | DiW | [m2/s] | | |
| 2.41e-9 | DOW | [m2/s] | | |
| 0.708 | Yi | [Kg/Kg] | | |
| 0.341 | YOi | [Kg/Kg] | | |
| 0.27 | mi | [-] | | |
| 34.4 | mO | [-] | | |
| 275 | C[o] | [g/m3] | | |
| 18.70 | Volume | [m3] | | |
| 1.82e-2 | Surface | [m^2] | | |
| 133 33 | As | [m-1] | | |
| 0.3 | Alnha | [] | | |
| 6.04e-3 | Ка | [m/h] | | |
| 2.254e-5 | Kd | [m/n] [σ/σ] | | |
| 0.3 | Porosity | [-] | | |
| 428 | RhoP | [kø/m3] | | |
| 0.96 | l/n | [This is $1/n$] | | |
| 10 | If 20 use OL | If 20 use OLD initial profile below | | |
| 42.last | | | | |
| 1e-6 | Error for OE | DESSA | | |
| | | | | |

include (partial)

operation.h

* Concentrations

real*8 cgB00,cgo00,Clo,Vplume,dilution real*8 inlet(0:ntmax) common/concen/cgB00,cgo00,Clo,Vplume,dilution,inlet

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