

Honour School: Engineering Science

Modelling the Removal of Oestrogen from Wastewater in an Activated Sludge Process



**Department of Engineering Science
Fourth Year Project**

Ezzat Nasr, 2006

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Oxford University Department of Engineering Science

2006 Fourth Year Project

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Certificate of Own Work

I certify that this is my own work and any assistance that has been received throughout the project has been acknowledged.

Ezzat Nasr

18th May 2006

Acknowledgements

I would like to express thanks to Dr P. Martin and Prof R. Darton at Oxford University Engineering Science and Mr A. Johnson and Ms M. Juergens for their help throughout this project.

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Abstract

The increased concentrations of steroid estrogens found in wastewater treatment plant effluents have raised a serious environmental concern. Artificial estrogens, constituting the birth control pill and hormone replacement treatment (HRT), are believed to contribute heavily to the problem. The feminisation of river fish populations has been documented, however, the wider impact of increased oestrogen concentrations in wastewater remains unknown.

The activated sludge process has been identified as the key process that removes steroid estrogens in a wastewater treatment plant. Despite the availability of more effective technologies for the removal of oestrogen, the high costs of implementation of these technologies at the industrial levels required point to optimising the activated sludge process.

Due to the difficulties in measuring oestrogen concentrations (which are in the order of ng/L), a mathematical model of the process is required. This project seeks to develop the modelling of the activated sludge process with particular emphasis on oestrogen degradation. Previous models developed have been improved using a MATLAB solver to carry out extensive parameter and dimensional analysis. The results enabled the development of a more sophisticated degradation model and more accurate parameter estimations based on the Great Billing sewage works.

Data for estrone (E1) was used throughout. It was concluded that lowering the average dispersion in the tank while also maximising the ability of activated sludge to biodegrade were key in increasing E1 removal. This led to adding fixed surfaces (packing) into the tank in order to increase microbial growth (and hence biodegradation) and create more plug flow like behaviour (and hence lower average dispersion). The model was used to investigate optimum packing lengths and arrangements and a realistic configuration was shown to improve E1 removal from 91% to 97%.

Work is currently underway at Great Billing to attain experimental data required to justify the model.

1.0 Introduction

1.1 Environmental Concern

The presence of endocrine disrupting compounds in rivers downstream of sewage treatment plants is a growing concern for many scientists and water quality regulators.¹ Purdom et al was the first to point out that fish exposed to the effluent produced by sewage treatment plants showed estrogenic responses.² Vitellogenin, an estrogenic responsive protein usually only found in female fish, was present in male fish in very high plasma concentrations, which suggested the exposure to estrogenic chemicals. Subsequent studies on intersex roach fish, downstream of many domestic sewage effluents in the U.K, reported the presence of oocytes in the testes³ which, similarly, is most likely to be the result of estrogenic exposure. This is still a long way from demonstrating that a serious threat exists to whole fish populations and aquatic life in general, but it raises a potential threat which is serious enough to warrant some action.

1.2 Possible Causes

A toxicity identification and evaluation procedure, which examined eight different sewage treatment plants in the U.K, identified the steroid oestrogen component of the effluent as contributing the greatest proportion of the overall estrogenic activity.⁴ The source of steroid estrogens entering the sewage plants is the human population. A recent study shows that most steroid estrogens are excreted by pregnant and menstrual females with menopausal females and males making a less considerable contribution.⁵ The rising levels of natural steroid estrogens in sewage could, therefore, be a result of general population increase. Hormone replacement therapy (HRT) and increased demand of the contraceptive pill could be the cause of rising concentrations in synthetic steroid estrogens.

1.3 Current Removal Technology

Modern sewage treatment efficiency has increased considerably in the past 50-100 years. Significant improvements in water quality have seen the return of a range of previously absent flora and fauna to many fresh water systems.⁶ The overall organic (and microorganic, in the case of estrogenic chemicals) loading has been reduced, particularly with the introduction of the activated sludge process in 1913.⁷ The activated sludge process very effectively converts organic contaminants in the water into biomass, which is then separated from the aqueous phase by settlement. Influent biological oxygen demands of 300mg/L can be reduced to less than 10mg/L in most activated sludge processes.⁸ Accordingly, field data suggests that up to 85% of steroid estrogens can be removed,⁵ however, steroid estrogens are known to be potent at very low concentrations, as is evident from the environmental concerns outlined earlier, and special consideration is required.

Water purification techniques such as UV photolysis or activated carbon could significantly remove steroid estrogens from wastewater but the high cost required in implementing these technologies on a large scale points to research in the potential optimisation of the activated sludge treatment process.

1.4 Project Objective

Previous projects, most recently conducted by E. Jeremy and J. Lupton, suggest that the removal of estrogens can be improved by inserting fixed surfaces (packing) into the activated sludge process tank offering more opportunity for the biomass to grow.⁹ There is a need for a mathematical model of the activated sludge process to develop an understanding of the key factors that affect the removal of estrogens. Subsequently, the model can be extended to include the effects of inserting packing into the tank.

The key objectives of this project are, therefore, to improve previous models of the process by wide-ranging solution analyses using MATLAB and, in the light of this, review the fundamental parameters and mechanisms of the process. To

achieve this, the project also aims to obtain beneficial results from extensive dimensional analysis. The final objective is to correlate and predict performance of the model with the inclusion of packing, where different positional arrangements and physical configurations can be explored.

Overall, the model will provide researchers with a tool to theoretically investigate alternative wastewater treatment systems. This report will be based on parameters relating to the process at Great Billing Sewage Works, some experimentally obtained, others estimated.

2.0 Wastewater Treatment Overview

2.1 Wastewater Contaminants

Domestic, industrial and agricultural sources make up the broad range of contaminants found in wastewater.¹⁰ Domestic waste mainly consists of faeces and urine and is therefore high in nutritional and bacterial content. It also carries relatively small amounts of metals, detergents and soaps. Industrial and agricultural waste, on the other hand, is responsible for more heavy metals, specialised chemicals, acids, alkalis, oils, fuels and, more in the case of agricultural contaminants, fertilisers and livestock excrement.

2.1.1 Endocrine Disrupting Compounds (EDCs)

EDCs are chemicals that alter the normal function of the endocrine system (a collection of glands in an animal's body for the secretion of hormones responsible for healthy growth, development and reproduction) and have adverse health effects. Examples include heavy metals, pesticides, ethoxylates, carboxylates, alkylphenols and synthetic/natural hormones. Outlined earlier, steroid estrogens had been identified as the EDCs of interest concerning estrogenic responses in fish populations. Therefore, a review of the origin, classification and nature of steroid estrogens was necessary.

2.1.2 Steroid Estrogens

The natural and synthetic steroid estrogens of interest were:

- E1 (estrone)
- E2 (estradiol)
- EE2 (ethinylestradiol)
- E3 (estratriol)

Although E3 could be found in high concentrations in the effluent of sewage treatment plants, the effects it had on aquatic life proved negligible and so it was not considered further in this report. Of the three remaining estrogens, E1 and E2 occur naturally whereas EE2 is synthetic and mainly constitutes the contraceptive pill.

2.1.3 Sewage Effluent Oestrogen Characterisation

Table 2.1 compares the relative potencies, effluent concentrations and potential impacts on wildlife of estrogens and other EDCs (alkylphenols – 4t-NP & 4t-OP, ethoxylates – NPEOs, and carboxylates – NPECs & CNPECs). The column under ‘in vitro E2 equiv’ in Table 2.1 indicates the potencies of all the listed compounds relative to E2 in an effluent solution. The in vivo vitellogenin (VTG – an estrogenic responsive protein mentioned in section 1.1) response in male trout, also relative to E2, combined with the respective effluent concentration of each compound, gives a clear indication of the serious environmental impact of steroid estrogens.

Table 2.1 Relating EDC Concs. in Sewage Effluent to Potential Impacts on Wildlife⁸

compd	in vitro E2 equiv	typical effluent concn (ng L ⁻¹)	in vivo VTG response in trout E2 equiv
E1	0.5	5	0.5
E2	1	1.5	1
E3	0.005	20	0.001
EE2	1–2	0.5	25
4t-NP or 4t-OP	0.0001	2 000	0.001
NPEOs, NPECs, & CNPECs	0.00001	20 000	no significant NPEO mixture effect at 100 µg/L

This lead to the following assessments:

(i) E1; despite being half as potent as E2, it was frequently found at concentrations in effluents consistently greater than double that of E2. On the basis of in vitro potency and concentration, E1 appeared to be the most

important endocrine disrupter. More efficient removal of E1 could therefore have a significant effect on overall estrogenicity since sewage treatment plants were found to be less effective at removing this compound compared to the other steroid estrogens.

(ii) E2; lower concentrations have reduced the overall impact compared with E1. There also appeared to be good removal performance of E2, some Dutch, Canadian and Brazilian sewage treatment plants have reported complete elimination of the compound.⁸

(iii) EE2; although in vivo vitellogenin responses in trout show EE2 to be the most potent (Table 2.1), low potencies in general in vitro tests revealed it not to be a key player. In addition, very low concentrations, to the point of measuring so close to detection limits of most analytical techniques, made EE2 properties the most difficult to evaluate.

For these reasons (and other reasons to be mentioned in the next section) the model for this project utilised estimations and relative data solely based on E1. However, this does not go to say that E2 and EE2 are less important or less threatening. As more information about these estrogens surfaces the easier it may be to adapt the model to E2 and EE2 removal.

2.1.4 Sewage Influent Oestrogen Characterisation

It was a matter of interest to explore the sources of these steroid estrogens in the hope of gaining a better understanding of their degradation behaviour. The main source of steroid estrogens in wastewater is the human population.⁵ With this knowledge, a recent study of human excretion was carried out by A. Johnson and R. Williams to predict sewage treatment plant influent concentrations.⁵ The predicted results proved to be reasonably accurate when tested against recent measurements of estrogens in influents of sewage treatment plants. These results are presented in Table 2.2.

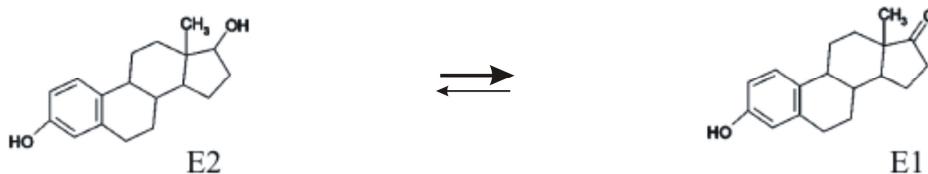
Table 2.2. Observed Influent Concs. (ng/L) for Various STWs Compared to Predicted Values.⁵

STW with population and flow	E1 influent		E2 influent		EE2 influent	
	observed mean	model mean	observed mean	model mean	observed mean	model mean
Cobis (40 000 pop and 10 000 m ³ /d)	71	55	16	13	4	3.6
Fregene (120 000 pop and 42 000 m ³ /d)	67	40	9	9	3.4	2.5
Ostia (350 000 pop and 112 000 m ³ /d)	51	43	14	10	2.5	2.8
Roma Sud (1 200 000 pop and 734 000 m ³ /d)	35	23	9	5	2.9	1.5
Roma Est (800 000 pop and 265 000 m ³ /d)	50	42	9	10	2.3	2.7
Roma Nord (800 000 pop and 354 000 m ³ /d)	37	31	11	8	2.9	2.0
Wiesbaden (300 000 pop and 66 000 m ³ /d)	66	63	16	15	8	4.0

The ‘model mean’ concentrations (theoretical mean predictions from the study) of E1, E2 and EE2 are compared to mean experimental measurements (‘observed mean’) in nanograms per litre (ng/L) for various sewage treatment works (STW). It has to be mentioned that the difficulty in measuring these extremely dilute concentrations should allow for large errors in the ‘observed’ data. Nevertheless, the results outlined the relative quantities of E1, E2 and EE2 to be expected in sewage influent. Also, considering Great Billing wastewater treatment plant, which receives sewage flows from a population similar in size to that of Cobis listed in Table 2.2, the results gave a rough idea of the magnitudes of oestrogen influent concentrations to be anticipated.

Figure 2.1 shows the molecular structures of both E1 and E2 which both comprise mainly of a complex chain of pentagonal carbon loops the only difference being that E2 has an extra hydroxyl group (–OH) in place of a double bonded oxygen atom (=O). An interesting assumption made in the construction of the model predicting wastewater influent composition was that 50% of all the E2 excreted would oxidise to E1 in transit through the sewage system to the STW.

Figure 2.1. Oxidation of E2 to E1



This turned out to be a valid assumption since, according to Table 2.2, the mean predicted value divided by the observed value gave a mean ratio of:

- 0.78 for E1
- 0.85 for E2
- 0.80 for EE2

which were good theoretical estimates. When the model was run ignoring 50% E2 oxidation, despite slightly improved estimates for E1 and EE2 (both having mean ratios of 1.00), the mean ratio for E2 turned out considerably worse at 2.20.⁵ This should be noted for future models when taking the removal of E2 into consideration. For the context of this project, however, it backed the importance to focus on E1 removal, as previously mentioned.

2.1.5 Steroid Oestrogen Sources

In addition to total concentrations, it is worth noting the contribution of estrogens made by different members of the population. The study indicated:⁵

(i) for E1; 34% amounted from pregnant women, 26% from menstrual females, 10% from males, 4% from menopausal women on HRT, 2% from menopausal women and the remaining 24% formed by conversion from E2.

(ii) for E2; 52% amounted from pregnant women, 14% from menstrual females, 15% from males, 17% from menopausal women on HRT and 2% from menopausal women.

(iii) The contraceptive pill contributes mostly to EE2 contamination since HRT treatment relies mainly on doses of E1 and E2. It is a fair estimate to say (in a typically western culture) that 17% of females take the contraceptive pill.

2.2 Wastewater Treatment Process Stages

A typical sewage treatment plant would generally consist of the following process stages:¹¹

(i) Preliminary; for the removal of large objects such as stones, grit and grease. Most malodorous gases are also biofiltered off at this stage.

(ii) Primary; mainly for sedimentation of wastes susceptible to floating and settling such as oils, greases, heavy metals and some organic nitrogen and phosphorous. Aluminium and iron salts are also added at this stage to form hydrolysed salts and help remove clay and organic compounds by adsorption. A 25% reduction in the bulk organic matter can be achieved in this manner.¹²

(iii) Secondary; remaining organic compounds are further degraded, mostly by biological means.

(iv) Tertiary; if very low levels of phosphorous and nitrogen are required, further unit operations have to be implemented. Specialised biological treatment and high level filtration are of the most common used here. Alternatively, natural systems such as ponds, lakes and fields can provide the chemical, physical and biological mechanisms that are required at this stage. It has been suggested that natural open-air death, sedimentation and biodegradation can be more effective than most advanced tertiary wastewater systems.¹²

Finally, if the water is to be reused for drinking, remaining pathogens and bacteria can be eliminated through disinfection by chlorine.

2.3 Wastewater Treatment Technology

Industrial use of domestic sewers has increased significantly over the past 20-30 years. The number of industrially synthesised organic compounds now exceeds half a million and it is estimated that some 10,000 new compounds are added each year.¹¹ Public health and environmental concerns have therefore urged the design and selection of new treatment facilities.

(i) UV Photolysis; classified as a tertiary wastewater treatment process and is highly effective in breaking down microorganic contaminants. In practice, however, low efficiency results due to absorption by chromophores and general scattering of UV light through the bulk of organic matter (degradation of most endocrine disrupting compounds (EDCs) require residence times of up to 100 hours).¹⁰ Despite possible catalytic improvements, it is unfeasible to use UV photolysis on a large scale due to high costs.

(ii) Activated Carbon; active surface hydrophobic reactions allow for effective removal of EDCs, pharmaceuticals and pesticides.¹² But, similarly, the costs of installing and maintaining granular bed reactors, in order to use activated carbon on a large scale, would be unsustainable.

It was therefore necessary to research existing technologies and potentially optimise current performance for the removal of trace microorganic contaminants.

2.4 The Activated Sludge Treatment Process

Classified as a secondary process stage and first put into practice in 1913, the activated sludge process has proved effective in removing trace organic compounds.⁷ Field studies suggest the elimination of up to 85% of steroid estrogens alone.⁸ Table 2.3 lists a compilation of recorded E1, E2 and EE2 removal values for activated sludge treatment plants worldwide. The data further consolidated the importance of focusing solely on E1 for the remainder of the project as E1 had the poorest worldwide mean removal at 64.7% compared with 81.7% and 85.2% for E2 and EE2 respectively.

Table 2.3. Steroid Oestrogen Removal Values for Activated Sludge Plants.⁵

country	E2% removal	E1% removal	EE2% removal
European av (<i>n</i> = 8)	88	74	NA
Italy (<i>n</i> = 30)	87	62	85
Canada (<i>n</i> = 6)	99*	71	NA
Japan (<i>n</i> = 27)	67	NA	NA
Italy (<i>n</i> = 18)	85	61	NA
Germany (<i>n</i> = 1)	98	98	90
worldwide mean removal	81.7 (± 10.6)	64.7 (± 5.8)	85.2 (± 5.1)

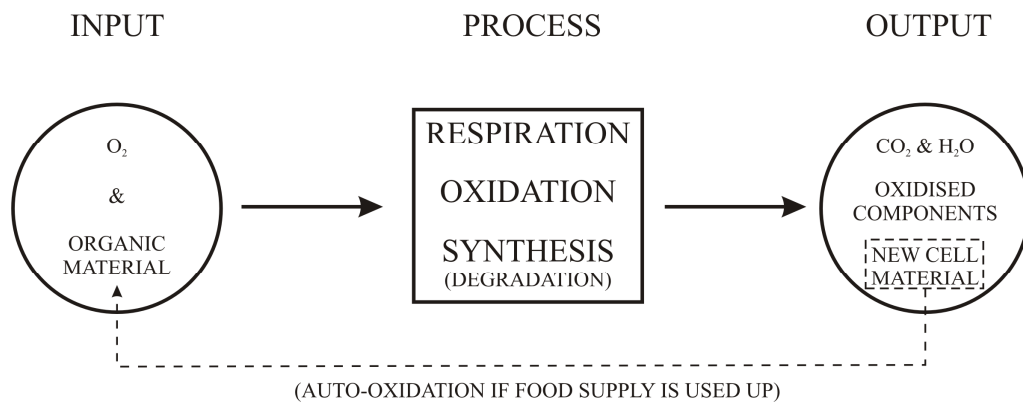
*E2 was largely undetectable in Canadian effluents and therefore 100% removal was reported in most cases.

The following sections discuss the process in more detail.

2.4.1 Activated Sludge

The content of sludge remains poorly defined. It mainly contains a biomass of over 100 different types of heterotrophic (dependent on complex organic substances for nutrition) and autotrophic (synthesising its own nutrition from inorganic material and energy) bacteria including a range of protozoa.¹³ It is the aerobic (and heterotrophic) bacteria responsible for degrading most organic matter. Organic matter present in wastewater (i.e steroid estrogens) acts as a vital source of food for the survival and successful propagation of some of these bacteria. Figure 2.3 outlines the basic process.

Figure 2.3. Action of Aerobic Organisms on Wastewater Organic Contaminants.¹³

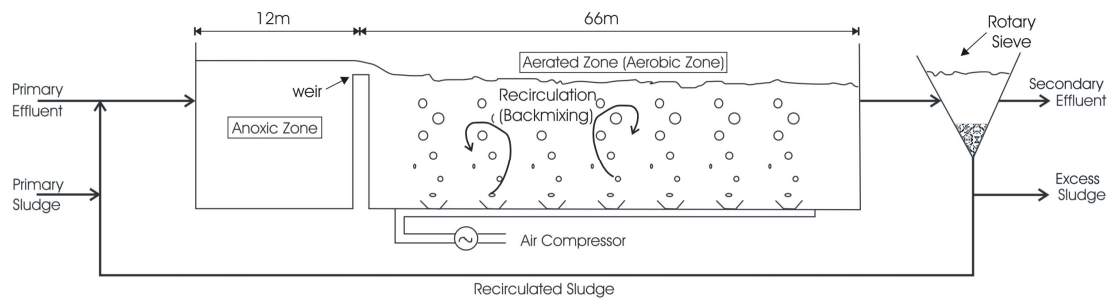


The aerobic organism is presented as a rectangle in Figure 2.3 where the process of organic contaminant removal is governed by respiration, oxidation and synthesis (or degradation). Oxygen and the organic material present in wastewater mainly constitute the input to the process whereas new cell material, oxidised components, carbon dioxide and water make up the output. Note the dotted line indicating cell material digestion when nutrition becomes scarce, ultimately leading to cell population death.

2.4.2 Sewage Treatment Plant Integration

Effluent from the primary stages is directed towards the input of the activated sludge system. The system consists of anoxic and aerated zones (Figure 2.4). The anoxic zone in this case was 12m in length and was where denitrification took place. Primary sludge (fresh sludge) is combined with recirculated sludge and subsequently mixed with the wastewater. The solution in the anoxic zone was assumed well mixed.

Figure 2.4. Schematic of the Activated Sludge Treatment Tanks.



Iron salts (Fe(ii)Cl_2) are added to the wastewater prior to being mixed with the sludge in the anoxic zone which made the water appear black in colour. Figures 2.5 & 2.6 show sludge (brown) and iron rich wastewater (black) travelling to the denitrifying tank and subsequently being mixed.

Figure 2.5. Sludge and Wastewater Transportation.

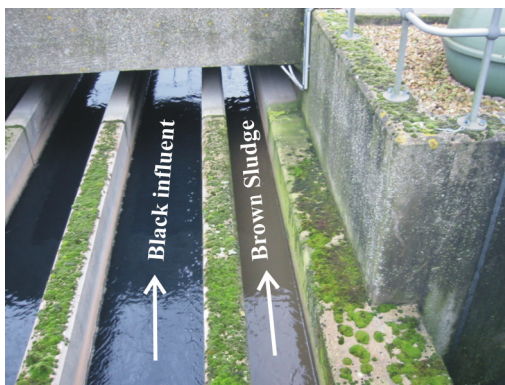


Figure 2.6. Anoxic Zone Mixing.



The aerated zone, or nitrifying tank, follows over a weir where vast quantities of air are pumped into the solution causing plumes of recirculating flow (Figure 2.4). This allows for oxidation of the iron salts (to Fe(iii)) followed by precipitation with phosphates.¹⁴ The high oxygen levels ‘activate’ the biomass and biodegradation of organic trace contaminants takes place. It is worth pointing out that the major cost of the whole process is powering air compressors to achieve these high levels of oxygen.¹⁴ In Great Billing, the

wastewater flows down a 66m length aerated tank before settling in a rotary sieve, where a low velocity circular flow ensures the separation of sludge from wastewater. Figure 2.7 shows the aerated tank with the surface flow pattern produced by the masses of pumped air. The rotary sieve which follows is pictured in Figure 2.8. The sludge is then mostly internally recirculated to the denitrifying tank while the separated secondary effluent is released into the environment. Excess sludge is then dewatered before being pumped and treated thermophilically (200°C) in a digester. What remains is then purged which, of course, has an environmental setback.¹⁴

Figure 2.7. Aerated Zone.

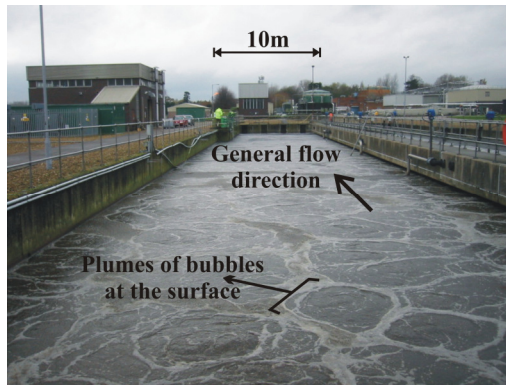


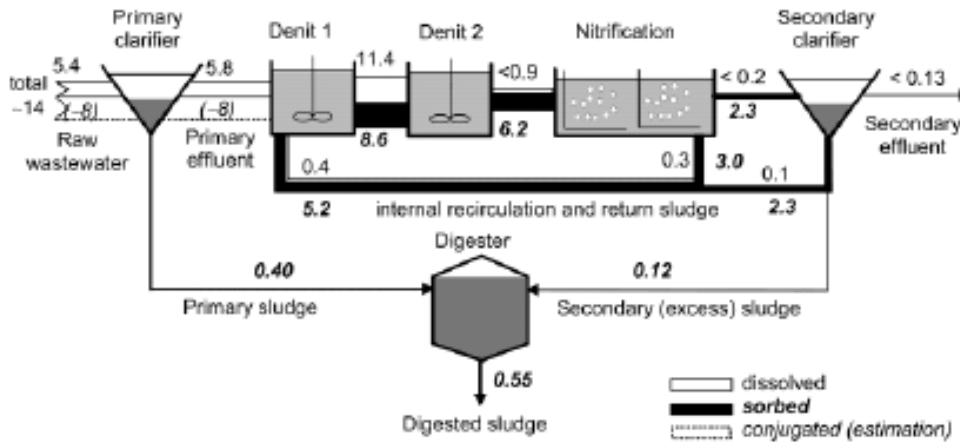
Figure 2.8. Rotary Sludge Separation.



2.4.3 Removal Mechanism

The science behind oestrogen removal in the activated sludge process is still largely unknown but recent studies suggest the key principles are possibly governed by aqueous phase biodegradation, solid phase biodegradation and adsorption onto solid surfaces.¹⁵ Estimated adsorbed and dissolved (aqueous phase) mass fluxes of E1, in grams per day, are presented in Figure 2.9 for an activated sludge plant in Wiesbaden, Germany.

Figure 2.9. Flow Scheme of Dissolved and Adsorped E1 for Wiesbaden Plant.



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For this particular case, roughly 85% of all the E1 present was estimated to be adsorped at the inlet of the nitrification tank (aeration tank) and about 95% adsorped at the outlet. This clearly shows the importance in considering adsorption of E1 onto biomass surfaces in the construction of the model.

3.0 Modelling Steroid Oestrogen Removal

The difficulty in modelling oestrogen removal from wastewater arose from the fact that very little information on the physical or biochemical removal properties was currently available. This was largely due to the very low steroid oestrogen concentrations in sewage (ng/L), and the difficulty in obtaining any experimental data on which to build a theory. In addition, the non-ideal nature of the activated sludge process (the complex nature of the flow in an aerated tank, the varying influent composition, the erratic effect of environmental factors, etc.) and the ambiguity of sludge composition further complicated matters.

Therefore, improving the model devised by E. Jeremy and presented in the previous report to this was considered the preferred means in achieving the project objectives. This section analyses the possible factors affecting E1 removal from wastewater, improving formulations utilised in the previous model, in an attempt to develop more accurate equations governing the removal process.

E. Jeremy highlighted the importance to include hydrodynamic factors in dealing with the aerated zone of the activated sludge process. The factors which could affect removal efficiency also include:¹⁶

- Influent wastewater composition
- Environmental factors
- Tank geometry
- Biochemical and physiochemical characterisation
- Flow dynamics, aeration and kinetic parameters

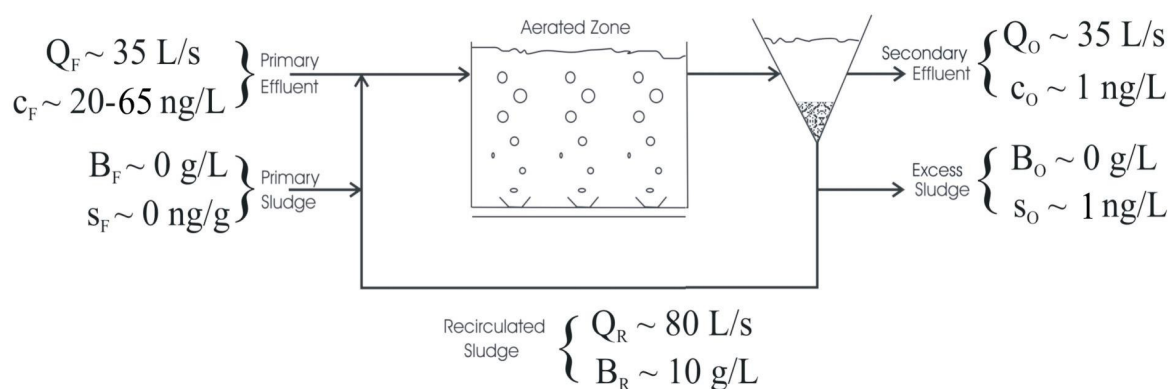
3.1 Steroid Oestrogen Removal Factors

Each factor listed above was analysed in detail.

3.1.1 Influent Wastewater Composition

The model was to be based on parameters relating to the **aeration lane** of the activated sludge treatment plant in Great Billing. Rough estimates of the influent, effluent and return concentrations of E1 both in solution and adsorped to solids is presented in Figure 3.1.

Figure 3.1. Great Billing Aeration Lane E1 Mass Balance.^{17,18}



Since accurate data is unavailable, some assumptions and simplifications have been made. Taking the aqueous concentration of E1 in the feed (c_F) to be between 20-65 ng/L with a feed volumetric flow rate (Q_F) of about 35 L/s is commonplace for Great Billing. Similarly, a reasonable estimate of the total output concentration of E1 was around 3 ng/L (assuming ~ 70% adsorped (s_o) and ~ 30% in solution (c_o)). Primary and excess sludge biomass loading (B_F & B_o respectively) and E1 concentrations (s_F & s_o respectively) have been ignored for model simplification. Considering estimates for return sludge biomass loading and return volumetric flow rate (B_R & Q_R respectively), and setting the overall tank biomass loading to $B = 3$ g/L, allowed for a reasonable estimation of the inlet E1 concentrations adsorped and in solution: (see appendix 10.1 for calculation)

- 0.7 ng/L adsorped, hence, $[s_{E1}]_{in} = 0.2$ ng adsorped/g biomass (3.1)

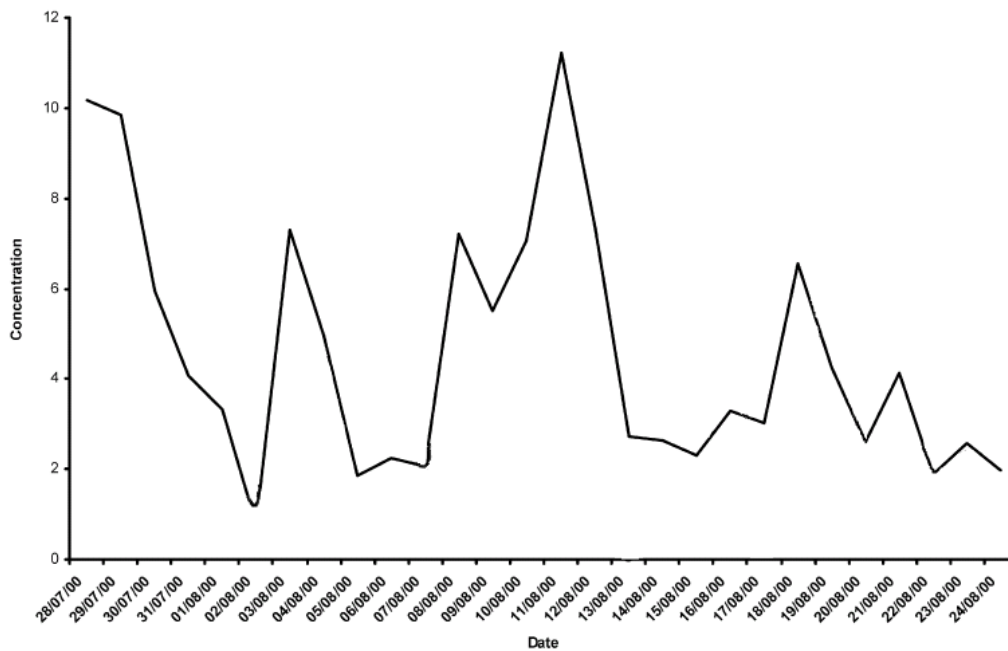
- and in solution, $[c_{E1}]_{in} = 20$ ng/L (3.2)

Conjugated forms of E1 at the inlet were ignored.

3.1.2 Environmental Factors

Rainfall, temperature and time of day are to name but a few important factors which affect flow rates, concentrations and degradation efficiency. Figure 3.2 demonstrates the inconsistency of measurements due to environmental change at Great Billing. Concentrations of E1 in the effluent of the treatment plant were analysed by R. Williams et al over a period of just one month.

Figure 3.2. Time Series of E1 Concentrations (ng/L) from Great Billing.¹⁷



For these reasons, inlet E1 concentrations were assumed constant and an average volumetric flow rate was taken. Temperature changes were ignored.

3.1.3 Tank Geometry

The aeration tank dimensions were:

- $L = 66 \text{ m}$ (3.3)

- $H = 3 \text{ m}$ (3.4)

- $W = 10\text{m}$ (3.5)

3.1.4 Biochemical and Physiochemical Characterisation

(i) Sludge Characterisation; there are current investigations into optimising the growth of selective oestrogen dependable microorganisms in activated sludge,¹⁶ but uncertainty still remains about the exact bacterial content. Despite this, it has been proven that removal efficiency of oestrogen increases with sludge age.¹⁹ It was therefore assumed that the sludge in the model was at least seven days old and had been pretreated at 30°C, since best effects have been achieved under these conditions.¹⁹

(ii) Rate of Degradation; in the previous model, the rate of degradation of E1 (r) was simply proportional to the E1 solution concentration (c_{E1}):¹⁶

$$r = -K_{E1}[c_{E1}] \quad (\text{ng L}^{-1} \text{ s}^{-1})^* \quad (3.6)$$

*units here are ng of E1 in sol. /L of effluent /s

where K_{E1} is the rate constant and has units of /s. This proved to be an inaccurate estimation. Since the degradation depends on bacterial activity, higher densities of bacteria populations should give a higher degradation rate. Increasing the biomass loading (B) in this model had no effect on biodegradation and, in fact, impaired overall E1 removal performance (see appendix 10.2).

Assuming the degradation rate also depended on biomass loading was, therefore, considered a reasonable improvement to make. This was also backed by a recent study on sludge biodegradation of estrogens by A. Joss et al.²⁰ The rate equation thus became:

$$r = -K_{E1}[B][c_{E1}] \quad (\text{ng L}^{-1} \text{ s}^{-1})^* \quad (3.7)$$

*units here are ng of E1 in sol. /L of effluent /s

where the biomass loading (B) has units of g/L (grams of biomass per litre of effluent). K_{E1} has been adapted to take the value:

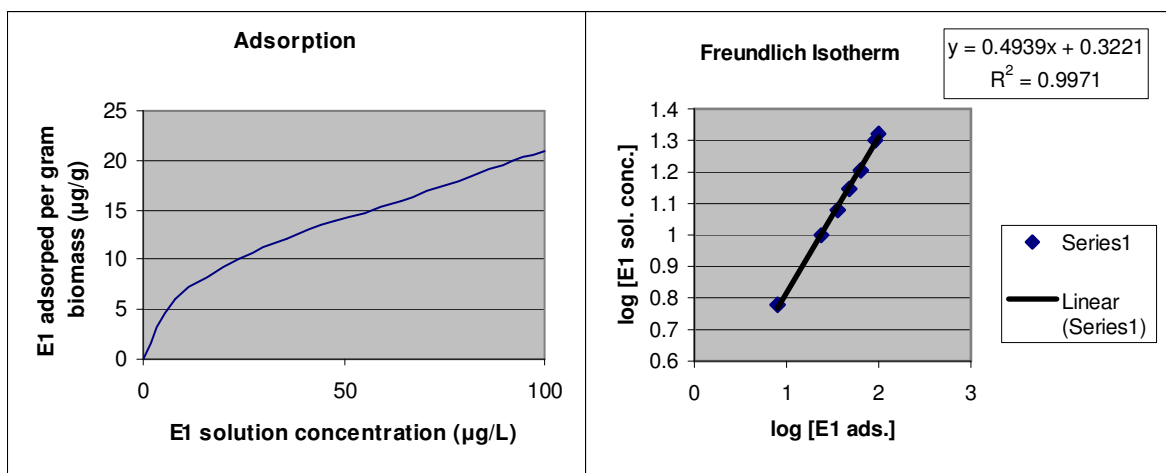
$$K_{E1} = 3.93 \times 10^{-5} \quad (\text{L g}^{-1} \text{ s}^{-1})^* \quad (3.8)$$

*units here are L of effluent /g of Biomass /s

Aqueous degradation was only considered in this model as information on solid degradation is currently unavailable.

(iii) Adsorption; as mentioned earlier, adsorption on the surface of the biomass played a large part in the removal process.

Figure 3.3. Freundlich Isotherm Relating E1 adsorped to E1 in solution.



(a)

(b)

Quantifying this phenomenon, however, was extremely difficult at the minute concentrations of E1 being dealt with. In the previous model, a relationship to predict the amount of E1 which would be adsorped on to biomass surfaces was derived from available experimental data.¹⁶ Figure 3.3(a) shows a plot of E1 adsorped onto biomass surfaces against E1 solution concentration for a series of experiments. The log (base 10) of each set of data was then plotted (Figure 3.3(b)) and a Freundlich isotherm calculated for the best linear fit. It was concluded that:

$$s_{E1} = c_{E1}^F, \text{ where } F = 0.4939, \quad (3.9)$$

and s_{E1} being the amount of E1 adsorped per gram of biomass, with units of $\mu\text{g/g}$.

This was later simplified to:

$$s_{E1} = pc_{E1}, \text{ where } p = 0.27 \text{ ('Distribution Coefficient', units L/g)*} \quad (3.10)$$

*units here are L of effluent /g of biomass

These correlations applied to E1 concentrations taken in the region of 20-100 $\mu\text{g/L}$ indicated by the linear part of Figure 3.3(a). For E1 concentrations below 20 $\mu\text{g/L}$, however, the graph had been forced through the origin, which deemed the Freundlich relationship unreliable for wastewater E1 concentrations in the order of ng/L . An improvement based on a recent study of adsorption for E1 at the required concentrations calculated a distribution coefficient (p) of 0.9 ± 0.1 L/g.¹⁵ Hence, the model became:

$$s_{E1} = pc_{E1}, \text{ where } p = 0.9 \text{ (L/g)} \quad (3.11)$$

This concluded that the amount of E1 adsorped on to biomass surfaces was assumed in equilibrium with the E1 solution concentration throughout the tank.

3.1.5 Flow Dynamics, Aeration and Kinetic Parameters

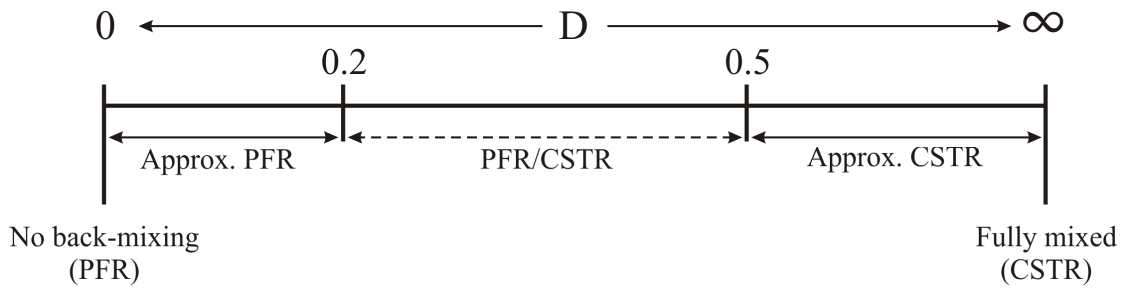
Flow properties have been known to affect the nature and period of contact with oestrogen molecules. The flow was considered quite irregular due to aeration throughout the tank and was further complicated by its heterogenous phase content.

To begin to classify the flow, the degree of mixing had to be considered. The submerged diffusers pumping air into the mixture would suggest that the tank contents were, on the whole, well mixed leading to Continuously Stirred Tank Reactor (CSTR) like behaviour. More specifically, due to the plumes resulting from the pumped air, the tank could be suggested to act more like a long series of CSTRs. Further still from ideal CSTR behaviour, previous tests on biomass in solution have shown locations in the tank with more enhanced microbial growth than others, suggesting Plug Flow Reactor (PFR) like behaviour.⁹ Tracer studies to experimentally determine the degree of mixing are unavailable, however, good theoretical progress in categorising non-ideal flow has been made in the past century.²¹ The dispersion coefficient (D) categorises the degree of ‘back mixing’ and was estimated by a formula developed by Murphy and Boyko which depended on the width of the tank (W) and the aeration rate (q_a):²²

$$D = 3.118 \times W^2 \times q_a^{0.344} \quad (\text{m}^2 \text{ s}^{-1}) \quad (3.12)$$

the dispersion coefficient was classified according to Figure 3.4. For values of $D \leq 0.2$, the flow is approximated to PFR. When $D \geq 0.5$ the conditions were approximated to be CSTR. For values of $0.2 \leq D \leq 0.5$, the flow is said to be a mixture of both PFR and CSTR.¹⁶

Figure 3.4. Dispersion Coefficient Classification.



For the aerated lane at Great Billing, the dispersion coefficient was calculated:¹⁶

$$D = 0.33 \quad (\text{m}^2 \text{ s}^{-1}) \quad (3.13)$$

which concluded that the flow for the activated sludge process had to be modelled as combined PFR and CSTR.

The remaining compulsory kinetic parameters were also previously calculated. Having the average hydraulic residence time (hrt)²³ enabled the calculation of a mean effluent velocity (u):

$$u = \frac{L}{hrt} = \frac{66}{8.91} = 7.4 \quad (\text{m hr}^{-1}) \quad (3.14)$$

a mean volumetric flow rate was also provided:¹⁶

$$Q = 36 \quad (\text{L s}^{-1}) \quad (3.15)$$

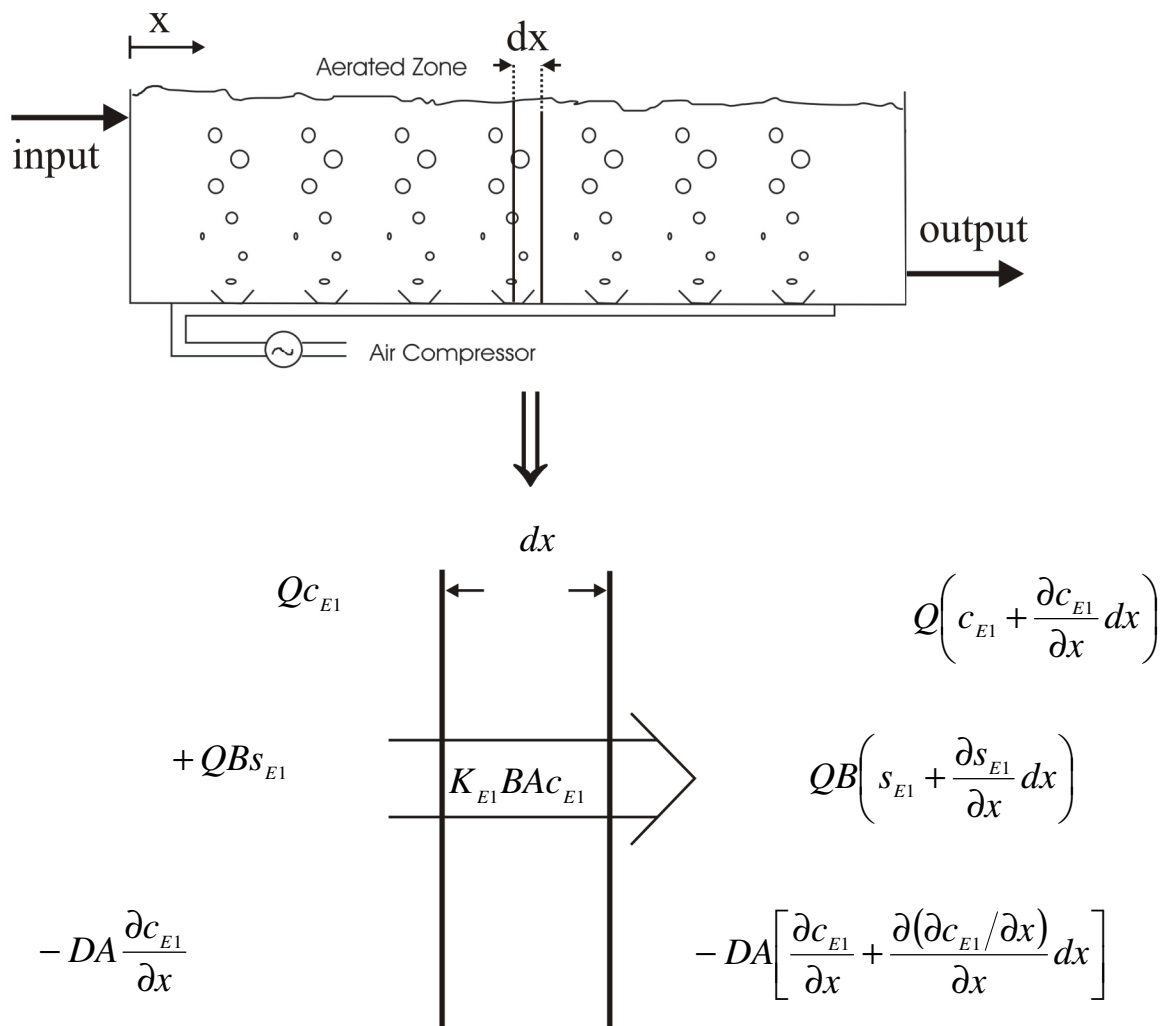
With all the necessary factors discussed and parameters listed, the next section deals with devising suitable equations.

3.2 Deriving the Equations

3.2.1 E1 Mass Balance

Within the activated sludge aeration lane, the following mass balance (Figure 3.5) over an infinitely small 2-d section of length dx was carried out .

Figure 3.5. E1 Mass Balance Over Segment dx .



'A' and 'V' are the elemental cross section area and volume respectively and 'QB' equates to the mass flow rate of biomass in g biomass/s. Balancing the input and output fluxes obtained an expression for the rate of change of E1 solution concentration with time :

$$V \frac{\partial c_{E1}}{\partial t} = \text{Input Flux} - \text{Output Flux} - \text{Quantity Biodegraded} \quad (3.16)$$

Substituting from Figure 3.5 gave,

$$V \frac{\partial c_{E1}}{\partial t} = -Q \frac{\partial c_{E1}}{\partial x} dx - QB \frac{\partial s_{E1}}{\partial x} dx + DA \frac{\partial^2 c_{E1}}{\partial x^2} dx - K_{E1} B A c_{E1} dx \quad (3.17)$$

Assuming steady state and dividing by 'A' in the limit as dx tends to zero, equation (3.17) gave,

$$D \frac{d^2 c_{E1}}{dx^2} - u \left(\frac{dc_{E1}}{dx} + B \frac{ds_{E1}}{dx} \right) - K_{E1} B c_{E1} = 0 \quad (3.18)$$

finally, substituting for s_{E1} from equation (3.11) yielded,

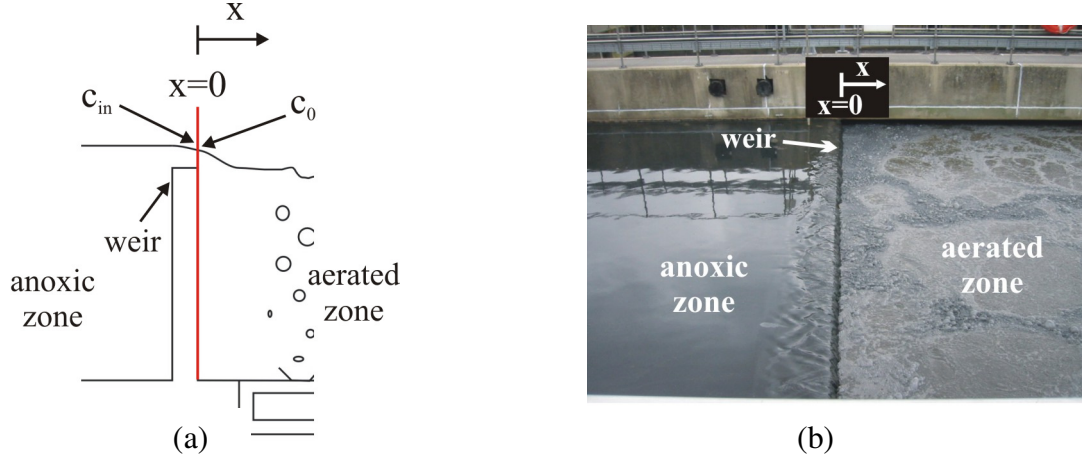
$$D \frac{d^2 c_{E1}}{dx^2} - u(1 + Bp) \frac{dc_{E1}}{dx} - K_{E1} B c_{E1} = 0 \quad (3.19)$$

3.2.2 Boundary Conditions

Dankwerts conducted revolutionary work on the boundary conditions of non-ideal flows within reactors in.²⁴ The boundary conditions were as follows:

- Inlet

Figure 3.6. Inlet Boundary Schematic and Great Billing Counterpart.



With reference to Figure 3.6(a) (Figure 3.6(b) shows a photograph of the real inlet boundary at Great Billing being modelled), the inlet boundary was considered at the weir just at the beginning of the aerated zone. Dankwert acknowledged that a sharp drop in E1 concentration should be expected across the inlet boundary due to acute difference in the degrees of mixing. The inlet boundary was thus defined:²⁴

at $x = 0$,

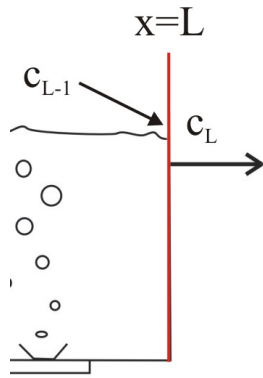
$$u[c_{E1}]_{in} + uB[s_{E1}]_{in} = u[c_{E1}]_0 + uB[s_{E1}]_0 - D \left. \frac{dc_{E1}}{dx} \right|_0 \quad (3.20)$$

and substituting for s_{E1} from equation (11) yielded,

$$u([c_{E1}]_{in} + B[s_{E1}]_{in}) = u(1 + Bp)[c_{E1}]_0 - D \left. \frac{dc_{E1}}{dx} \right|_0 \quad (3.21)$$

- Outlet

Figure 3.7. Outlet Boundary Schematic and Great Billing Counterpart.



(a)



(b)

According to Dankwert, there would be no change in E1 concentration at the outlet ($c_{L-1} = c_L$) leading to the second boundary condition:

at $x = L$,

$$\left. \frac{dc_{E1}}{dx} \right|_L = 0 \quad (3.22)$$

This chapter has shown how the previous model was improved on. The main changes made were to the biodegradation rate equation and adsorption isotherm. These changes, along with more accurate estimations of the inlet concentrations of E1, should create a considerably more realistic model. The mass balance equation (3.19) and the two boundary condition equations (3.21) and (3.22) formed the basis of the model to be analysed for the remainder of the project.

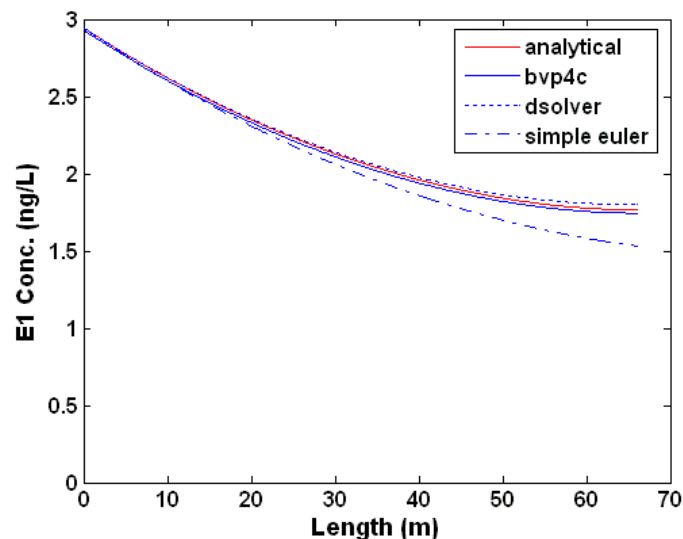
4.0 Solving the Equations

As well as developing the mathematical model, improving the solving techniques previously employed was vital in achieving the project objective. With a more sophisticated MATLAB solver, a multitude of solutions could be analysed in good time, and with more advanced graphical presentations, steady progress could be made.

4.1 Selection of Suitable MATLAB Solver and Step Size

An analytical solution for equation (3.19), with the boundary conditions specified, had been determined by Dankwerts²⁴ (see appendix 10.3) and is plotted in Figure 4.1 in red. MATLAB defines these set of equations as a ‘boundary value problem,’ the most appropriate internal solver in this case being bvp4c. A comparison of solutions by various MATLAB solvers with the analytical solution was carried out to verify this and plotted in Figure 4.1.

Figure 4.1. MATLAB Solver Comparison with Analytical Solution.

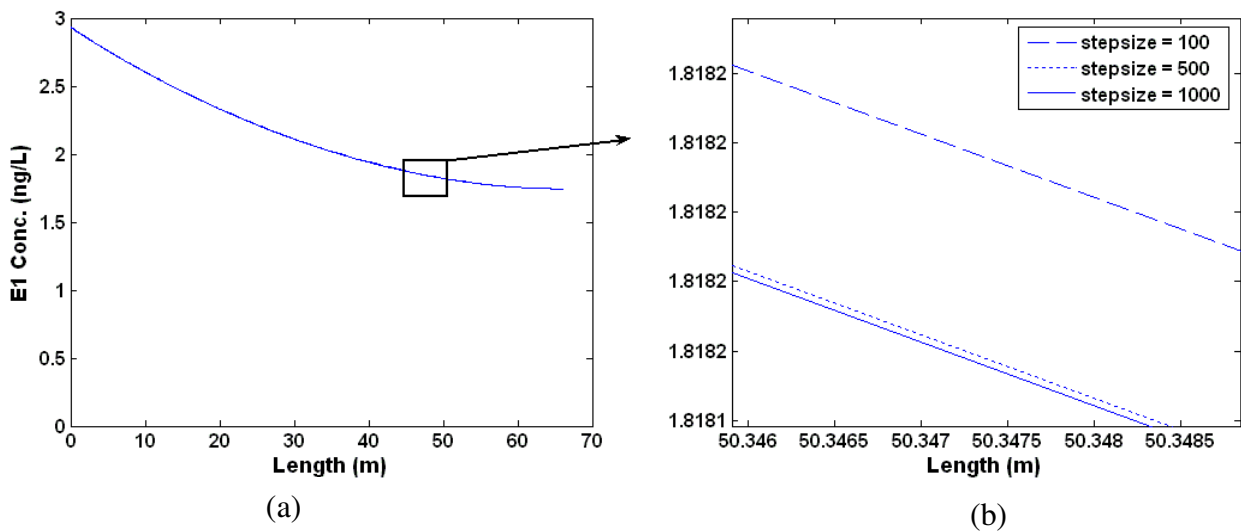


It has to be noted that the initial conditions for the simple euler algorithm were copied straight from the analytical solution. A simple euler algorithm was employed in the previous model, which showed that major improvements have

been made since the simple euler solution was furthest from the analytical (Figure 4.1).

Varying the solving step size (the solving accuracy which in turn affects the number of iterations performed) in `bvp4c` did not have a major effect on the solution. Figure 4.2(a) displays three different plots which were all so similar that they appeared as a single curve. The scale had to be reduced to over 10000 times (!) in order to reveal any discrepancy (see figure 4.2(b)). In the end, a step size of 1000 was used.

Figure 4.2. The Effect of Varying `bvp4c` Step Size.

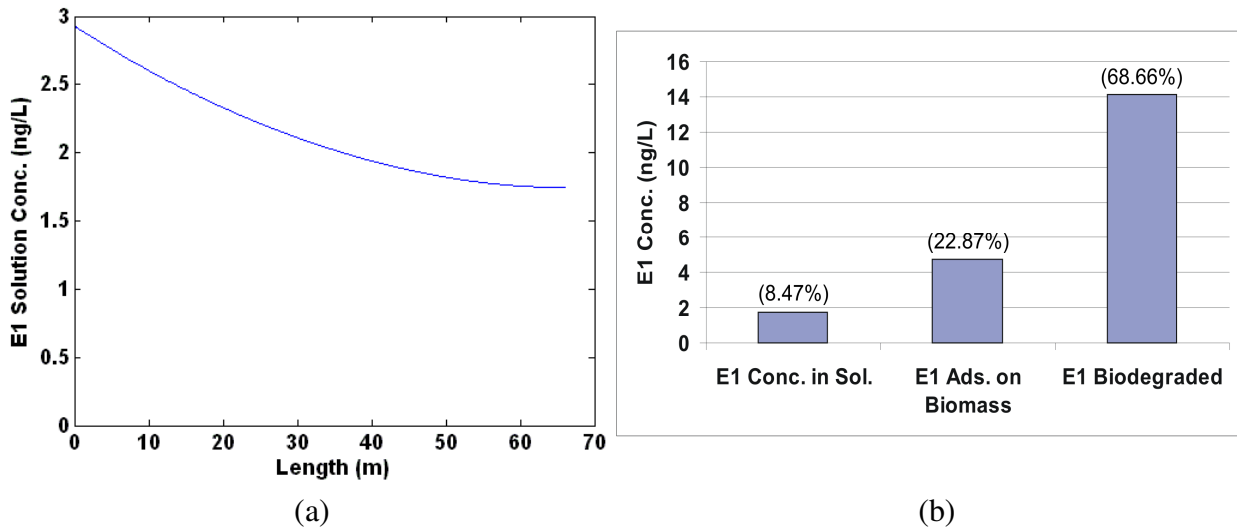


4.2 Results - Solution Analysis

With the Great Billing (GB) activated sludge treatment plant parameters, given in section 3.1, the model solved for an E1 solution concentration (C_{E1}) profile down the full length (L) of the aerated tank (Figure 4.3(a)). Despite the relatively high total inlet E1 concentration (both in solution and adsorbed on biomass) of 20.6 ng/L, C_{E1} at $x=0$ was around 2.9 ng/L.

This was due to the tank contents being well mixed for which the derivative in the inlet boundary condition was necessary.

Figure 4.3. c_{E1} Tank Profile for GB and Overall Fate of E1 at Outlet.



Further analysis of the output data revealed the resulting proportion of E1 adsorped, degraded and left in solution (Figure 4.3(b)). E1 adsorped at the output was attained from the E1 remaining in solution due to equilibrium (section 3.1.4, equation (3.11)). The difference with the total input E1 concentration was then calculated and contributed wholly to biodegradation. A removal of about 69% (91% assuming adsorped E1 is considered ‘removed’) can be seen here which was within the bounds of experimental records (Table 2.3).

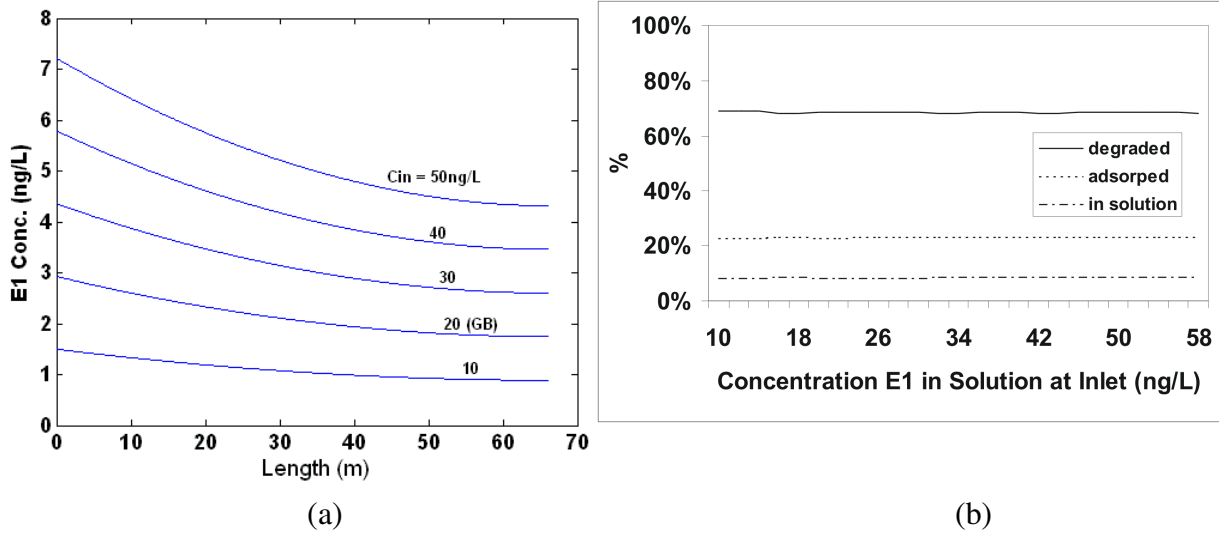
4.2.1 Solution Analysis with Parameter Variation

Figures 4.4-4.9 consider how the model would interpret variations in key parameters including flow properties, reaction kinetics and inlet concentrations.

(i) Inlet E1 Solution Concentration, $[c_{E1}]_{in}$; the procedure outlined in section 4.1 was iterated over a variation of inlet concentration values. Although the outlet E1 solution concentrations (c_{E1} at $x=66m$ in Figure 4.4(a)) increased

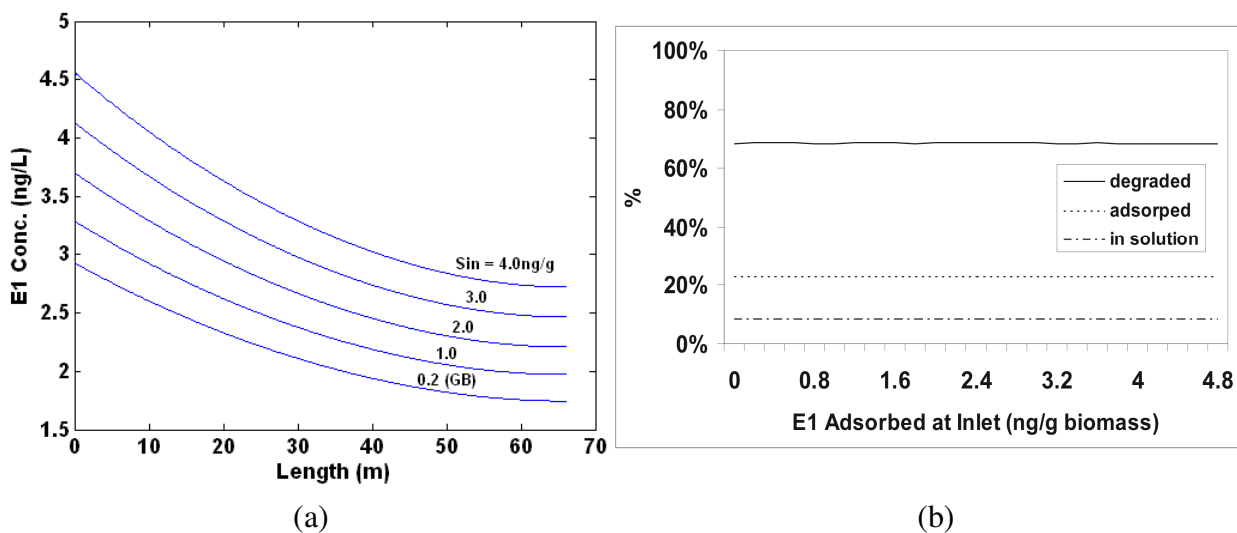
slightly with higher inlet concentrations, the overall removal of E1 was increased since there was negligible variation in the proportions adsorped and biodegraded (Figure 4.4(b)).

Figure 4.4. C_{EI} Tank Profile for a Range of $[C_{EI}]_{in}$ and Overall Fate of E1 at Outlet.



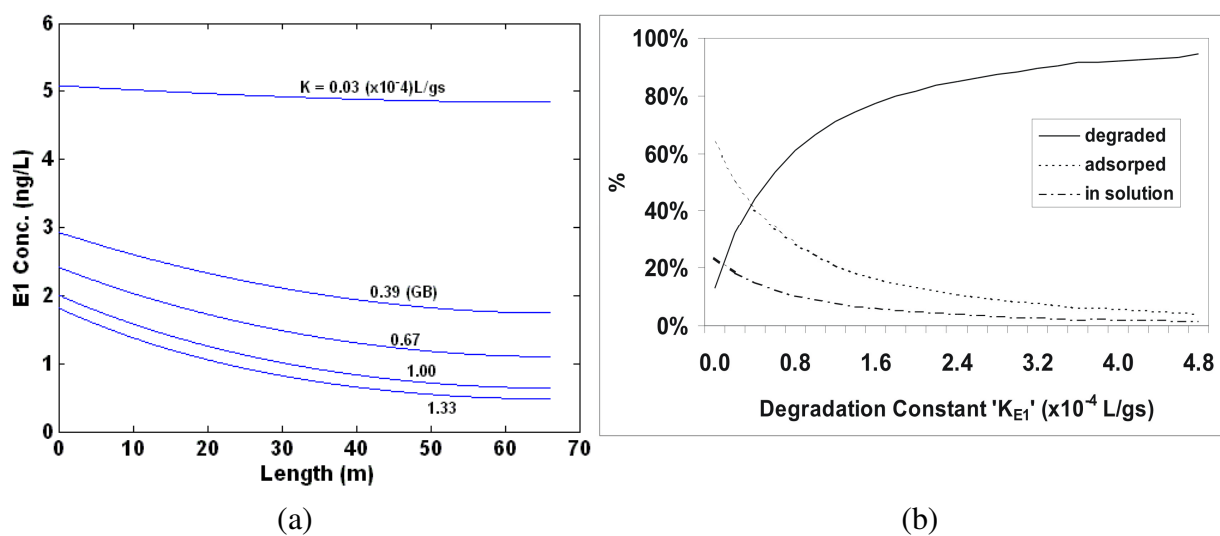
(ii) Inlet Adsorped E1, $[C_{EI}]_{in}$; similar behaviour was seen with varying adsorped E1 concentrations at the inlet (Figure 4.5).

Figure 4.5. C_{EI} Tank Profile for a Range of $[s_{EI}]_{in}$ and Overall Fate of E1 at Outlet.



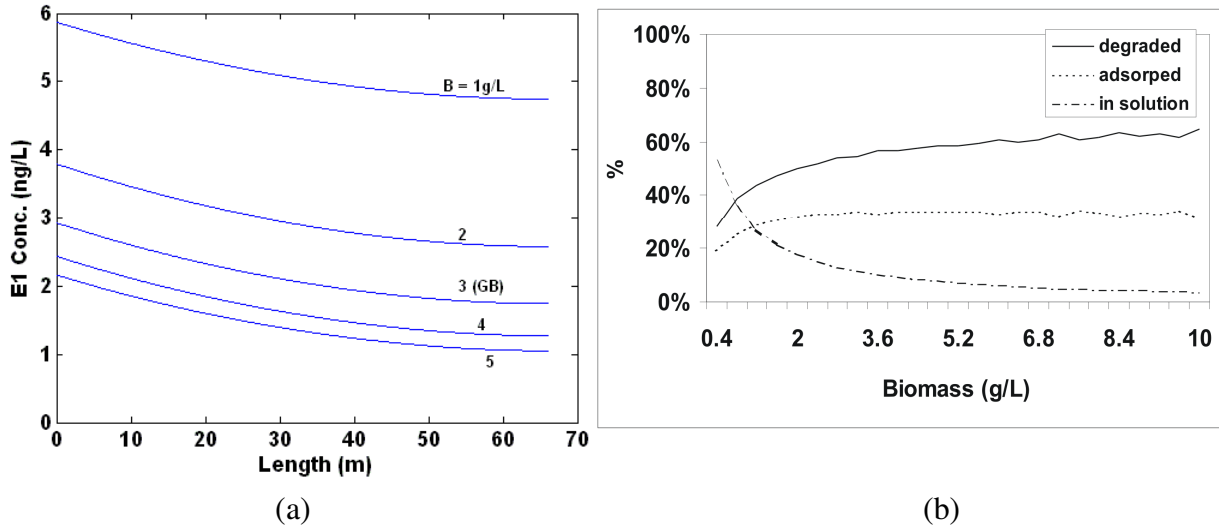
(iii) Degradation Coefficient, K_{EI} ; low values of K_{EI} yielded poor results. When $K_{EI}=0$ L/gs, the c_{EI} profile became flat (Figure 4.6(a)) and removal relied entirely on adsorption (Figure 4.6(b)). But as K_{EI} increased, performance was rapidly improved, decreasing solution concentration and greatly reducing the dependence on adsorption. This highlighted the importance of research into increasing flocs of bacteria responsible for steroid oestrogen biodegradation, as mentioned earlier.

Figure 4.6. c_{EI} Tank Profile for a Range of K_{EI} and Overall Fate of E1 at Outlet.



(iv) Biomass Loading, B ; attention had to be paid to the more complicated behaviour observed when varying biomass loading, B . B is proportional to degradation and hence as B increased c_{EI} was reduced (Figure 4.7(a)). More biomass should largely have increased adsorption due to the availability of more surface area, however, only a slight increase in adsorption was observed (Figure 4.7(b)) before levelling off at much higher B values.

Figure 4.7. c_{EI} Tank Profile for a Range of B and Overall Fate of E1 at Outlet.

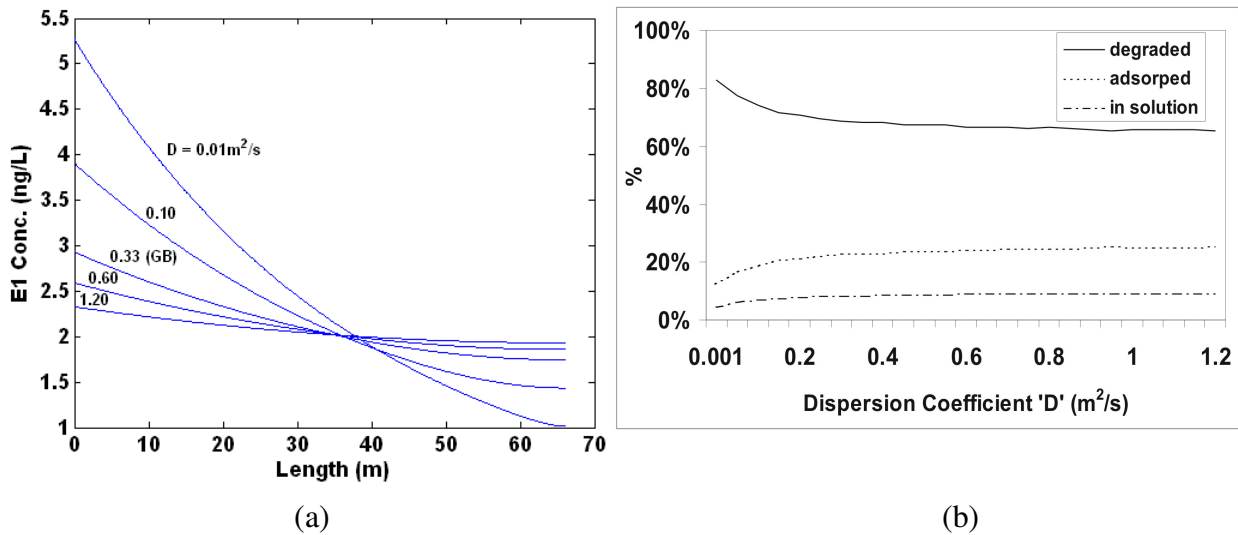


It was therefore clear that because the amount of E1 adsorped was proportional to c_{EI} , the model depended less on adsorption when c_{EI} became low. The model did indicate, however, that the net effect of adding more biomass was a slight increase in adsorption and degradation up until around 5-6 g/L (Figure 4.7(b)) before levelling off for larger amounts.

It is worth noting that the ‘adsorped’ and ‘degraded’ curves in Figure 4.7(b) are not completely smooth. This could be due to numerical round-off errors by the solver and may require more attention in future work.

(v) Dispersion Coefficient, D ; as dispersion coefficient determined the extent of PFR or CSTR behaviour, it was not surprising that at low values of D the model exhibited an exponential PFR profile (Figure 4.8(a)). Well mixed profiles and, hence, greater initial step drops appeared at higher values of D .

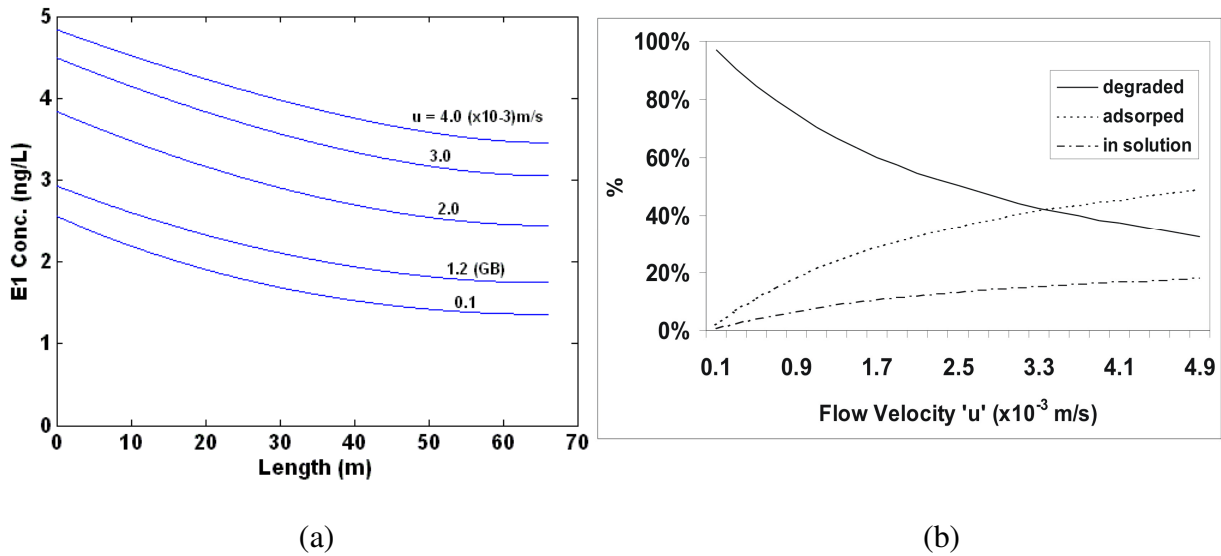
Figure 4.8. c_{EI} Tank Profile for a Range of D and Overall Fate of E1 at Outlet.



Interestingly, for very low D values (0-0.1 m^2/s), degradation was improved by 20-30% in return for slightly worse adsorption performance (Figure 4.8(b)). This was considered highly favourable and confirmed the relevance of inserting packing not only to increase K_{EI} and B , by allowing more bacteria to grow, but also to bring about more PFR like flow properties.

(vi) Mean Flow Velocity, u ; as u approaches zero, 100% degradation was achieved which was intuitive since an infinite residence time would allow for completion of the simple first order biochemical reaction. This was obviously of no use since we had to model a pretty steady flow of wastewater!

Figure 25. c_{E1} Tank Profile for a Range of u and Overall Fate of E1 at Outlet.



Hence, the model implied that a balance must be struck with flow velocity in order to achieve acceptable degradation which can be seen by Great Billing employing more than one activated sludge aerated lane all working in parallel.

5.0 Dimensional Analysis

The previous chapter showed that the model was sensitive to quite a large range of parameters. Due to this, it became exceedingly difficult to realise the importance of one parameter compared to the other. Moreover, in all cases analysed in section 4.2.1, one parameter was being varied while the rest remained constant. The combined effect of the variation of a few parameters on the model would be even more difficult to understand.

For these reasons, and to provide further insight into the combined contributions of the various key parameters mentioned previously, there was a need to group parameters and simplify the model analysis. This need was satisfied by dimensional analysis. Furthermore, dimensional analysis provided a conceptual tool which checked for correctness in the theoretically derived equations that made up the model.

5.1 Manipulating the Equations

The first step in making the mass balance and boundary condition equations dimensionless is to establish appropriate variables in place of c_{E1} and x . The obvious choice here would be $c_{E1}/[c_{E1}]_{in}$ and x/L , denoted by c_{E1}^* and x^* respectively. Therefore, equation (3.18) became:

$$D \frac{d^2 c_{E1}^*}{dx^{*2}} - uL(1 + Bp) \frac{dc_{E1}^*}{dx^*} - L^2 K_{E1} B c_{E1} = 0 \quad (5.1)$$

Further manipulation yielded:

$$\frac{d^2 c_{E1}^*}{dx^{*2}} - \left(\frac{uL}{D} \right) (1 + Bp) \frac{dc_{E1}^*}{dx^*} - \left(\frac{uL}{D} \right) \left(\frac{K_{E1} BL}{u} \right) c_{E1} = 0 \quad (5.2)$$

which identified the three key dimensionless groups of interest, those being:

- $\frac{uL}{D}$ - 'Peclet number', Pe
- Bp - 'Gamma group', γ
- $\frac{K_{E1}BL}{u}$ - 'K group', K

Similar treatment of the boundary conditions gave:

$$Pe \left[1 + \gamma \left(\frac{[s_{E1}]_{in}}{p[c_{E1}]_{in}} \right) \right] = Pe(1 + \gamma)[c_{E1}^*]_0 - \left. \frac{dc_{E1}^*}{dx^*} \right|_0 \quad (5.3)$$

and

$$\left. \frac{dc_{E1}^*}{dx^*} \right|_L = 0 \quad (5.4)$$

which gave the additional dimensionless group

- $\frac{[s_{E1}]_{in}}{p[c_{E1}]_{in}}$ - 'Inlet group', θ

5.2 Group Characterisation

c_{E1}^* , x^* , Pe , γ , K and θ made up the six expected dimensionless groups from a system which contained nine variables and three dimensions. θ characterised input concentrations of E1 and would not be investigated further due to $[c_{E1}]_{in}$ and $[s_{E1}]_{in}$ having had almost no impact on the overall 'effectiveness' of the system (Figure 4.4 & 4.5). Solutions in terms of c_{E1}^* and x^* were, therefore, solved and the effects of the groups of particular interest, Pe , γ and K were explored.

(i) Pe ; the Peclet number conventionally relates the forced convection of a system to its *heat conduction* and is equivalent to the product of the Reynolds number with the Prandtl number. The only difference here was that Pe exhibited the dispersion coefficient (D) instead of a thermal diffusion coefficient in turn relating the ratio of forced convection to the degree of *backmixing* present in the system.

(ii) γ ; proportional to the amount of biomass in solution and its capacity to adsorb E1 molecules in equilibrium, γ was interpreted as the ratio of E1 adsorbed on solid surfaces to the E1 present in solution.

(iii) K ; due to the adapted nature of K_{E1} (equation (3.8)), K related the mixture residence time in the aerated tank to the biodegradation reaction time.

5.3 Results - Dimensionless Plots and Comments

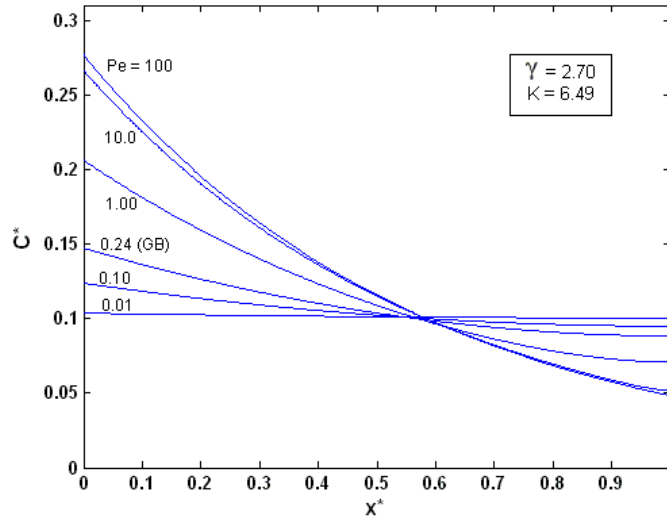
To understand the effects of Pe , γ and K on the model, data had to be appropriately plotted. The following section graphically explores the contribution of each of these three groups.

5.3.1 Singular Variation

To begin with, each group was varied between 0 and 100 while, in each case, the remaining two groups were kept constant at Great Billing values. The results were plotted on graphs of c_{E1}^* vs x^* .

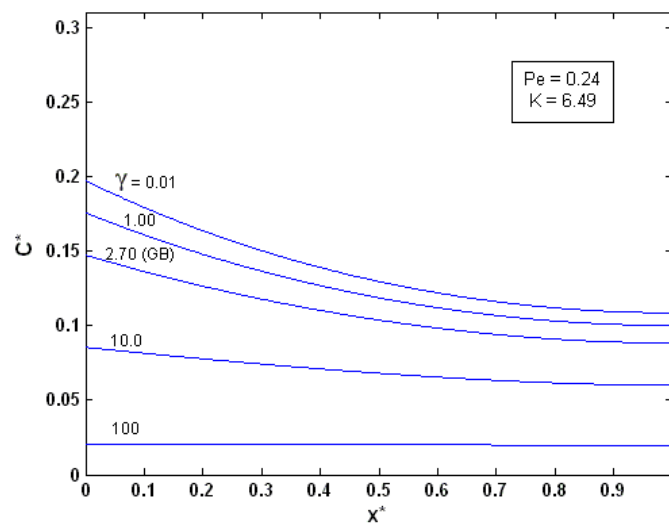
(i) Pe ; in keeping with what was observed when varying the dispersion coefficient (D) in section 4.2 (Figure 4.8), it was no surprise that the Peclet number effected the flow characteristics of the model.

Figure 5.1. Variation of C_{E1}^* Profile with Pe .



As Pe approached infinity, the system assumed plug flow behaviour, the limit at the inlet of about 0.28 (Figure 5.1) being solely determined by the amount adsorbed. As Pe approached zero, perfect mixing was exhibited, which complied, of course, with an infinite value of D .

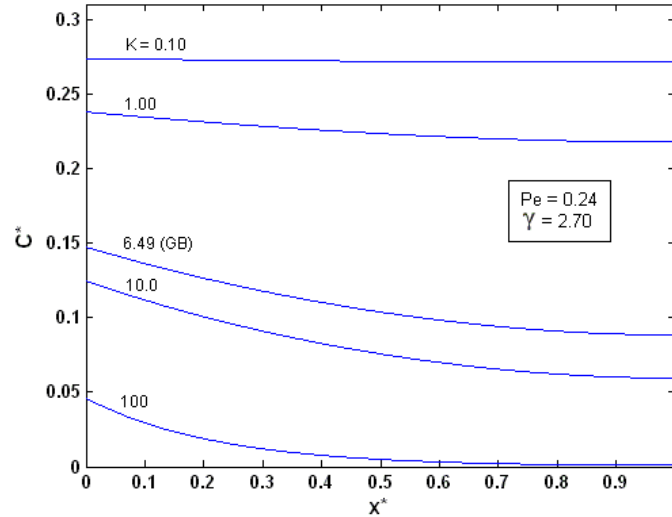
Figure 5.2. Variation of C_{E1}^* Profile with γ .



(ii) γ ; as γ decreased, so did the overall removal which agreed with Figure 4.7. The distinct property of Figure 5.2 was that the profile flattened as γ tended to infinity and did not eventually merge with the x^* axis. This, however, was intuitive since despite an increased biodegradation rate, resulting from larger γ values, the adsorption equilibrium set up by the model required for an amount of E1 to remain in solution (an aspect requiring refinement). As γ decreased, performance worsened to the point where biomass contributed to neither degradation nor adsorption.

(iii) K ; the limit of 0.28 at the inlet was reached here (Figure 5.3), as K approached zero, which again revealed the effect of adsorption alone (a flat profile as the same amount was adsorped down the length of the tank due to the lack of degradation).

Figure 5.3. Variation of C_{E1}^* Profile with K .



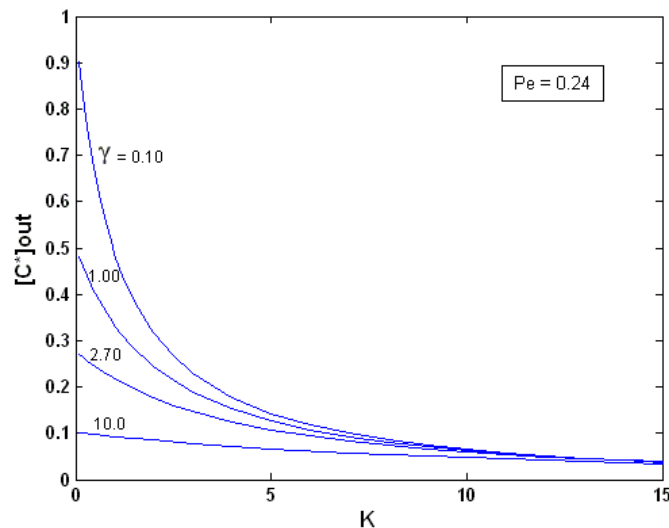
As K reached infinity, full removal was achieved which signified the importance of long tank residence times and short biodegradation reaction times.

5.3.2 Relative Variation

Varying one group would, in reality, have a knock on effect on the values of the other two groups and so keeping the rest of the groups constant while changing one group, as in the previous section, may give impractical results. For this reason, it was necessary to investigate how two groups would vary relative to each other. In order to achieve this, only values of c_{E1}^* at the outlet (at $x^* = 1$) were calculated in the solution. Values of $[c_{E1}^*]_{out}$ (c_{E1}^* at $x^* = 1$) were plotted for the variation of two groups while the third in each case was kept constant at the Great Billing value.

(i) Keeping Pe constant; when the flow properties were unchanged ($Pe = 0.24$), the relationship between γ and K in the model could be studied in more detail. As both γ and K approached zero, no E1 removal was achieved and $[c_{E1}^*]_{out}$ quite rightly became 1 (Figure 5.4).

Figure 5.4. Variation of $[c_{E1}^*]_{out}$ with K and γ .

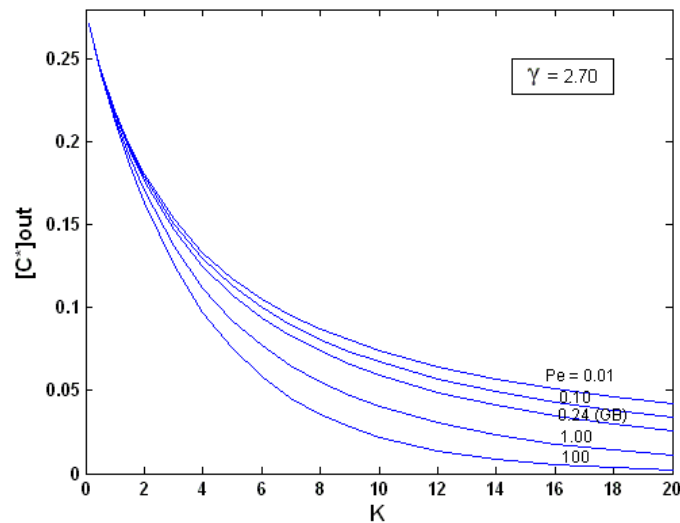


As γ increased, similar properties to Figure 5.2 arose with the gradually flattening profile (see section 5.3.1). Interestingly, for large values of K (long

residence times and short reaction times) removal ceased to depend on γ , and complete removal was attained as K reached infinity. The model became more dependent on γ when $K < 10$.

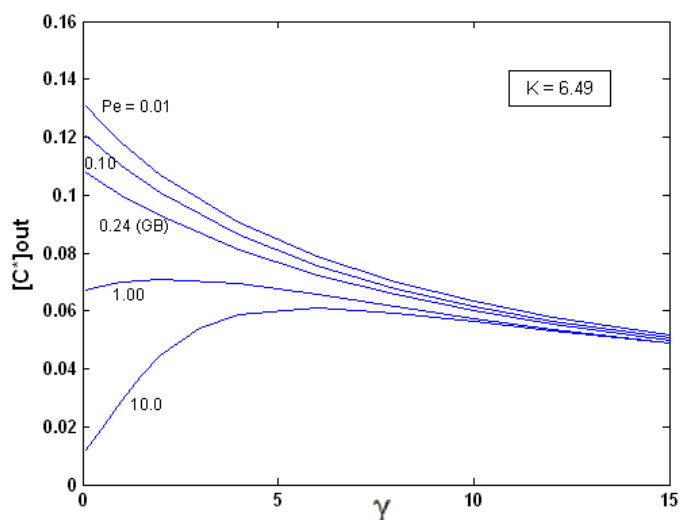
(ii) Keeping γ constant; keeping available solid surface area and adsorption rate constant, gave useful insight into how performance fared with variation in Pe and K (Figure 5.5). When K was small, the limit of 0.28 for $[c_{E1}^*]_{out}$ was revisited (Figures 5.1&5.3) which confirmed removal by adsorption alone. As K increased, so did the removal's dependence on Pe . Figure 5.5 shows that increasing PFR behaviour effected removal performance the greatest when $4 < K < 20$. This agreed with the effects of plug flow discussed earlier.

Figure 5.5. Variation of $[c_{E1}^*]_{out}$ with K and Pe .



(iii) Keeping K constant; altering flow characteristics while keeping biodegradation at a constant rate gave an important illustration of the how the model functioned.

Figure 5.6. Variation of $[c_{E1}^*]_{out}$ with γ and Pe .



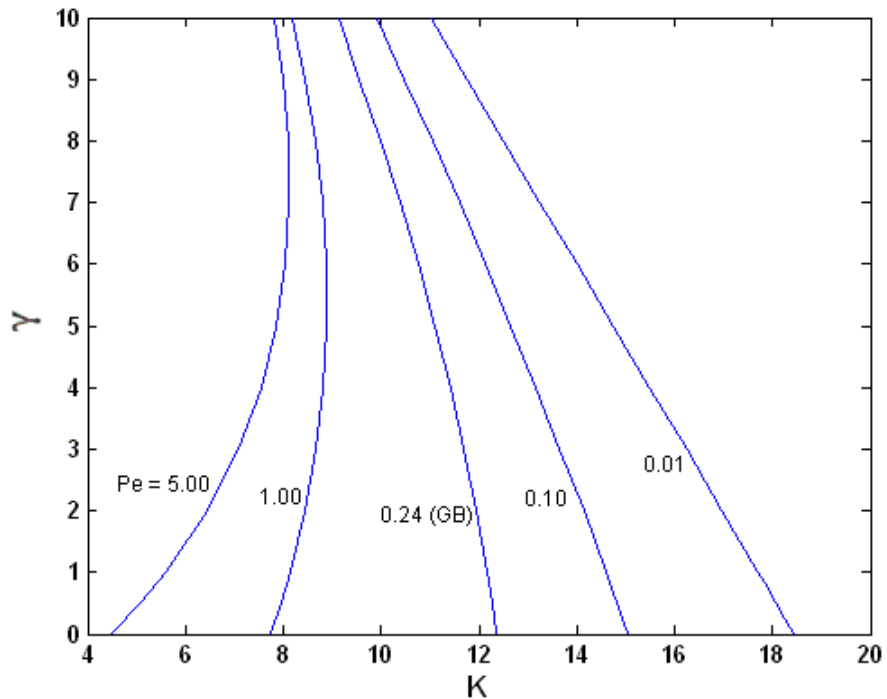
Contrary to K , as γ increased flow properties tended to have less of an impact (Figure 5.6), but the feature worth noting here is the solution when $\gamma < 10$. Since the rate of biodegradation was proportional to the E1 solution concentration (equation (3.7)) it was possible that the tank could be more effective in E1 removal with more E1 in solution. Figure 5.6 points out that as the flow became more PFR like (which allowed for more efficient biodegradation - Figure 5.5), it was more favourable to have less adsorption. In the case of Great Billing ($Pe = 0.24$), however, the model predicted the opposite behaviour – so long as the flow is considered more ‘well mixed’ than PFR, increasing γ would always aid overall performance.

5.3.3 Cumulative Variation

Finally, for a full picture of the cumulative effect all three groups have on the model, an iterative scheme was set up. Defining an ‘acceptable effluent

concentration' of E1 to be 5% of the total influent concentration, all possible values of Pe , γ and K were iterated to give the solution $[c_{E1}^*]_{out} = 0.05$. The results are plotted in Figure 5.7.

Figure 5.7. Variation of Pe , γ and K for $[c_{E1}^*]_{out} = 0.05$.



The features of Figure 5.7 help conclude the key features of the model arising from dimensional analysis:

- When the nature of the flow approached PFR (plug flow), E1 removal was enhanced and lower values of K (shorter residence times and longer reaction times) would suffice.
- When the nature of the flow became CSTR (well mixed – $Pe = 0.01$), K decreased linearly as γ (the ratio of E1 adsorbed to E1 in solution) was increased to maintain E1 removal. This meant that as more E1 was adsorbed during CSTR conditions, longer reaction times (or shorter

residence times) would be ample to deal with the ever lowering E1 solution concentration. However, in accordance with the previous statement, higher overall values of K were required (10-20) at CSTR conditions.

- On the other hand, PFR conditions ($Pe = 5.00$) induced the opposite (and also parabolic) relationship between γ and K . In other words, K would now **increase** non-linearly as γ was increased in order to maintain E1 removal. This now meant that because of more E1 being adsorped, shorter reaction times (or longer residence times) were required to make up for the slow degradation rate resulting from low E1 solution concentration. Nevertheless, much lower overall values of K were required (4-8) at PFR conditions.
- It is interesting to point out that the curve where $Pe = 5.00$ (approximated PFR conditions) reached a maximum at $K \approx 8$ ($\gamma \approx 6.6$ - 8.2). Similar behaviour can also be seen for the $Pe = 1.00$ (near PFR conditions) curve with a maximum at $K \approx 8.5$ ($\gamma \approx 4.7$ - 6.2). This revealed that for larger values of γ (where adsorption dominated the removal of E1), for PFR like conditions, the relationship between γ and K approached that under CSTR conditions.

Dimensional analysis has clearly lead to a greater understanding of the inner workings of this model and the conclusions of this chapter firmly endorse the addition of packing as is discussed in the next chapter.

6.0 Insertion of Packing

The results of the extensive analysis carried out in previous chapters predicted that adding fixed surfaces to the aerated tank would greatly enhance E1 removal. Generally, it was concluded that three physically viable changes had the largest impact on overall E1 removal efficiency. These were:

- To increase the rate of biodegradation through higher biomass concentrations.
- To increase free surface area for adsorption (also through higher biomass concentrations) so much so as not to reduce biodegradation.
- Creating more PFR (plug flow) like conditions.

Therefore, it was predicted that inserting packing into the aeration lane would, most probably, lower dispersion and provide a structure for more biomass to grow on, subsequently increasing biodegradation and adsorption capacity.

6.1 Modelling Packing

The same model was used but with the dispersion coefficient (D) set to zero and a substantially higher biomass concentration (B). According to experiments conducted previous to this report, for packing with a surface area of $300 \text{ m}^2/\text{m}^3$ (Rauschert RFK 25B packing – Figure 6.1) a suitable value for B was:⁹

Figure 6.1. Rauschert RFK 25B.



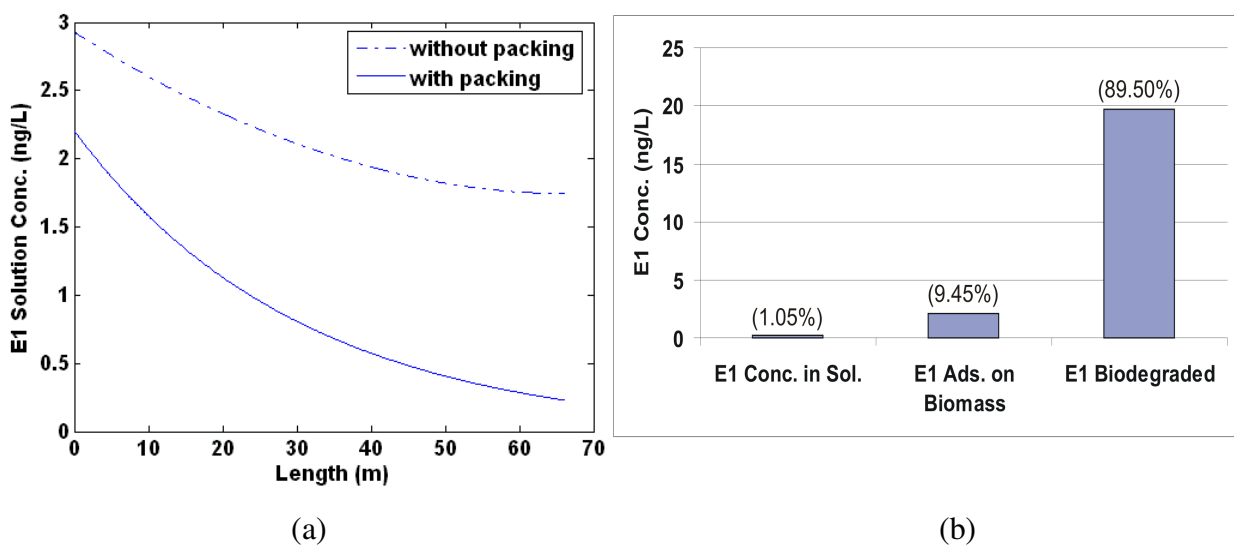
$$B = 10 \quad (\text{g L}^{-1})^* \quad (6.1)$$

*units here are g of Biomass /L of effluent

6.2 Results - Solution Analysis

For the purpose of showing how the results now fared compared to standard aerated flow the model was solved for a 66m long block of packing inserted into the tank (!) with the same initial conditions as before. This was obviously impractical but gave a good idea of how the model interpreted the E1 solution concentration profile and overall fate of E1 for a (long) packing segment.

Figure 6.2. C_{E1} Profile Over a 66m Length of Packing and Overall Fate of E1 at Outlet.



The dotted line in Figure 6.2(a) is identical to the profile presented in Figure 4.3(a) earlier, the profile of the packing proving more efficient in the removal of E1 from the solution. Figure 6.2(b) shows the effectiveness of packing due to the fact that much more E1 was biodegraded (the same initial conditions as before were used here).

6.2.1 Solution Analysis with Parameter Variation

Similar to section 4.2.1, the following diagrams explore the effect of varying key parameters within the model for a length of packing alone.

(i) Length of packing segment; the extent of sustained PFR flow at higher biomass concentrations within the tank would have a considerable impact on E1 removal. Figure 6.3(a) shows how well 5, 10, 15, 20 and 25m long segments of packing reduced the solution concentration of E1.

Figure 6.3. c_{E1} Profiles Over a Range of Packing Lengths and Overall Fate at Output.

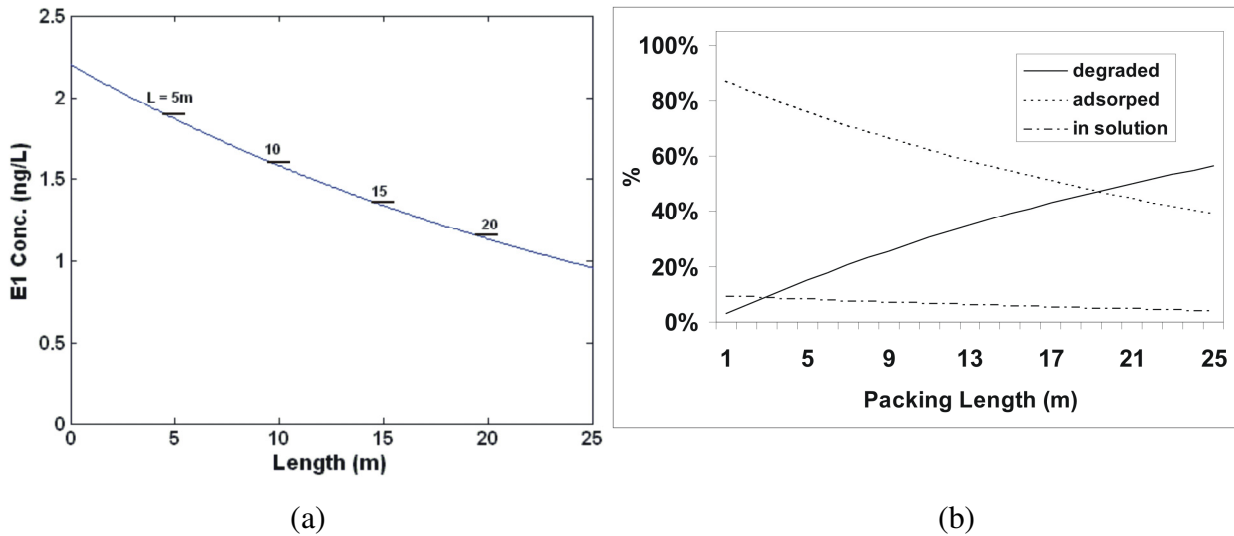
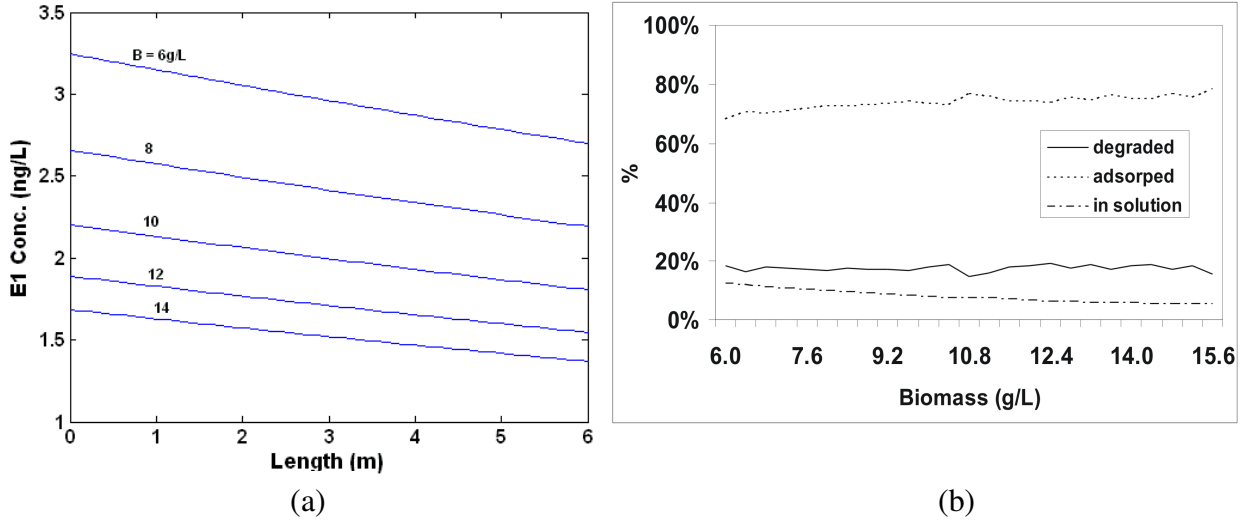


Figure 6.3(b) shows that as well as decreasing solution concentration of E1, increased packing lengths effectively removed E1 by providing better degradation.

(ii) Biomass Loading, B ; it has already been established that a biomass loading of 10 g/L was appropriate to model the ability of packing to retain more bacterial growth. Nevertheless, it was worth analysing how the results varied with other quantities of B .

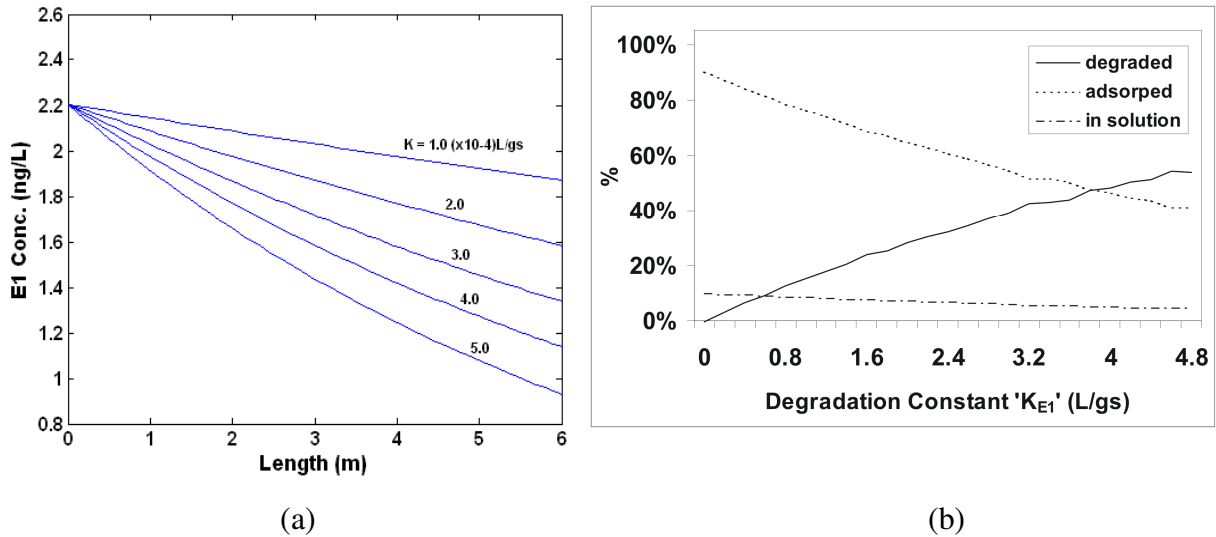
Figure 6.4. c_{EI} Profiles for 6m Packing Over a Range of B and Overall Fate of E1 at Outlet.



Increasing B clearly improved solution concentrations of E1 within a segment of packing (Figure 6.4(a) - 6m length arbitrarily used). The percentage of E1 adsorped increased gradually with higher values of B whereas the proportion of E1 degraded appeared to reflect this by decreasing gradually in an equal and opposite fashion (Figure 6.4(b)).

(iii) Degradation Coefficient, K_{EI} ; as K_{EI} did not affect the initial concentrations of E1 at the inlet (unlike B), varying K_{EI} alone did not change c_{EI} at $L = 0m$ due to no back mixing within packing (Figure 6.5(a)).

Figure 6.5. C_{EI} Profiles for 6m Packing Over a Range of K_{EI} and Overall Fate of E1 at Outlet.

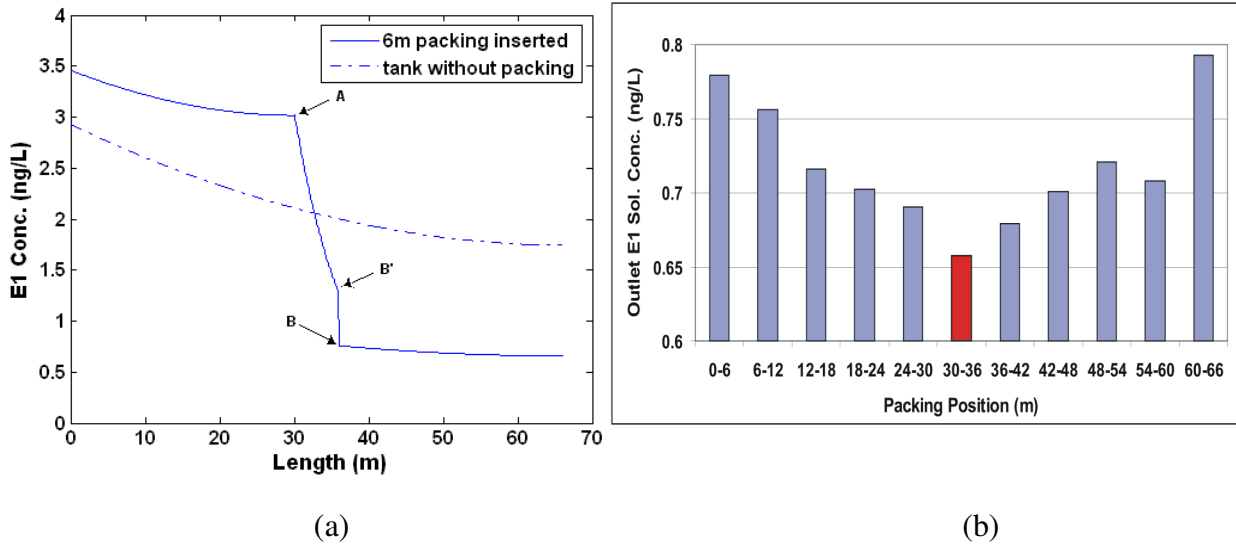


With reference to Figure 4.6(b) (varying K_{EI} for the original model), Figure 6.5(b) shows that the model had a similar but more linear response to the increase of K_{EI} for packing.

6.2.2 Incorporating Packing Segments into the Tank

The first two quantities to consider before adding packing segments to the model were the position of the packing in the tank and the length of each segment to be used. In order to find the optimum positioning, output E1 solution concentrations were explored for various packing locations down the full length of the tank using an arbitrary length of packing (6m).

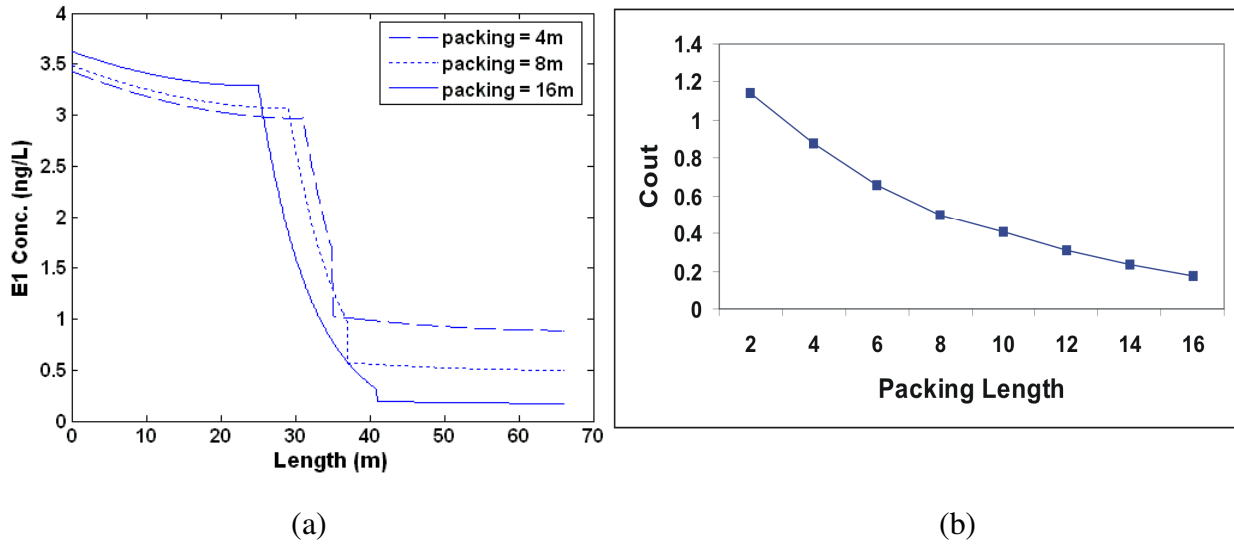
Figure 6.6. c_{E1} Profile Comparison for Model with 6m Packing and c_{E1} at Outlet for Various Positions.



From this analysis it could be concluded that positioning the packing segment exactly in the middle of the tank gave the best result (highlighted red in Figure 6.6(b)). It has to be noted that the unexpected result when placing the packing at 54-60m must have been due to a numerical round-off error for this set of data. Further work must be done in this area to rectify this particular problem in the MATLAB solver. Despite E1 outlet solution concentration not giving a clear idea of how effective each case was in fully removing (biodegrading) E1, it was a good measure to go by since, essentially, the technology is being implemented to achieve the lowest possible E1 sewage effluent concentrations. The solution concentration profile for the packing positioned at 30-36m is shown in more detail in Figure 6.6(a). Compared with the model for no packing (dotted line), outlet solution concentration of E1 was reduced from ~ 1.75 ng/L to 0.66 ng/L which was about a 5.5% increase in performance considering a 20 ng/L inlet solution concentration. Taking into account the E1 adsorbed on surfaces at the inlet and outlet then the performance increase would be about 19.7%. The profile within the packing is marked in the interval from A to B.

B'B shows the step decrease in concentration due to the difference in mixing between zones (Dankwerts boundary conditions, discussed in section 3.2.2).

Figure 6.7. c_{E1} Profile Comparison for Various Packing Lengths and c_{E1} at Outlet.

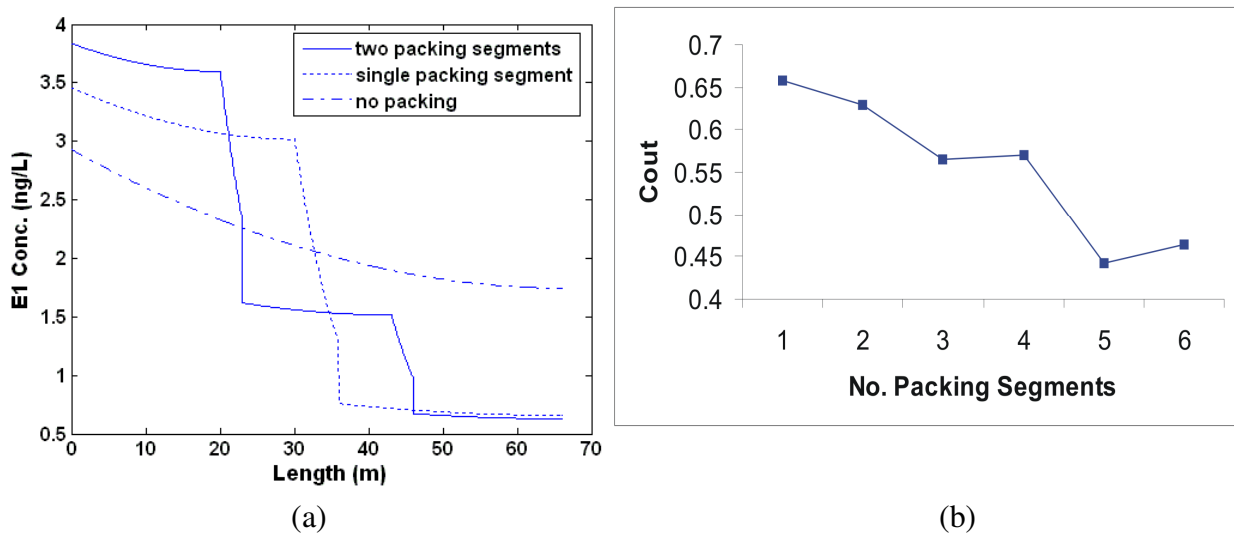


To find an appropriate length for the packing segment, results with various lengths of packing placed half way down the tank were examined. The E1 solution concentration profiles for the tank fitted with a 4, 8 and 16m long segment of packing are plotted in Figure 6.7(a). Plotting the outlet solution concentration of E1 for various lengths of centralised packing (Figure 6.7(b)), it was evident that as the packing segment length increased, more overall E1 removal resulted. However, the rate of increase of performance diminished with the length of packing employed (the graph in Figure 6.7(b) becomes flatter as the packing length increases) which would be an important factor when considering the cost of the packing material. Another factor in selecting an ideal length of packing would be clogging and the expense of cleaning.

6.2.3 Multiple Segment Arrangement

Minimising segment length to prevent clogging and high maintenance costs was essential in ensuring optimum utilisation of packing.

Figure 6.8. c_{EI} Profile for Two Packing Segments and c_{EI} at Outlet Comparison for Various Arrangements.



This could be achieved by using a number of shorter segments arranged to ensure equal lengths of well-mixed stretches. This was discovered through model iteration but could also be deduced from the previous section – where placing the single segment of packing in the centre of the tank (and hence creating two aerated zones of equal length) yielded the best result. Figure 6.8(a) demonstrates the effect on the c_{EI} tank profile of having multiple packing segments. 6m of packing has been split up into 2, 3, 4, 5 and 6 segments of 3m, 2m, 1.5m, 1.2m and 1m lengths respectively and the outlet solution concentrations calculated and plotted in Figure 6.8(b) (c_{EI} profiles of 3, 4, 5 and 6 segment arrangements are plotted in appendix 10.4). This revealed that overall performance was enhanced when the packing was further distributed over the tank. However, a limit to the number of segments dividing the tank would be bound to the cost of installation. From these results, packing (6m) has

shown to improve E1 removal from sewage effluent by 5-7% improving overall E1 removal from 91% to 97%.

A physical model of the activated sludge aerated zone including two segments of packing is currently under construction (Figure 6.9). The photograph shows a binary arrangement of the Rauschert RFK 25B, which was the same packing modeled. This should allow for accurate experimental data in the near future to validate the model solutions with.

Figure 6.9. Experimental Model of Aerated Tank with Packing.



7.0 Conclusions and Recommendations for Future Work

7.1 Concluding Remarks

The previous model to this was reassessed and repeatedly solved by more sophisticated means using MATLAB. The numerical solver was able to solve the boundary value problem presented by the model equations more accurately than previous methods used.

Consequently, revisions were made by identifying limitations to the previous model through extensive parameter and dimensional analysis. Rigorous research in the field of the removal of estrogens in activated sludge processes also enabled major improvements to the previous model. The main modifications to the model were:

- More accurate inlet E1 concentrations
- Employing Dankwerts boundary conditions
- Improvement of the biodegradation rate equation
- Utilising an up to date sludge adsorption isotherm relationship

Solution analysis was repeated for the adapted model and presented in this report for future scrutiny.

Valuable insight into the fundamentals of the improved model was best achieved through extensive dimensional analysis. The three major dimensionless groups governing the behaviour of the model were identified as:

- Peclet number, Pe ; the ratio of forced convection to the degree of backmixing present in the flow of the activated sludge tank.
- Gamma, γ ; the ratio of E1 adsorbed on biomass surfaces to the E1 present in solution.
- K group, K ; relating the mixture (solution + biomass) tank residence time to the biodegradation reaction time.

Iterating solutions within MATLAB while varying these three dimensionless groups gave a good idea of how the groups were interrelated. The main conclusions were:

- Approximate CSTR flow was apparent at $Pe \geq 5$. Relatively low values of biodegradation reaction times and high tank residence times were required to achieve reasonable E1 removal in a CSTR system.
- Approximate PFR behaviour was apparent at $Pe \leq 1$. Relatively high values of biodegradation times and low tank residence times were required to achieve reasonable E1 removal in a PFR system. This confirmed the importance of obtaining more PFR like conditions.
- There was a clear change in the relationship between γ and K as the system varied from a CSTR regime to PFR. For CSTR flow, more adsorption was favoured whereas the opposite was observed for a PFR system. However, a threshold for γ was found above which PFR became to favour increased adsorption. This gave valuable insight into the limitations of each flow regime.

Dimensional analysis predicted the enhancements of adding fixed surfaces into the activated sludge tank. General requirements for improved E1 removal were outlined to be:

- To increase the rate of biodegradation through higher biomass concentrations.
- To increase free surface area for adsorption (also through higher biomass concentrations) so much so as not to reduce biodegradation.
- Creating more PFR (plug flow) like conditions.

The model was thus used to explore the possibilities of inserting packing. Removal of E1 was enhanced by up to 7% when just 6m (eleventh the length of the full tank) of packing was used. Analysis found that the introduction of packing affected performance due to principally inducing segmented PFR flow which enhanced biodegradation. Positioning a multitude of packing segments,

so as to lower the average dispersion in the tank, achieved optimum results. On this basis, the alternative, cheaper option of adding simple obstructions, such as mesh barriers or weirs, should be considered.

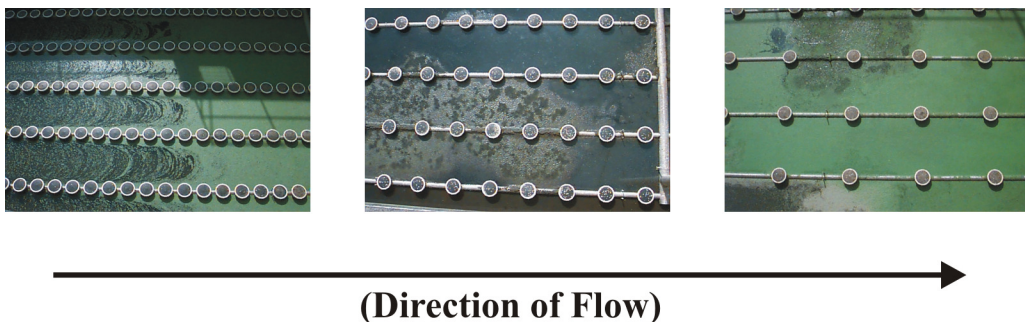
The model pointed to the importance of manipulating the behaviour of biomass to biodegrade E1 more efficiently by physically viable means. After all, it is biodegradation which in effect fully removes E1 from wastewater.

This project reaffirmed the need for experimental data concerning E1 concentrations in an activated sludge tank to justify the development of the model.

7.2 Recommendations for Future Work

- The first order biodegradation rate equation was a first guess at the nature of how biomass reacted with E1. The linear proportionality with biomass loading had also been a rough estimate. Further research has to be carried out to refine this relationship.
- Expanding the model to incorporate E2 and EE2 is required. The complex behaviour, such as E2 oxidising to E1, could also be integrated.
- Since the nutrients in wastewater on which the biomass sludge feed are finite, a limit to the amount of biomass allowable has to be considered. With the addition of packing, for example, bacterial population death could result from a shortage of nutrients.
- In considering overall tank dispersion, a more accurate estimation than that of Murphy and Boyko is needed. Microbial activity is thought to decrease down the length of the tank as organic nutrients in the wastewater are gradually depleted. This is reflected in the decreasing air flow rate down stream of the flow (figure 7.1).

Figure 7.1. Variation in Air Diffuser Density Down the Length of the Tank.



This will affect the dispersion coefficient and refinement to the model would be needed to take this into account.

- The assumption that biodegradation of E1 favours plug flow will have to be investigated since it is possible that bacteria activity far down the tank relies on back mixing to migrate to more nutrient rich zones further up stream.



- On the same principle, the ability of biomass to grow on packing far down stream may be hindered by less microbial activity requiring further study into the nature of biomass formation on packing surfaces.
- Recent studies suggest that the boundary between flows of relatively equal cross sections (like the flow between fluid in the tank and that within the packing) have less clear cut boundary conditions than those of Dankwerts. This is an area of interest which would shed more light on the supposed flow advantages of inserting packing which the current model strongly advocates.
- Concerning the dimensional analysis results, further work needs to be done in order to obtain a clear idea of the proportion of oestrogen in solution, biodegraded and adsorped. In the end, conclusions were drawn up from iterations based on 95% 'removal' with no emphasis on the overall fate of E1.
- Some solutions were found to be 'unsmooth' and contained 'glitches' which was put down to round-off errors within the numerical MATLAB solver. Refinement of the solver may be required to eradicate these errors.


8.0 References

- ¹ Belfroid, A. C.; Van der Horst, A.; Vethaak, A. D.; Schafer, A. J.; Rijs, G. B. J.; Wegener, J.; Cofino, W. P. *Sci. Total Environ.* **1999**, 225, 101-108.
- ² Purdom, C. E.; Hardiman, P. A.; Bye, V. J.; Eno, N. C.; Tyler, C. R.; Sumpter, J. P. *Chem. Ecol.* **1994**, 8, 275-285.
- ³ Jobling, S.; Nolan, M.; Tyler, C. R.; Brighty, G.; Sumpter, J.P.; *Environ. Sci. Technol.* **1998**, 32, 2498-2506.
- ⁴ Desbrow, C.; Routledge, E. J.; Brighty, G. C.; Sumpter, J. P.; Waldock, M. *Environ. Sci. Technol.* **1998**, 32, 1549-1558.
- ⁵ Johnson, A. C.; Williams, R. J. *Environ. Sci. Technol.* **2004**, 38, 3649-3658.
- ⁶ Eklöv, A. G.; Greenberg, L. A.; Brönmark, C.; Larsson, P.; Berglund, O. *Freshwater Biol.* **1998**, 40, 771-782.
- ⁷ Cooper, P. F.; Downing, A. L. J. *Chem. Inst. Water Environ. Manage.* **1998**, 12, 303-313.
- ⁸ Johnson, A. C.; Sumpter, J. P. *Environ. Sci. Technol.* **2001**, 35, 4697-4703.
- ⁹ Lupton, J. 'The Removal of Estrogens from Water', **2004**, 4YP Report, Oxford University Engineering Department.
- ¹⁰ Land and Water Development Division, www.fao.org/landandwater/gho/waterquality/treatproc.stm (viewed on 20/03/2006).
- ¹¹ Das, D. B. 'Wastewater Treatment', **2006**, C5B Lectures, Oxford University Engineering Department.
- ¹² Kookana, R.; Waite, T. D.; Xing, G. G. 'Australian Water Conservation and Reuse Research Program', www.clw.csiro.au/priorities (viewed on 20/03/2006).
- ¹³ Metcalf and Eddy, 'Wastewater Engineering', **1981**, 3rd Edition.
- ¹⁴ Andersen, H.; Siegrist, H.; Halling-Sørensen, B.; Ternes, T. A. *Environ. Sci. Technol.* **2003**, 37, 4021-4026.
- ¹⁵ Joss, A.; Anderson, H.; Ternes, T.; Richle, R. P.; Siegrist, H. *Environ. Sci. Technol.* **2004**, 38, 3047-3055.
- ¹⁶ Jeremy, E. 'Modelling Oestrogen Removal from Wastewater in an Activated Sludge Process', **2005**, 4YP Report, Oxford University Engineering Department.
- ¹⁷ Williams, R. J.; Johnson, A. C.; Smith, J. J. L.; Kanda, R. *Environ. Sci. Technol.* **2003**, 37, 1744-1750.

- ¹⁸ Johnson, A. C.; Jurgen, M.; Darton, R.; Martin, P. '*Oestrogen Removal at Great Billing*', Personal Contact, **2006**.
- ¹⁹ Richardson, M. '*Water Treating for Steroid Removal*', **2000**, 4YP Report, Oxford University Engineering Department.
- ²⁰ Joss, A.; Anderson, H.; Ternes, T.; Richle, R. P.; Siegrist, H. *Environ. Sci. Technol.* **2004**, 38, 3047-3055.
- ²¹ Dankwerts, P. V. *Insights into Chemical Engineering*, '*Adsorption by Simultaneous Diffusion and Chemical Reaction*', **1949**, Paper A2, pgs 6-11.
- ²² Makinia, J.; Wells, S. A. '*Evaluation of Empirical Formulae for Estimation of the Longitudinal Dispersion in Activated Sludge Reactors*', **2005**, Water Research.
- ²³ Hurford, T. '*Wastewater Treating*', **2003**, 4YP Report, Oxford University Engineering Department.
- ²⁴ Dankwerts, P. V. '*Continuous Flow Systems and Distribution of Residence Times*', *Chem. Eng. Sci.* **1953**, 2, 1-13

9.0 Risk Assessment

Risk Assessment		Modelling the Removal of Oestr ogen from Wastewater		Page 1 of 1
In Building				
Assessment	Ezzat Nasr	Signed		Date: 17/11/05
Assessment supervisor	Peter Martin	Signed		Date: 17/11/05
Hazard	Persons at Risk	Risk Controls In Place	Further Action Necessary To Control Risk	
240V Electrical Shock	Ezzat Nasr	Ensuring electrical equipment is tested.		
Eyestrain	"	Ensuring monitor is in working order; taking regular intervals to rest eyes from screen.		
Backpain	"	Adjusting seat orientation; taking regular intervals to move about.		
Neckpain	"	Ensuring screen is at correct height; taking regular intervals for simple exercises.		
Aching Arms/Legs	"	Creating plenty of space for legs to rest comfortably; providing armrest support at keyboard level.		
Tripping on Cables	(and others)	Making sure all cables and connections are tucked away safely or stuck securely to the floor.		

Your E-mail Address: ezzat.nasr@spc.ox.ac.uk Checked by D J Reed  date 17/11/05

10.0 Appendices

10.1 Inlet E1 Concentration Calculations

$$0.7 \text{ ng/L adsorped at inlet} = \frac{Q_R}{Q_R + Q_F} \times s_0 = \frac{80}{80 + 35} \times 1 \approx 0.7 \text{ ng/L}$$

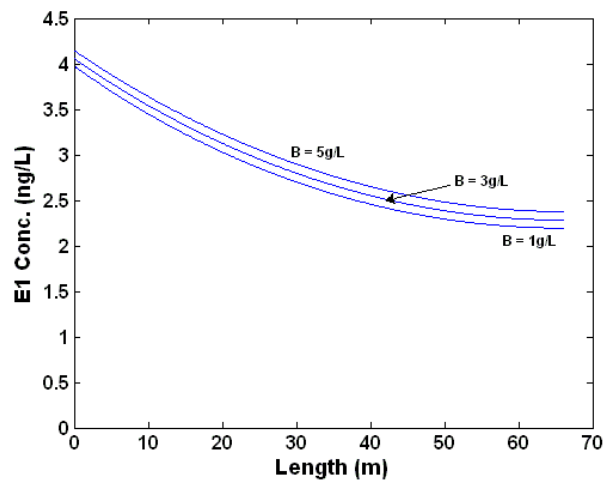
$$\text{Therefore, } [s_{E1}]_{in} = \frac{0.7}{B} = \frac{0.7}{3} \approx 0.2 \text{ ng/g}$$

$$[c_{E1}]_{in} = \frac{Q_F}{Q_F + Q_R} \times c_F = \frac{35}{35 + 80} \times 65 \approx 20 \text{ ng/L (note that max value for } c_F$$

used, $c_F = 65 \text{ ng/L}$).

10.2 Biomass Variation in Previous Model

Figure 10.1. Variation of cE1 profile for varying Biomass loadings for previous model.



10.3 Dankwerts Analytical Solution

$$c_{E1} = [c_{E1}]_{in} \exp\left(\frac{u(1+Bp)x}{2D}\right) \left[2(1+a) \exp\left(\frac{u(1+Bp)a(L-x)}{2D}\right) - 2(1-a) \exp\left(\frac{u(1+Bp)a(x-L)}{2D}\right) \right] \div m$$

where,

$$m = (1+a)^2 \exp\left(\frac{u(1+Bp)aL}{2D}\right) - (1-a)^2 \exp\left(\frac{-u(1+Bp)aL}{2D}\right)$$

and

$$a = \sqrt{1 + \frac{4DBK_{E1}}{[u(1+Bp)]^2}}$$

Due to the boundary conditions involving an adsorption term (unlike Dankwerts BCs), the corrected values were used:

$$u = 4.44 \times 10^{-3} \text{ and } [c_{E1}]_{in} = \frac{2.472 \times 10^{-8}}{u}$$

10.4 Multiple Packing Configurations

Figure. 10.2. Three (a) and Four (b) Segment Packing Configuration.

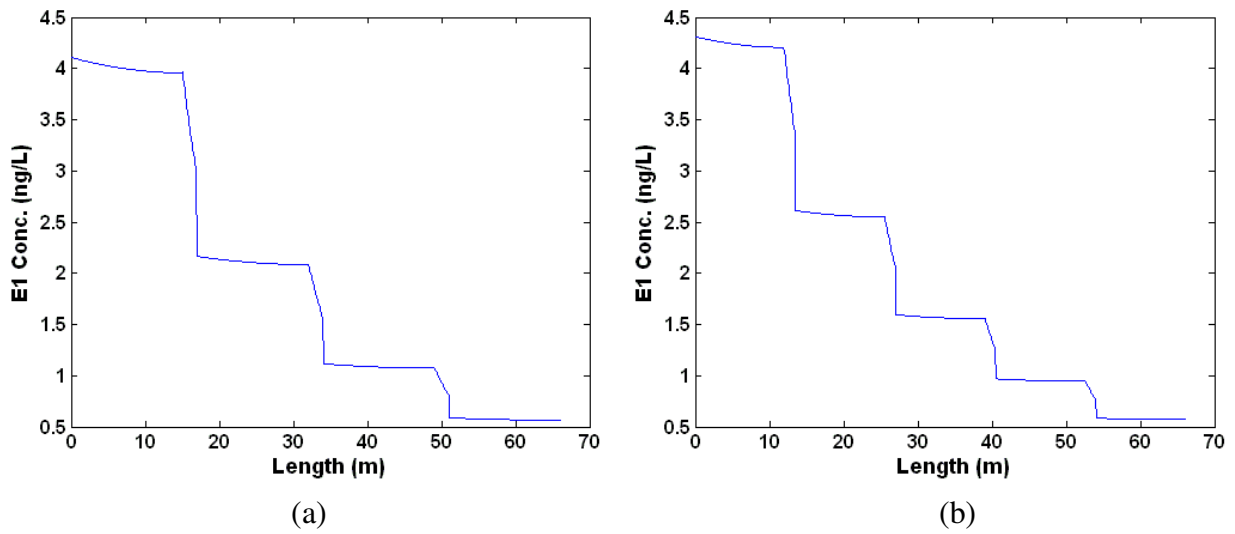
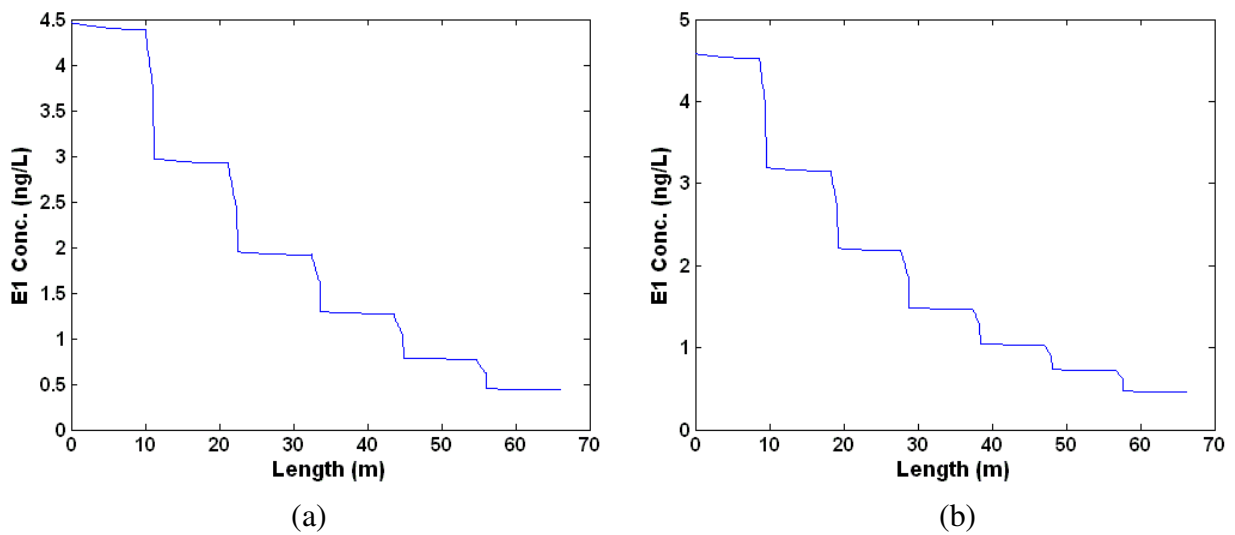


Figure 10.3. Five (a) and Six (b) Segment Packing Configuration.



10.5 MATLAB Code

Model

```
function y = model(x)

solinit = bvpinit(linspace(0,66,1000),[5 0]);
options = bvpset('Stats','on','RelTol',1e-5);
sol = bvp4c(@modelode,@modelbc,solinit,options);

x = sol.x;
y = sol.y;

plot(x,y(1,:)*1e6)
title('Model')
ylabel('E1 Conc. (ng/L)')
xlabel('Length (m)')
```

```
function dydx = modelode(x,y)

B = 3; % (kg/m^3)
D = 0.33; % (m^2/s)
k = 1.18e-4/3; % (1/gs)
u = 1.2e-3; % (m/s)
p = 0.9; % (m^3/kg)

dydx = [y(2)
        (1/D)*( u*y(2) + u*B*p*y(2) + k*B*y(1) ) ];
```

```
function res = modelbc(ya,yb)

D = 0.33; % (m^2/s)
u = 1.2e-3; % (m/s)
B = 3; % (kg/m^3)
p = 0.9; % (m^3/kg)
Cin = 20e-6; % (kg/m^3)
Sin = 0.2e-6; % (kg/kg biomass)

res = [u*Cin + u*B*Sin + D*ya(2) - u*ya(1) - u*B*p*ya(1)
       yb(2)];
```

Packing

```
function y = packing(x)

solinit = bvpinit(linspace(0,6,60),[5 0]);
options = bvpset('Stats','on','RelTol',1e2);
```

```

sol = bvp4c(@packode,@packbc,solinit,options);

x = sol.x;
y = sol.y;

plot(x,y(1,:)*1e6)
title('Packing')
ylabel('E1 Conc. (ng/L)')
xlabel('Length (m)')

function dydx = packode(x,y)

B = 10; % (kg/m^3)
D = 1e-6; % (m^2/s)
k = (5e-4/3)*B; % (/s)
u = 1.2e-3; % (m/s)
p = 0.9; % (m^3/kg)

dydx = [y(2)
        (1/D)*( u*y(2) + u*B*p*y(2) + k*y(1) ) ];

function res = packbc(ya,yb)

D = 1e-6; % (m^2/s)
u = 1.2e-3; % (m/s)
B = 10; % (kg/m^3)
p = 0.9; % (m^3/kg)
Cin = ; % (kg/m^3)
Sin = p*Cin; % (kg/kg biomass)

res = [u*Cin + u*B*Sin + D*ya(2) - u*ya(1) - u*B*p*ya(1)
       yb(2)];

```

Dimensionless

```

% Peclet = u*L/D
% gamma = p*B
% Kgroup = K*B*L/u
% Sgroup = Sin/p*Cin
% also C/Cin & x/L

function y = dimless_groups(x)

solinit = bvpinit(linspace(0,1,660),[5 0]);

options = bvpset('Stats','on','RelTol',1e-5);

sol = bvp4c(@ode,@bc,solinit,options);

x = sol.x;
y = sol.y;

```

```

plot(x,y(1,:))
title('Dimensionless Groups')
ylabel('E1 C/Cin')
xlabel('x/L')
axis([0 1 0 1])

```

```

function dydx = ode(x,y)

```

```

gamma = ; %2.7
Kgroup = ; %6.49
peclet = ; %0.24

```

```

dydx = [y(2)
        peclet*y(2) + peclet*gamma*y(2) + Kgroup*peclet*y(1) ];

```

```

function res = bc(ya,yb)

```

```

Theta = 0.2/(20*0.9);
gamma = ; %2.7
peclet = ; %0.24
Cin = 20e-6;

```

```

res = [peclet + peclet*gamma*Theta + ya(2) - peclet*ya(1) -
       peclet*gamma*ya(1)
       yb(2)];

```