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Pressurised Membrane Bioreactor Treatment of an Inhibitory Petrochemical Wastewater

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ABSTRACT

Environmental regulations impose limitations on a wide variety of organic pollutants in industrial wastewater. One of the current water quality management strategies is that of separating particular wastewater streams for specific treatment. The reason for this is that the cleaner water can be recycled, reducing fresh water intake, whereas the highly polluted water can be treated separately by specialised means. Treating highly polluted wastewater requires modification of the conventional activated sludge design approach.

An inhibitory petrochemical wastewater (phenol content 948 mg/l, organic content 11500 mg/l and total dissolved solid 5,4 g/l) had to be treated to remove most of the organic material and toxic compounds from the wastewater. The purpose of this study was to develop and evaluate a bioreactor with biomass membrane separation, which operates under 3 bar pressure. The inhibitory wastewater was selected to assess the high pressure bioreactor's (HPB) performance, since this wastewater represents a typical toxic effluent expected to be treated at the petrochemical complex.

A laboratory scale activated sludge reactor (ASP) was operated as a control for the HPB, and to evaluate the toxic effects of the petrochemical effluent. The toxic effects were determined by evaluating the growth kinetics of the biomass under different reactor operating conditions. Volatilisation of organic compounds during treatment was also measured as a pathway of organic removal. The microbial kinetics and volatilisation were combined to produce a reactor model able to predict the HPB performance.

The microbial growth kinetics were determined using chemical oxygen demand (COD) removal rate and a newly proposed oxygen utilisation rate (OUR) technique. The COD and OUR determined kinetics gave comparable results. The inhibition kinetics can be represented by the Haldane kinetic inhibition model with constants K_s *= 1142 mg/l;* K_i *= 786 mg/l;* μ_{max} *= 0,428* h^{-1}.

The HPB biomass was separated using an ultra-filtration membrane with a mean pore size of 0,05 µm to achieve a 100% effective biomass separation with organic loading rates of 4-28 kgCOD/m^3*.d and flux rates of up to 10 l/*m^2*.h. The activated sludge in the ASP was separated in a settling tank with hydraulic retention time of 1-5 h to achieve a biomass*

concentration of 0,1-1,8 g/l with an organic loading rate of 4-15 kgCOD/m^3.d. Effective MLSS separation could not be achieved by the ASP settler.

The maximum operating conditions for the two reactors are shown in the following table:

	Activated sludge control	***HPB***
COD reduction (filtered) %	*70-92*	*86-92*
COD loading [kg COD/m^3.d]	*15*	*28*
Hydraulic retention time [h]	*12*	*8*
Sludge age [days]	*2*	*7,5*
MLSS reactor[g/l]	*2,5*	*18*
$MLSS_{out}$ [g/l]	*1*	*0*

The ASP became unstable twice, whereas the HPB achieved a steady 90% COD removal. Excessive foaming stopped further testing at higher organic loads in the HPB, while oxygen transfer became limiting in the ASP.

It was found that volatilisation accounted for less than 1% of the organic removal from the HPB reactor.

A methodology and model was set up to facilitate treatment of other toxic waste streams. The model was evaluated against reactor steady state operations using the growth kinetics and included VOC volatilisation. The model predicted cell mass to 99% accuracy, while the predicted organic effluent concentration was within 87% of observed values.

It is concluded that the HPB effectively reduced the organic as well as the toxic content of the wastewater with stable operation throughout the test period. This exceeded the performance of the ASP control. These results indicate that the HPB is a viable technology to treat high strength inhibitory wastewaters.

Opsomming

Omgewings regulasies plaas druk op die industrie om verskye organiese besoedelstowwe in industriële afvalwater te verminder. Een van die watergehaltebestuurs praktyke is om spesifieke uitvloeisels afsonderlik te be behandel. Die rede hiervoor is dat skoner water hergebruik kan word om sodoende varswater inname te verminder, terwyl erg besoedelde water met gespesialiseerde metodes afsonderlik behandel kan word. Om die meer besoedelde strome te kan behandel moet modifikasies aan die konvensionele geaktiveerdeslykproses aangebring word.

'n Inhiberende petrochemiese uitvloeisel (fenol 948 mg/l, organiese inhoud 11500 mg/l en totale opgeloste soute 5,4 g/l) moes behandel word met die doel om meeste van die organiese materiaal en die toksiese stowwe te verwyder. Die doel van hierdie studie was om die tegnologie van 'n bioreaktor met biomassamembraanskyding wat teen 3 bar druk werk te evalueer. Die bogenoemde uitvloeisel is gekies as 'n tipiese industriële afvalwater wat gebruik kan word om die hoëdrukmembraanbioreaktor (HPB) te toets.

'n Laboratoruim grootte geaktiveerdeslykproses het gedien as kontrole vir die HPB en om die toksiese effek van die afvalwater te evalueer. Die toksiese effekte is geëvalueer deur die groeikinetika van die biomassa onder reaktor kondidies waar te neem. Vervlugtiging van organiese stowwe tydens aerobiese behandeling is ook gemeet as 'n roete van organiese verwydering. Die mikrobiese kinetika en vervlugtiging is gekombineer om 'n reaktor model te produseer wat die HPB se werkverigting kan voorspel.

Die groeikinetika van die biomassa is bepaal deur van chemiesesuurstofbehoefte (CSB) verwyderings tempo en 'n nuwe suurstofverbruikstempo tegniek (OUR) gebruik te maak. Die CSB en OUR groeikinetika het vergelykbare resultate opgelewer. Die inhibisiekinetika kan voorgestel word deur van die Haldane kinetiese model gebruik te maak (K_s = 1142 mg/l; K_i = 786 mg/l; μ_{maks} = 0,428 h^{-1}).

Die HPB biomassa is deur 'n ultrafiltrasie membraan geskei met 'n gemiddelde porie grootte van 0,05μm. 'n 100% effektiewe biomassa skeiding is bewerkstellig teen organieseverwyderingstempos van 4-28 kgCSB/m^3.d en vloedingstempos van 10 l/m^2.h. Die geaktiveerdeslyk in die geaktiveerdeslykaanleg is deur 'n besinktenk met hidroulise

retensietyd van 1-5 h besink om 'n finale uitvloeisel met 0,1-1,8 g/l gesuspendeerde stowwe teen 'n organiese lading van 4-15 kgCSB/m^3.d te lewer. Effektiewe skeiding kon nie deur die geaktiveerslykproses bewerkstellig word nie.

Die maksimum stabiele bedryfs parameters word in die onderstaande tabel getoon:

	Geaktiveerde slyk	***HPB***
CSB verwydering (gefilter) %	*70-92*	*86-92*
CSB lading [kg CSB/m^3.d]	*15*	*28*
Hidroulise retensietyd [h]	*12*	*8*
Slyk ouderdom [dae]	*2*	*7,5*
Slyk konsentrasie in reaktor [g/l]	*2,5*	*18*
Slyk konsentrasie uit [g/l]	*1*	*0*

Die geaktiveerdeslykproses het twee keer onstabiel geraak terwyl die HPB 'n konstante 90% CSB verwydering getoon het. Skuimvorming het toetswerk by hoër organiese ladings belemmer in die HPB, terwyl suurstofoordrag in die geaktiveerdeslykproses die beperkende faktor was.

Daar is gevind dat die verlies aan vlugtige stowwe slegs verantwoordelik was vir 1% van die organiese verwydering van die HPB.

'n Metodologie en model is opgestel om verdere ondersoeke op die behandeling van organiese stowwe te vergemaklik. Die model is teen gestadigde toestande in die reaktore geëvalueer en sluit die mikrobiese kinetika en vervlugtiging in. Die model voorspel die biomassa met 99% akkuraatheid en die organiese konsentrasie in die uitvloeisel met 87% akkuraatheid in vergelyking waargenome waardes.

Die ondersoek het getoon dat die HPB effektief CSB en toksiese organiese stowwe vanuit die afvalwater kan verwyder en dat die reaktor stabiele bedryf getoon het tydens die hele toetsperiode. Die HPB het beter as die geaktiveerdeslykproses kontrole presteer. Die resultate toon dat die HPB 'n toepaslike tegnologie is wat gebruik kan word vir die verwydering van hoë organiese ladings in afvalwaterstrome.

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NOMENCLATURE

ASP	activated sludge plant
CIP	cleaning in place
COD	chemical oxygen demand
CSTR	continual stirred tank reactor
DO	dissolved oxygen concentration [mg/*l*]
E	enzyme
ES	enzyme-substrate complex
EC_{50}	the concentration of a compound or wastewater that inhibits 50% normal respiration of a particular micro-organism or active sludge.
F	mass flow rate [kg/h]
f_e	net endogenous fraction
F_r	mass recycle flow rate [kg/h]
F_s	oxidation reaction mole fraction
F_w	mass wastage flow rate [kg/h]
FI	Flow indicator
HPB	high pressure bioreactor
H	dimensionless Henry's law constant
k_b	overall decay rate [h^{-1}]
K_i	inhibition constant [mg/*l*]
K_{i2}	second inhibition constant [mg/*l*]
k_d	specific decay rate [h^{-1}]
K_{La}	overall mass transfer coefficient
K_s	half saturation constant [mg/*l*]
K_v	overall first order volatilisation constant [h^{-1}]
LC	level controller
LC_{50}	the concentration which is lethal to 50% of a population.
MLVSS	mixed liquor volatile suspended solids concentration [mg VSS/*l*]
MLSS	mixed liquor suspended solids concentration [mg TSS/*l*]
OUR	oxygen utilisation rate [mg/*l*.h]
P	pressure [bar]
Q_g	air flow rate [*l*/h]
r_d	rate of cell decay [mg VSS/*l*.h]
r	rate of cell growth [mg VSS/*l*.h]
S	substrate [mg/*l*]
SES	substrate enzyme inactive complex
S_e	readily biodegradable substrate concentration in effluent from reactor [mg/*l*]
S_0	readily biodegradable substrate concentration in influent to reactor [mg/*l*]
SVI	sludge volume index [ml/g]

T	temperature [°C]
t	time [h]
V_l	liquid volume [*l*]
VOC	volatile organic carbon
WAS	waste activated sludge mass flow rate [kg/h]
X	biomass concentration [mg/*l*]
X_v	volatile biomass concentration [g/*l*]
X_d	dead biomass concentration [g/*l*]
Y_o	observed cell yield [mg MLSS/mg COD]
Y_t	true cell yield [mg MLSS/mg COD]
α	recycle ratio
γ	specific death rate constant [h^{-1}]
μ	specific growth rate [h^{-1}]
μ_{max}	maximum specific growth rate [h^{-1}]
θ	cell retention time or sludge age = reactor volume/waste flow rate [days]
τ	space time = reactor volume/flow rate [h]

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1. INTRODUCTION

Increasing industrialisation and population growth are placing greater strain on the supply and quality of water resources (Swerdlow, 1998). This is especially true in semi-arid South Africa where water is scarce (Department of Water Affairs and Forestry; 1991).

One of the current water quality management strategies is the segregation of the different wastewaters for specific treatment (Eckenfelder, 1989). The reason for this is that the cleaner water can be recycled, thereby reducing water intake, whereas the highly polluted water can be treated separately by specialised means. The overall effect is the reduction of water intake and a better quality effluent.

A high strength wastewater stream from a South African Petrochemical complex has proven difficult to treat in the past according to Du Toit (1997). This wastewater inhibited anaerobic activity, while aerobic treatment resulted in an effluent high in microbial solids. Analysis of the water showed that the high phenolic concentrations (948 mg/*l*), organic content (11500 mg/*l*) and total dissolved solid (TDS) (5,4 g/*l*) have the biggest impact on the water quality.

Toxic compounds and difficult degradable organic molecules have been shown not to degrade in a normal activated sludge process and may inhibit normal biological activity (Tabak *et al.*, 1981; Eckenfelder & Englande, 1998). High TDS wastewaters also influence the effluent quality of the activated sludge process, usually resulting in high biological suspended solids in the outflow (Eckenfelder & Musterman, 1995). Rozich *et al.* (1983) showed that toxic compounds negatively influences sludge settleability. A specialised means to treat the wastewater biologically and to retain the biological solids is therefore required. A high pressure bioreactor with membrane biomass separation system was selected as possible means to treat the high strength wastewater and retain biomass (Krauth, 1996; Krauth & Staab, 1993).

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If this technology is successful it could be employed to not only treat the current wastewater, but also the ever-increasing number of high strength industrial wastewaters. The purpose of this project was therefore to develop, build and operate a laboratory-scale high-pressure bioreactor (HPB) system with membrane biomass separation. The treatment of a toxic high strength effluent allowed the comparison of such a system's performance to a normal activated sludge system.

The following study objectives were identified:

- Determine bio-degradation kinetics, which must include the toxicity or inhibitory effect the wastewater has on a microbial population.
- Quantify the volatile organic compounds (VOC) stripping during bioreactor aeration.
- Design, build and operate the high-pressure membrane reactor system using a conventional activated sludge treatment pilot plant as a control.
- Compare the performance of the two reactor systems in terms of the chemical oxygen demand (COD) removal achieved and stability, while treating the inhibitory wastewater.
- Develop a model for a biological membrane system treating toxic or inhibitory wastewaters and include VOC stripping.

2. LITERATURE REVIEW

The first water quality and management goal of the Department of Water Affairs and Forestry is the encouragement of source reduction, recycling, detoxifying and neutralisation of wastes (Department of Water Affairs and Forestry, 1991; Department of Water Affairs and Forestry and Water Research Commission, 1995). This is also the policy being implemented at the petrochemical complex in South Africa. The optimisation of water usage leads to the reuse of relatively unpolluted streams, thereby decreasing water intake. The highly polluted streams however remain undiluted. The major effects of these streams on the environment are due to COD, toxic chemicals, VOC, total dissolved solids (TDS), priority pollutants (a list of toxic recalcitrant compounds compiled by the United States environmental protection agency) and heavy metals (Eckenfelder, 1989; Eckenfelder & Englande, 1998).

The major water quality impacts of the petrochemical wastewater are its high organic content, which include toxic compounds, and high salt concentration as can be seen in Table 2.1. The priority pollutant, phenol is also present, representing 17% of the COD content of the wastewater.

Table 2.1: The major chemical components of the petrochemical effluent.

Analysis	
pH	8,7
COD	11500 mg/*l*
Alkalinity as $CaCO_3$	4233 mg/*l*
NH_3 as N	252 mg/*l*
Phosphate as P	18 mg/*l*
Acetone	27 mg/*l*
Ethanol	46 mg/*l*
Phenol	840 mg/*l*
Total Phenols	948 mg/*l*
Methanol	13 mg/*l*
Cresols	108 mg/*l*
SO_4^{2-}	2227 mg/*l*
Cl^-	455 mg/*l*
Hg	<5 µg/*l*
Conductivity	17 mS/cm
Suspended solids	188 mg/*l*
TDS	5450 mg/*l*

2.1. Organic removal

The major removal pathways of organic compounds are through biological oxidation, volatile organic stripping and adsorption (Parker *et al.*, 1993; Namkung & Rittmann, 1987).

Biological treatment methods are the most commonly used pathway in the removal of organic compounds from wastewater streams (Eckenfelder & Englande, 1998). The growth kinetics of the biological solids coupled with reactor design theory is used to predict the removal of organic compounds and the production of biomass. The kinetic theory of microbial growth on soluble substrates has been studied for many years (Monod, 1949; Grady & Lim, 1980; Edwards, 1970). This theory is well developed and is used to predict the steady-state response of biochemical processes, including those of wastewater treatment (Water Research Commission (WRC), 1984). If toxic compounds are degraded however, these models fail to predict biological system behavior (Maier, 1989; Gaudy *et al.*, 1986; D'Adamo *et al.*, 1984).

2.1.1. Dynamics of microbial growth on toxic compounds

Interest has been shown in the biodegradation of toxic compounds and inhibitory carbon sources in wastewater treatment. Phenol has been the most widely studied inhibitory compound (Rozich *et al.*, 1983). Singer *et al.* (1978) as quoted by Rozich *et al.* (1985) stated that phenols would become more prevalent toxic contaminants. As the number of industrial toxic wastewaters is expected to increase in the future, it is imperative to understand the behavior of the microbial systems expected to treat these inhibitory effluents.

The most common growth rate equation used, proposed by Monod (1949), describes the relationship between the specific growth rate and the concentration of a growth limiting substrate as seen in Equation 2.1. Equation 2.1 is used to model microbial growth on readily biodegradable substrates.

$$\mu = \frac{\mu_{max} S}{K_s + S} \qquad (2.1)$$

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The saturation constant K_s determines how rapidly the curve approaches the maximum growth rate (μ_{max}). This equation applies to the growth limiting substrate, which is the organic content (COD) of the wastewater if all the essential nutrients are present in excess (Grady & Lim, 1980).

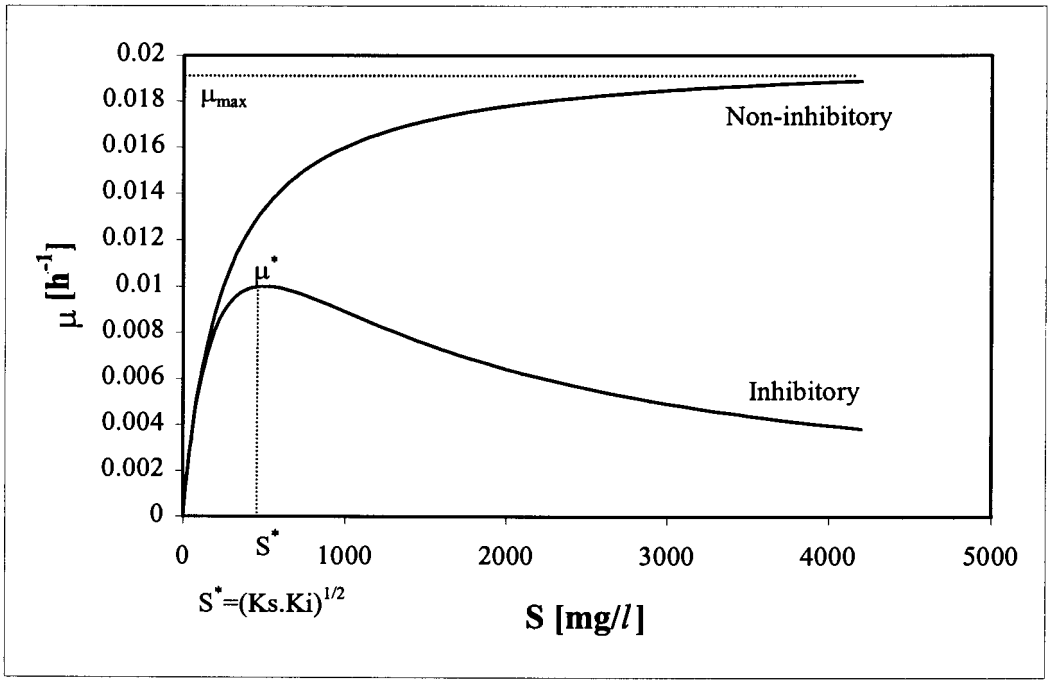

Figure 2.1: Relationship between μ and S according to non-inhibitory (Monod) and inhibitory (Haldane) models. The decreased growth rate at higher substrate concentrations can be seen for inhibited growth.

Several investigators found that the Monod kinetic model did not fit their growth kinetics, as they observed a decrease in biological growth at higher organic concentration, as illustrated in Figure 2.1 (Godrej & Sherrard, 1988; D'Adamo *et al.*, 1984; Palowsky & Howell, 1973; Edwards, 1970).

It was realised that inhibition of the microbial growth was taking place at higher substrate concentrations. Inhibition manifests as a reduction in the metabolic activities of a cell (Webb, 1963).

Phenol inhibition is a result of bonds formed with components of the cell (Edwards, 1970). Pelzcar *et al.* (1996) stated that phenolic compounds alter the cell membrane permeability and also bind to enzymes. This kind of inhibition is expected in the treatment of the study wastewater, since the phenolic concentration was high (948 mg/*l*).

Several equations have been proposed (Edwards, 1970) to model the inhibition effects of toxic substrates.

One mechanism for substrate inhibition would be a reduction in the enzyme activity due to the enzyme complexing with excess substrate to form one inactive site. From the following enzyme reactions Haldane (1930) derived an equation similar to Equation 2.3 but for enzyme kinetics:

$$E + S \xleftrightarrow{K_s} ES \xrightarrow{k} E + P$$
$$ES + S \xleftrightarrow{K_i} SES \ (inactive) \qquad (2.2)$$

In vitro substrate inhibition of an individual enzyme reaction is usually caused by a mechanism of this type. Equation 2.3 is totally empirical if used for growth kinetics although it is erroneously assumed to have a theoretical basis. The situation is analogous to the use of the theoretical Michaelis-Menten (derived from enzyme reactions) relationship for growth kinetics when the empirical Monod (Equation 2.1) should be used.

$$\mu = \frac{\mu_{max} S}{S + K_s + S^2/K_i} \qquad (2.3)$$

If two inactive sites are assumed Webb (1963) showed that the following Equation could be derived:

$$\mu = \frac{\mu_{max} S}{S + K_s + (S^2/K_i)(1 + S/K_{i2})} \qquad (2.4)$$

He further showed that allosteric substrate inhibition could be represented by:

$$\mu = \frac{\mu_{max} S(1 + S/K_{i2})}{S + K_s + S^2/K_i} \qquad (2.5)$$

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Aiba *et al.* (1968) correlated alcohol fermentation inhibition data using an empirical growth model described by:

$$\mu = \frac{\mu_{max} S.e^{-S/K_i}}{S + K_s} \qquad (2.6)$$

A protective diffusional-limitation of high and inhibitory substrate concentrations leads to the semi-empirical Equation 2.7 (Edwards, 1970):

$$\mu = \mu_{max}(e^{-S/K_i} - e^{-S/K_s}) \qquad (2.7)$$

All of the above equations should be considered empirical when used to model growth kinetics. All five equations have been used to model growth kinetics of microbial populations. Equation 2.3, named the Haldane equation, has been used most often, because it can more easily be manipulated mathematically than the other equations (Rozich *et al.*, 1985; Edwards, 1970).

The significance of substrate inhibition is most commonly displayed during reactor failures when treating toxic wastes. This occurs when the system parameters change (during a system upset such as a sudden feed rate increase) resulting in a sudden increase in COD concentration. The cell generation and wastage is usually in dynamic equilibrium. When the COD increases beyond the maximum growth rate, indicated by the maximum on the inhibition curve Figure 2.1, the growth rate decreases leading to lower cell production and subsequent (often sudden) washout and system failure.

This aspect of inhibitory wastewater biological systems was observed by Gaudy *et al.* (1986). Rozich *et al.* (1985) went further and concluded that if the values for μ_{max}, K_i and K_s are known the dilution rate at which washout occurs can be determined. Rozich (1992) reviewed three case studies where inhibitory kinetics predicted values closer to the actual operating condition than the standard growth kinetic models.

The growth kinetics of microbes is therefore a crucial part of the dynamic response of any biological system. Biological systems are designed and operated around their dynamic

responses. This is especially true when designing or modeling systems treating inhibitory wastewater.

2.1.2. Selection mechanisms

When a microbial population is exposed to a specific environment, two fundamental changes occur to the population as it adapts or acclimatises to that environment according to selective pressures (Daigger & Grady, 1982; Pretorius, 1987). These same changes occur when a microbial population is transferred from one environment to another, or from one operating condition to another.

The first change that occurs is in the biochemical composition of each specific microbial species and is known as physiological adaption. Daigger and Grady (1982) stated that physiological adaption can be considered to be the primary element of transient response. The major biochemical components that vary are the primary macromolecules (i.e. ribonucleic acid, protein, carbohydrate and lipid), activity of enzymes and metabolic intermediates.

The second adaption that occurs is the shift in the relative amount of specific species present in a microbial population. This response is a result of selective pressures on the population, in which the microbial species better suited to the new environment out-grows the rest of the population (Pretoruis, 1987). This adaption usually occurs more slowly than the physiological adaption. Lund and Rodriguez (1984) showed that it took up to four weeks for a microbial population to adapt to metabolize various mono-substituted phenolic compounds.

A stable and adapted microbial population is therefore important when conducting microbial tests (Rozich, 1992). This applies especially when determining the kinetics of biological wastewater treatment or the biodegradability of a potential toxic wastewater.

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2.1.3. Growth kinetics

The kinetic constants are either determined using the steady state response of a continuously fed CSTR (WRC, 1984; Grady & Lim, 1980) or by measuring the initial dynamic behavior of several batch reactors (Rozich *et al.*, 1985; Grady & Lim, 1980). Kinetic constants obtained through the use of batch reactors can be used to design or model a CSTR as well. It is imperative to realise, as discussed in section 2.1.2, that only a fully acclimated microbial population be used in either of the two tests, otherwise representative kinetic parameters will not be obtained.

A continuous system can be operated at different steady states. The reactor equations, including the kinetics can then be linearised and plotted, as shown by Grady & Lim (1980), to determine the kinetic parameters. This is straightforward for systems exhibiting Monod kinetics, since the equations can be linearised. If inhibition kinetics are expected the Haldane or equivalent equation (Eq. 2.3-2.7) should be used, which cannot be linearised. The CSTR approach is also time consuming, requiring at least 2 sludge ages to reach steady state (which can be up to 60 days for each steady state). The advantage of this system is that population shifts are measured as the new steady states are reached.

In the batch reactor system, acclimated activated sludge from a CSTR with cell recycle must be used to reflect the kinetics of a typical population. Several batch reactors are set-up to measure increase in activity of the microbes in the exponential growth phase when exposed to different substrate concentrations (Kappeler & Gujer, 1992). The test can be completed in 6 to 12 hours.

Several methods are used to measure the growth rate of microorganisms. These include cell mass increase, COD reduction rate or respiration rate. Respiration rate has been used to determine uninhibited cell growth (Ekama *et al.*, 1986). Equation 2.8 shows that a logarithmic linearisation of the differential equation (only for exponential growth) can be used to determine the growth rate minus decay rate of the microbial population at different substrate concentrations.

$$r_s = \frac{dS}{dt} = (\mu - k_b)S = -Y_t \frac{dX}{dt} = -Y_t(\mu - k_b)X \qquad (2.8)$$

Kappeler and Gujer (1992) stated that for a batch test with no substrate or oxygen limitation the respiration rate can be given by Equation 2.9 and that combining with Equation 2.8 yields Equation 2.10. The slope from the plot of Equation 2.10 consequently yields the growth rate minus the decay rate of the population.

$$r_{resp}(t) = -[(1-Y_h)/Y_h].\mu_{max}X(t)-(1-f_p)k_bX(t) \quad (2.9)$$

$$\ln\left[\frac{r_{resp}(t)}{r_{resp}(t_0)}\right] = (\mu - k_b)t \quad (2.10)$$

If the decay rate is known Equations 2.8 and 2.10 can be used to determine the growth rate. To determine the activated sludge decay rate using respirometry, Marais and Ekama (1976) derived Equation 2.11.

$$\ln OUR = \ln [(1-f_e)k_bX_0] - k_bt \quad (2.11)$$

The microbial kinetics (growth and decay) for a specific wastewater can therefore be determined by using Equations 2.8 to 2.11.

2.1.4. Volatile organic stripping

The second method of organic removal from aerobic treatment systems, after biological oxidation, is the volatilisation of organic compounds (Narayanan *et al.,* 1993). Organic compounds with low vapour pressures will move from the liquid phase into the vapour phase, if exposed to a liquid-air interface. Equilibrium between gas phase and liquid phase concentrations can be calculated using Henry's law, with volatile organic compounds having large Henry's law constants. The degree to which the gas/water system deviates from equilibrium provides the driving force for mass transfer.

Eckenfelder and Englande (1998) found that the microbial degradation of organic material influences the amount of VOC stripped, decreasing the liquid phase concentration, thereby decreasing the driving force for mass transfer. Researchers found that non-chlorinated VOC

are readily degraded under aerobic conditions encountered in wastewater plants (Zhu *et al.*, 1997; Bell *et al.*, 1993; Narayanan *et al.*, 1993; Parker *et al.*, 1993). Namkung & Rittmann (1987) found that only 2-3% of both benzene and toluene were stripped and that 97% were degraded in an activated sludge plant. Parker *et al.*, (1993) found that 15% of toluene were volatilised in their pilot plant.

The fraction of VOC stripped depends on several factors such as Henry's Law constant, the compound's biodegradation rate, reactor design factors, liquid:air ratio, temperature, sludge age and pH of mixture (Eckenfelder & Musterman, 1995; Parker *et al.*, 1993). Table 2.2 shows the amount of toluene and benzene stripped in an activated sludge process (Eckenfelder & Musterman, 1995).

Table 2.2: Amount of volatile toluene and benzene stripped as a function of sludge age.

Compound	Influent concentration [mg/l]	Sludge Age [days]	Amount stripped [mass %]
Toluene	100	3	12-16
	0.1	3	17
	40	3	15
	40	12	5
	0.1	6	22
Benzene	153	6	<1
	0.1	6	15

The rate of volatilisation, in a completely mixed reactor with steady air flow, follows first order kinetics (Watkin & Eckenfelder, 1984):

$$\frac{dS}{dt} = -K_v S \qquad (2.12)$$

When using diffused bubble aerators the liquid to air volume is small and minimal stripping occurs compared to mechanical aerators. For diffused bubble aerators, Roberts *et al.* (1984) developed the following expression for the mass transfer of volatile compounds from a completely mixed reactor:

$$\frac{dS_l}{dt} = -\frac{Q_g H}{V_l}\left[1 - \exp\left(-\frac{K_L a V_l}{H\, Q_g}\right)\right] S_l \qquad (2.13)$$

Comparing Equation 2.13 and Equation 2.12 shows that the term in front of S equals K_v. Equation 2.13 shows that the air holdup, V_l/Q_g, and overall mass transfer coefficient, K_La, are the physical parameters that influence VOC stripping.

If K_v can be determined experimentally for a certain wastewater, Equation 2.12 can be used in the activated sludge biodegradation equation to produce a concurrent biodegradation/ volatilisation model.

From the literature it is clear that primary removal of volatile compounds is through biodegradation and not volatilisation, but that volatilisation could play a significant role.

2.1.5. Reactor model

A model is a representation of the actual situation in which the most important elements are identified and their interactions described. The complexity of a model will usually depend upon the precision of the estimate required (Daigger & Grady, 1982) and the more complex a model the more specific it becomes. The complexity of the model depends also upon how well the phenomena being modelled are understood. If the process is poorly understood it would be a waste of time to use a complex, and therefore highly specific, mathematical model. Conversely if a simpler model can be used it becomes more general and applicable.

A model to predict the bioreactor treatment of not only the current wastewater but also future wastewaters must be developed to fulfill the requirements proposed in the introduction. This model will facilitate the design of new HPBs treating other wastewaters. The model must include all organic removal mechanisms such as the growth and decay kinetics of the microbial population and VOC stripping. These will then be included in a mass balance equation for a CSTR with cell recycle.

In addition to growth (Equation 2.15) a microbial population also undergoes cell *death* and endogenous *decay*. A cell is defined as dead when it losses the ability to reproduce (Grady & Lim, 1980). A "dead" cell can therefore still contribute to the removal of organic compounds. Natural predation amongst other complex mechanisms also contributes to death. Rate equations can be written for both death and decay. The two rate constants can

only be determined separately with difficulty (WRC, 1984). The combined effect can, however easily be determined as an equivalent endogenous mass loss (Equation 2.14) and has been shown to yield reliable predictions (Ekama & Marais, 1977; Kappeler & Gujer, 1992):

$$r_d = \frac{dX_v}{dt} = k_d X_v \qquad (2.14)$$

$$r_g = \frac{dX_v}{dt} = \mu X_v \qquad (2.15)$$

Figure 2.2 shows a CSTR system that can be used to define the membrane operation and from which a model mass balance can be derived.

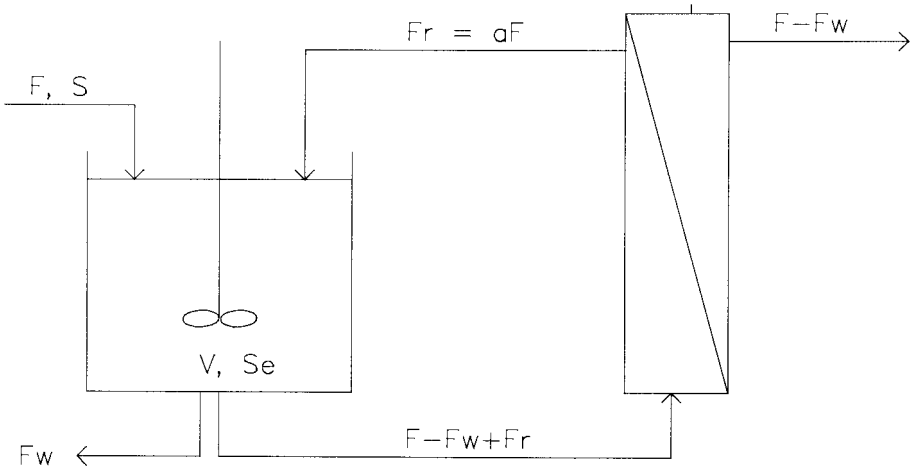

Figure 2.2: Process flow diagram indicating flows for the HPB.

This process model is also used for activated sludge, when the membrane is replaced by a settling tank. Grady & Lim (1980) have shown that for carbon removal in the system described above, growth rate is a function of decay rate and cell age:

$$1/\theta = \mu - k_b \qquad (2.16)$$

μ is the growth rate, usually represented by the Monod growth rate equation. For growth on inhibitory substances μ is replaced by one of the Equations 2.3 to 2.7.

The volatile cell mass is then determined by:

$$X_v = \frac{Y_g(S_0 - S)}{(1/\theta + k_b)\tau} \qquad (2.17)$$

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In the development of the above equations the following assumptions were made:

- All soluble substrate removal and cell decay occurs only in the reactor and none in the membrane or settling tank. This is a valid assumption for the membrane system but not for cell removal by settling tank, where retention times in the settler may be up to 2 hours.
- The mass of the organisms in the recycle stream and membrane or settler is small compared to the cell mass in the reactor.
- All substrates are biodegradable. No nonbiodegradable COD enters the equations.
- No substrates are removed by volatilisation or adsorption.
- The membrane or settler retains all biomass and no dissolved organic matter. This is a good assumption for the ultra filtration (UF) membrane, but not always for the activated sludge settling tank.

The petrochemical wastewater has a volatile organic fraction and most of the COD is expected to be readily biodegradable (du Toit, 1997). The equations above do not include all removal mechanisms and were consequently modified in the experimental section to include volatilisation.

2.2. Treatment systems

A wide range of biological processes have been employed to treat petrochemical effluents. These technologies can be categorised into aerobic and anaerobic systems. This study only focuses on the aerobic treatment of wastewater, since the wastewater inhibited anaerobic metabolism (Du Toit, 1997).

2.2.1. Aerobic treatment

Aerobic means have been employed extensively to treat industrial chemical effluents (Eckenfelder & Englande, 1998; Eckenfelder & Musterman, 1995; Gaudy *et al.*, 1986, Rozich, 1992). Aerobic treatment can be divided into aerated lagoons and activated sludge treatment.

Aerated lagoons

In the aerated lagoon, wastewater is retained for a long period of time compared to the activated sludge process. Biodegradable organic material is removed by conversion into biomass and CO_2, while oxygen is used as terminal electron acceptor. Oxygen is supplied by diffused or mechanical aeration, which also induces mixing. Typical average operating values for aerated lagoons are shown in Table 2.3 (Tchobanoglous & Burton, 1991; Eckenfelder, 1989; Grady & Lim, 1980).

Table 2.3: Average operating data for aerobic lagoon.

Parameter	Chemical	Petroleum
Area [m^2]	125 000	62 700
Depth [m]	1,5	1,5
Retention [d]	10	25
Loading [$kgCOD/m^3.d$]	0,017	0,00314
BOD removal [%]	87	76
MLSS [mg/*l*]	150-250	100-200
Y_o [$mgSS/mgCOD_{rem}$]	0,3-0,5	0,3-0,5
Mixing energy required [W/m^3]	2-12	2-12

Advantages of aerated lagoons as treatment method are:

- Less sludge is produced compared to the activated sludge process (Tchobanoglous & Burton, 1991).

Disadvantages of aerated lagoons are:

- Large land areas are required compared to other treatment technologies (Tchobanoglous & Burton, 1991).
- Low removal rates during the colder seasons (Uhlman, 1978).
- High power consumption for aeration and mixing (Eckenfelder, 1989).
- The process is less resistant to toxic, pH and temperature shocks than the activated sludge plant. (Puskas *et al.*, 1991).

Activated sludge

The activated sludge system is the most widely used aerobic treatment process (Webb, 1991). Many variations exist such as plug-flow, complete mix, contact stabilization, step aeration, deep shaft and extended aeration (Eckenfelder, 1989). The typical operating

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parameters for the completely mixed activated sludge system are listed in Table 2.4 (Tchobanoglous & Burton, 1991; Grady & Lim, 1980).

Table 2.4: Average operating data for activated sludge plants.

Parameter	
Sludge age [d]	5-15
Retention [h]	3-5
Loading [$kgCOD/m^3.d$]	0.5-2
BOD removal [%]	75-90
MLSS [mg/*l*]	2000-4000
Y_o [$mgSS/mgCOD_{rem}$]	0,3-0,5
Energy requirements [W/m^3]	50-80

The advantages of activated sludge are (Tchobanoglous & Burton, 1991; Eckenfelder & Musterman, 1995; Gaudy & Gaudy, 1980; Tabak *et al.*, 1981; Watkin & Eckenfelder, 1989) that it:

- Can treat higher organic loads than aerated lagoons.
- Requires smaller land area than aerated lagoons.
- Removes COD more effectively than aerated lagoons and anaerobic systems.
- Is more resistant to shock loadings than aerated lagoons and anaerobic systems.
- Is less sensitive to inhibitory toxic compounds than anaerobic system..

While its disadvantages are:

- Production of large amounts of sludge.
- Requires large amounts of energy compared to aerated lagoons and anaerobic systems.
- Does not always remove inhibitory and difficult degradable organics.
- Unstable operation, when treating inhibitory compounds.

Membrane bioreactor system

A new activated sludge treatment system using membrane separation to retain biomass have recently been proposed by several investigators (Krauth, 1996; Staab & Krauth, 1988; Knoblock *et al.*, 1994; Sutton *et al.*, 1994; Magara & Itoh, 1991). Inhibitory biodegradable substances can be removed in a biological reactor if specialised microorganisms with long generation times are kept within the system. This can be accomplished by using micro- or ultrafiltration to retain biological solids.

Eckenfelder & Englande (1998) stated that high dissolved solids concentration and toxic compounds produce a biomass that does not settle, but that biodegradation kinetics are not influenced. They found 600 mg/*l* VSS in an effluent from activated sludge treatment works treating an industrial wastewater with 44 g/*l* TDS. Eckenfelder & Musterman (1995) showed that TDS values as low as 1 g/*l* can increase suspended solids concentration in the effluent. Work done previously showed an activated sludge effluent high in microbial solids when treating the petrochemical wastewater shown in Table 2.1 (Du Toit, 1997). Rozich *et al.* (1983) could not reduce their SS effluent concentration below 200 mg/*l*, while treating a synthetic inhibitory phenolic wastewater.

With the use of a membrane separator, high sludge concentration can be maintained within the reactor and a treated effluent, free of suspended solids, can be produced. The alternative is to use coagulants to remove solids from the effluent (Eckenfelder & Englande, 1998).

Pressure (2-4 bar) is required as driving force for the micro- or ultra-filtration membrane separation. As a result the reactor is also kept under pressure. A high crossflow velocity (1-4 m/s) over the membrane is necessary to prevent excessive membrane fouling (Krauth & Staab, 1993). The membranes are cleaned in place using a back pulse to remove solids once every few hours, while a more thorough chemical cleaning is required every few weeks.

The increased pressure has the advantage of increasing the oxygen transfer in the reactor. In addition CO_2 solubility is increased. Increased CO_2(aq) or H_2CO_3 can cause a significant pH drop if insufficient alkalinity is available to buffer the system (Ho & Shanahan, 1986).

Table 2.5 shows the operating values for membrane bioreactor systems. The values vary considerably from application to application.

Table 2.5: Operating data for membrane bioreactor plants.

Parameter	Krauth & Staab, 1993	Magara & Itoh, 1991	Sutton *et al.*, 1994
Sludge age [d]	15,9		75
Retention [d]	5,8	4-9	1,9
Loading [$kgCOD/m^3.d$]	7,431		2,7
COD removal [%]	99	96	91
MLSS [g/*l*]	3,18-10,9	10-15	4-34
Operation pressure [bar]	2-4	1-4	
Membrane flux [$m^3/m^2.h$]	0,066	0,0625	0,04-0,068
Membrane cross-flow rate [m/s]	2,53	1,1-2,2	
Temperature [°C]	31,5	33	28-31
Y_o [$gSS/gCOD_{rem}$]	0,094		0,12
Energy required [kW/m^3]	7,9		

Advantages of the membrane bioreactor system are (Krauth, 1996; Krauth & Staab, 1993; Magara & Itoh, 1991):

- The membrane provides an absolute barrier to suspended solids.
- Higher volumetric loading rates compared to both the activated sludge process and the aerated lagoon are attainable.
- Biomass can be effectively retained.
- Less sludge is produced per COD treated, compared to activated sludge systems.
- Higher oxygen transfer efficiency is achieved because of higher pressures.
- Removal of all microbial pathogens in effluent.

Disadvantages are:

- High operating cost due to crossflow recirculation over the membrane.
- High pressures required for both the membrane and reactor.
- High capital cost for pressure vessel and membrane. This is partially offset by the smaller reactor volume required because of better oxygen transfer.

Considering the above-mentioned processes it is expected that the HPB, with better oxygen transfer and cell retention than the other processes, will be the preferred choice when treating high strength inhibitory wastewater. While the aerated lagoon will be the least favourable process to treat the wastewater. The second best process, activated sludge, will be an effective control to compare the performance of the HPB to.

2.3. Literature Conclusions

From the literature survey the most important factors to consider when treating a high strength wastewater are:

- The inhibitory effect the wastewater might have on microbial populations, and the stability of the treatment process.
- The effluent quality attainable.
- The organic load that can be treated effectively.
- The oxygen requirements of the reactor system.

The results from this research should help predict the performance of the bioreactor-membrane system treating the current wastewater. The toxic effects of the wastewater should be considered by including them in the kinetic parameters. Not only must the current water be treated but a methodology should be developed to facilitate future treatment of toxic waste streams.

3. EXPERIMENTAL

The first experimental section is preliminary experimental work, which includes determination of the growth kinetics when treating the wastewater and evaluating the kinetic constants. The next step was the operation of the HPB and activated sludge plant (ASP) control. The final step involved setting up a model that was evaluated against the operating data.

3.1. Growth kinetics

COD reduction rate was used to determine the growth rate (μ-k_b term). In this study acclimated seed activated sludge was needed. This was obtained from a stable (constant maximum COD removal of 92%) laboratory activated sludge plant using the undiluted petrochemical wastewater as feed. The laboratory reactor was seeded with activated sludge from two ASP treating industrial and domestic wastewater.

A second faster method to determine the growth rate kinetics using oxygen utilisation rate (OUR) measurement was developed and is shown in Appendix C.

3.1.1. Growth rate determination using COD removal rate

To evaluate Equation 2.8 several batch reactors were needed each operating with a different initial COD concentration. The amount of petrochemical wastewater needed to give a diluted COD of 100, 300, 500, 1000, 2000, 3000, 4000, 5000 mg/*l*, was added to glass beakers respectively.

An ASP with settler was used as source of biomass. The sludge age varied between 5 and 8 days. The reactor was operated for more than 40 days to ensure that a stable and acclimated sludge developed. Grady & Lim (1980) stated that 2 to 3 sludge ages are required to ensure that steady operation is achieved after an operational change. Reactor stability was also evaluated by measuring cell mass concentration and COD removal using filtered COD determination. Optical examination on a Zeiss Axioskop optical microscope, Phase

Contrast, x150-x400 magnification was used to evaluate that an acclimated and stable microbial population was developing. This can be seen when higher life forms such as protozoa and fungi develop (Lankford *et al.*, 1988).

Settled sludge was added to the beakers to give a final suspended concentration of 300 mg/*l*. A small concentration of sludge is required, so as not to mask the lag growth phase and to obtain a clear linear region (D'Adamo *et al.*, 1984). Distilled water was used to dilute the mixture to 500 ml after nutrients were added to give the concentrations recommended by Rozich *et al.* (1985).

The beakers were immersed in a water bath at 30°C. pH was checked and corrected every 30 minutes to pH 7,8.

Samples were taken at 0, 30, 60, 120, 240, 420, 540 and 1220 minutes. For more dilute samples (100-500 mg/*l* COD) samples were taken 0, 30, 60, 90, 120, 240, 360, 520 minutes.

Each sample was filtered to determine the suspended solids concentration using Whatman Glass fiber B filters. The filtrate was collected and analysed for COD content.

The COD data obtained were plotted on logarithmic scale as a function of time. The growth rate term (μ-k_b) indicated by the slope of the initial linear region, was determined. After the decay rate k_b was determined the growth rate for each COD concentration could be calculated. The statistical Pearson function was used to determine whether the region was significantly linear. Values of r^2>0,95 were accepted, otherwise the particular experiment was repeated. Growth rate data was then plotted against initial COD concentration as determined for the samples at time 0.

A statistical software package Datafit® was used to fit the three inhibition kinetic equations to the data obtained using non-linear regression. Initial estimates were required to avoid unrealistic convergence. To test the ease of convergence of a particular equation a matrix of starting values were set-up and the number of iterations before convergence was achieved

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was logged. The package also indicated which model best fitted the data using the parameter R^2, coefficient of multiple determination, and the sum of the squares of the errors.

3.1.2. Determining endogenous decay rate

The slope of Equation 2.11 yields the endogenous aerobic decay rate. To determine this a batch reactor was set up and the decrease in the OUR rate over time was plotted.

A batch reactor consisting of a beaker was filled with settled sludge and diluted to 500ml using distilled water to a suspended solids concentration of 3-4g/*l*. The batch reactor was kept at 30°C and pH corrected to pH 7,8 using H_2SO_4 daily, if required. The water loss was made up daily using distilled water.

OUR was determined every day for 8 days using a dissolved oxygen (DO) probe and OUR meter calibrated daily.

Interference during the test may be encountered from nitrification bacteria influencing the OUR of the decay rate. Thio-urea was added (20mg/*l*) to inhibit nitrifiers (Ekama *et al.*, 1986).

A plot was prepared of LogOUR vs. time. The slope is k_b can be seen in Figure 4.3.

3.2. Reactor operation

To assess the performance of the HPB it was compared to a normal ASP, both reactors operated on the same wastewater. Both reactors were designed, built and operated in parallel receiving the same inhibitory petrochemical wastewater. Reactor performances were assessed comparing the effluent quality and reactor stability at different COD loadings.

The wastewater was transported from the source to tanks at the University of Pretoria's wastewater laboratories. The wastewater was stored at 4°C. This water was tested for biological degradation and adsorption onto the polymer container by measuring if any filtered COD reduction took place over time. No COD reduction was detected.

The stored wastewater was used to make up reactor feed daily, with nutrients added in the form of NH_4OH solution and KH_2PO_4 (COD:N:P ratio of 100:6:1 on mass basis), with the micro-nutrients Mg, Mn, Fe and Co added at the concentration recommended by Gaudy *et al.* (1986).

3.2.1. HPB

The HPB consists of a vessel with constant draw-off, which is sent to the membrane separator. The UF (50nm) membrane requires 0,5-3 bar pressure as driving force for separation of the treated water and the reactor content. It was decided to also keep the reactor content under pressure to prevent the biomass from being exposed to alternating cycles of high and low pressure which may damage the microbes (especially during the pressure letdown). Figure 3.1 shows the laboratory reactor setup with the control systems.

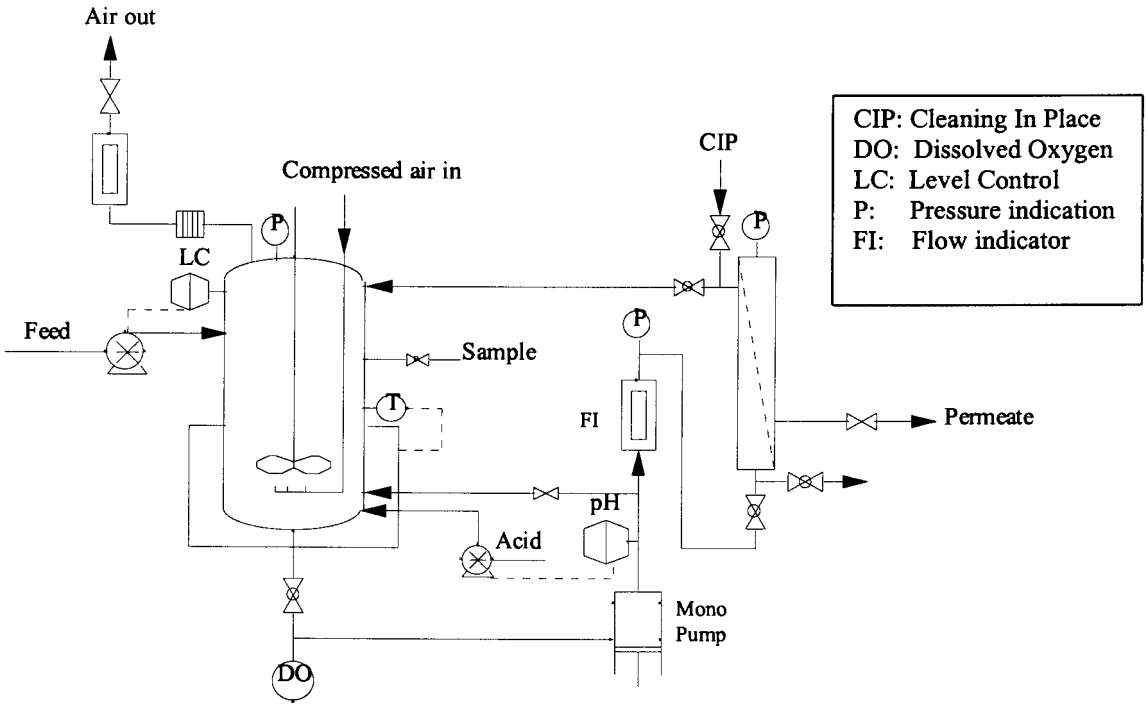

Figure 3.1: The HPB system setup, showing flow and control system.

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The HPB consisted of a converted 30*l* stainless steel fermentor, with agitator (100-300 rpm) and baffles. A peristaltic pump, fed the HPB with wastewater. The feed pump was controlled by a float Reed switch stainless steel level controller, which kept the volume of the reactor constant within ±0,3*l*. The sludge age was controlled by manually wasting biomass from the reactors twice daily.

The reactor-membrane was kept under pressure using compressed air. The pressure was controlled by adjusting the pressure regulator on the pressure header, while the airflow through the reactor was controlled by a manual valve and rotameter to achieve +2mgO_2/*l*. The air enters the reactor at the bottom through a coarse bubble diffuser below the agitator. A flow loop was provided to measure DO, and to determine oxygen utilisation rate using a OUR meter. The DO probe was calibrated daily before use.

The pH was measured using a pH probe, which fed the signal to a pH controller. The controller switched a pump dosing sulfuric acid into the reactor keeping pH 7,8±0,5. The probe was calibrated twice weekly.

Temperature was regulated using a thermocouple in the reactor, which controlled the temperature of water circulated in the mantle. The water served as heating or cooling medium depending on the ambient temperature. The temperature was controlled at 30±2°C. This temperature was chosen since this is the average temperature of wastewater and it was expected that the full-scale process will generate heat (microbiological and recirculating pump). It also provided a standard baseline temperature at which the microbial kinetics could be determined and ASP operation compared to.

The reactor content was recirculated across the membrane using a monopump model. The monopump provided a means of pumping sludge at a constant flow rate with little damage to the microbial cells. The flow rate over the membrane was set at 1-1,5 m/s using a Saunders valve and bypass line. A Membralox (AEC, Pretoria) tubular ceramic ultra filtration membrane with 50 nm pore size was used. Ceramics was chosen as material of choice to allow for easy cleaning in place as opposed to tubular polymeric membranes. The flux through the membrane was controlled using a Saunders valve on the permeate side,

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which was opened progressively over time as the membrane fouled. The membrane was designed to be isolated from the rest of the system to allow cleaning in place, either though back pulse or by chemical cleaning. The retentate is returned to the reactor, which completes the system.

3.2.2. Activated sludge

The activated sludge plant was designed according to the WRC report (1984). The ASP consisted of a 10*l* aerated Acrylic chamber and a 2,5*l* settling tank at an angle of 30° from the vertical as seen in Figure 3.2.

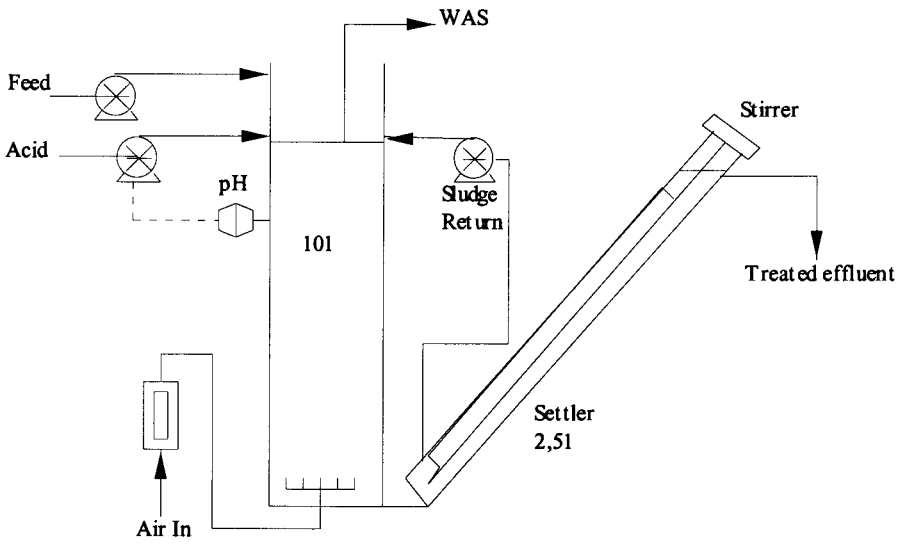

Figure 3.2: The activated sludge reactor setup.

Aeration and mixing were provided by two diffuse ceramic aerators at the bottom of the aeration chamber. The DO content and OUR were measured.. The aeration rate was controlled to ensure a DO concentration of 4±2 mg/*l*.

pH was controlled at pH 7,8±0,5 using pH probe connected to a pH controller, which switched a pump, dosing 0,46M dilute sulfuric acid. The probe was calibrated twice weekly.

The temperature was controlled through a heat exchange coil submerged in the aeration basin. Water served as the heating/cooling medium keeping the reactor content at 30±2°C.

Feed wastewater was delivered to the aeration chamber using a peristaltic pump. Sludge recycle was also accomplished using a peristaltic pump. The sludge recycle pump and scraper were switched on every half-hour for 5 minutes. A recycle ratio of 5-6 was employed. Sludge wastage occurred twice daily by manually removing a fixed quantity of sludge.

3.2.3. Planning & Analysis

The main aim of the reactor operation and testing was to evaluate the HPB technology to ASP technology and to evaluate a HPB reactor model treating inhibitory wastewater.

The HPB was operated at three steady states to complete mass balances around the system. The organic loading to the system was then systematically increased to determine the maximum COD removal that could be obtained from the HPB. The ASP was also operated at steady states and the organic loading to it increased to determine the maximum organic removal rate and resulting oxygen consumption rate. This was done over a 100-day test period.

The reactors were operated for at least two sludge ages until a COD mass balance could be calculated, before operating at the next steady state (Grady & Lim, 1980). The steady states were at 3,3; 5,3 and 10,2 kgCOD/m^3.d respectively. During the operating period MLSS, MLVSS, COD and OUR were measured as an indication of how the reactors were performing. The steady state data obtained was used to evaluate the steady state reactor model.

After the steady states were reached the COD load was increased to determine the highest practical organic loading. During this part of the experiment reactor stability and performance would be determined.

The methods shown in Table 3.1 were used during the study.

Table 3.1: Analytical methods used

Daily	Filtered COD of effluent, NH_3, MLSS, MLVSS, SVI DO, OUR Daily feed makeup to yield a COD:N:P ratio of 100:6:1 on a mass basis (addition of NH_4OH, KH_2PO_4), with micro-nutrients Mg, SO_4, Mn, Fe and Co added.	Standard methods (1989) no 2540D, 5220B, 2710 Ekama *et al.* (1986) Grady & Lim (1980) Gaudy *et al.* (1986)
Weekly	Influent COD, NH_3 as N and P concentrations. Filtered effluent NH_3, P. Microscope analysis, phase contrast, 150x, and 400x magnification	Standard Methods (1989), no 4500 N and P.
At each steady state	Phenol concentration	Merck Spectroquant 14551 & GC.

3.3. Model

The petrochemical wastewater has a volatile organic fraction and all of the COD is expected to be readily biodegradable. Grady & Lim's (1980) reactor model equations (literature survey) do not include all removal mechanisms and have consequently been modified to include volatilisation but not COD fractionation.

The following additional assumptions have been made during the modification of Grady & Lim's (1980) model (previous assumptions are still applicable):

- The readily biodegradable fraction contains the toxic compounds. This assumption is made because a high phenol concentration is expected, which can be considered a readily biodegradable compound to acclimated organisms (Gaudy *et al.*, 1986).
- The mass of the organisms in the recycle stream and membrane or settler is small compared to the cell mass in the reactor.

Equation 2.16 is manipulated to yield Eq. 3.1 with μ represented by one of the inhibition equations (2.3, 2.6 or 2.7).

$$0 = k_b + 1/\theta - \mu \qquad (3.1)$$

A mass balance on readily biodegradable substrate, including volatilisation, yields the volatile biomass fraction:

$$X_v = \frac{Y_g(S_0 - S)}{\tau\mu} - \frac{Y_g K_v S}{\mu} = \frac{Y_g(S_0 - S)}{\tau(1/\theta + k_b)} - \frac{Y_g K_v S}{(1/\theta + k_b)} \qquad (3.2)$$

The extra volatilisation term in the equation reduces the amount of COD available for conversion into cell mass. The sludge age and hydraulic retention time, influencing the volatile cell mass, are the parameters that can be used to control the process.

Equations 2.16 and 3.2 can be used not only for the membrane reactor but also for an activated sludge reactor system with a settler replacing the membrane, as long as no microbial solids are lost in the overflow.

A spreadsheet was used to setup the model, using Equations 2.3, 2.7, 3.1 and 3.2. The model required as input influent COD concentration, kinetic growth constants, volatilisation constant, observed cell yield, flow rate, sludge age and volume of reactor.

An effluent COD was assumed and Equation 3.1 was calculated using either Equation 2.3 or 2.7 to represent the growth kinetics. An equation was setup that measures the error of Equation 3.1 (against expected zero) and corrects by assuming a new effluent COD value. The whole process starts from the beginning until convergence is reached (error less that 1.10^{-5}). After the effluent COD has been calculated the cell mass in the reactor is calculated using Equation 3.2.

4. RESULTS & DISCUSSION

4.1. Growth kinetics

Equation 2.8 was plotted for different initial COD concentrations as shown in Figure 4.1.

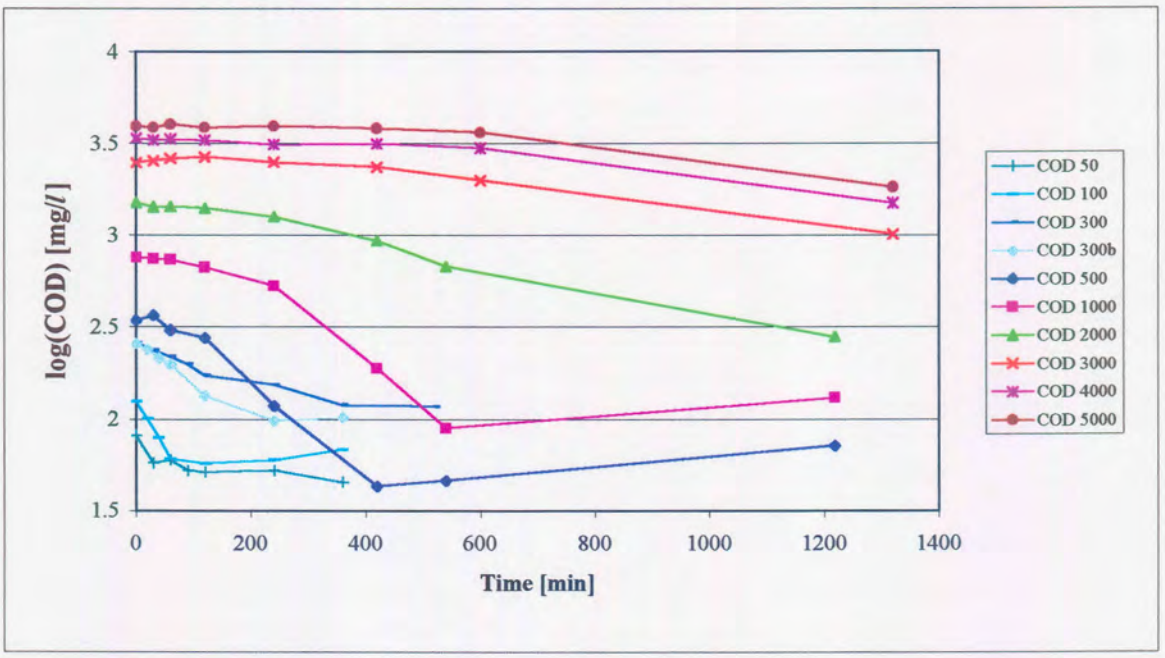

Figure 4.1: Logarithmic plot of COD concentration over time. The slope of the linear region is the term of interest in Equation 2.8.

From the Figure 4.1 it can be seen that the linear (exponential) growth region follows after a short lag phase followed by a log-linear region. Growth rate measurements at low COD (COD approaching MLSS concentration of 300mg/*l*) concentrations becomes less significant as the linear region becomes shorter. The slope of the linear region is then used to plot the growth rate as a function of substrate concentration as shown in Figure 4.2.

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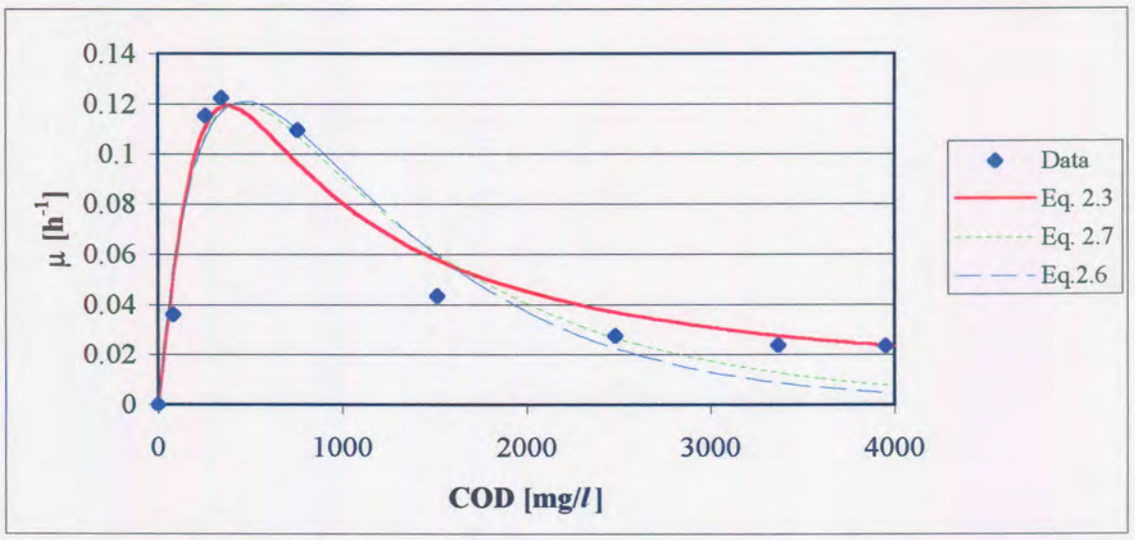

Figure 4.2: Growth rate data fitted to the inhibition Equations 2.3, 2.6 and 2.7, using COD reduction rate.

The kinetic parameters determined by minimising the sum of the square errors of the inhibition models are shown in Table 4.1. Equation 2.6 and 2.7 kinetic constants are comparable to literature values.

Table 4.1: Kinetic parameters determined using inhibition Equations 2.3, 2.6 and 2.7.

		μ_{max} [h^{-1}]	K_s [mg/l]	K_i [mg/l]	R^2	Sum of squared errors
COD fitted data	Eq. 2.3	2,39	7779,9	18,8	0,944	$0,725.10^{-3}$
	Eq. 2.6	0,429	519,9	901,62	0,927	$1,260.10^{-3}$
	Eq. 2.7	0,214	215,69	1198,5	0,940	$0,8760.10^{-3}$
Rozich *et al.* (1985) Phenol data	Eq. 2.3	0,16-0,36	5-266	200-1200		$0,8\text{-}1,6.e^{-3}$
	Eq. 2.6	0,16-0,35	30-247	281-1300		$0,7\text{-}12.e^{-3}$
	Eq. 2.7	0,16-0,24	24-272	350-1440		$0,6\text{-}4,4.e^{-3}$

Looking at Figure 4.2 all equations fitted the data well with errors comparable to literature values. From Table 4.1 it is seen that Eq. 2.3 and 2.7 gave the best fits with Eq 2.3 slightly better than 2.7, while Eq 2.6 gave the worst fit. This agrees with inhibition data on phenol presented by Rozich *et al.* (1985). The values for Eq 2.3 are high for μ_{max} and low for K_i. The Equation however yielded a graph close to the experimental and expected response. From the discussion Eq 2.7 gave the best results in terms of literature-compared results.

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Statistically there is however no significant difference between the equation results and all fitted the data well.

The determination of the endogenous decay rate is shown in Figure 4.3. The value obtained for microbial decay rate, 0,0074 h^{-1} compares well to other research's findings: 0,005 h^{-1} Rozich *et al.* (1985); 0,005-0,016 h^{-1} Kappeler & Gujer (1992); 0,01 h^{-1} Marais & Ekama (1976).

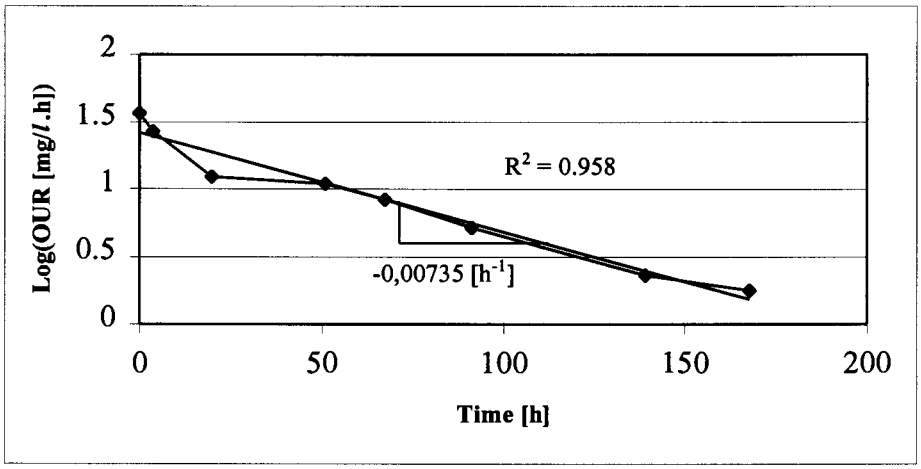

Figure 4.3: Determination of k_b using OUR data, with fitted trend line and slope indicated.

4.2. HPB vs. ASP

The COD removal as a percentage, COD reactor loading per reactor volume, sludge age, air flow rate per reactor volume and cell concentration in the reactor and overflow was plotted to indicate the reactor efficiencies. This is shown for both reactors except the cell concentration in the overflow is shown for the ASP only. The membrane and settler performances are evaluated qualitatively as biomass separators.

Three steady states for the HPB were evaluated and verified using a mass balance. These were used to validate the reactor model. The two reactors were started up at low COD loadings to acclimatise the microorganisms to the reactor operation. The HPB was operated for 2 sludge ages to achieve steady states. After the steady states the COD loading was steadily increased to assess the performance of the reactors by measuring the maximum attainable COD loading before oxygen consumption or toxicity became limiting.

4.2.1. Reactor Operations

It was determined that the maximum COD reduction of the wastewater attainable through biological means was 92%, decreasing the influent COD concentration (11,5 g/*l*) to 0,9 g/*l* and phenol concentration < 20mg/*l*.

Figure 4.4 indicates that all through the study a stable 90% COD reduction could be achieved, dropping to 86% only at high COD loadings of 28 kg/m^3.d. Phenol concentration of the treated water showed that the phenols were reduced to below 20mg/*l* during the steady states for both reactors. Few fluctuations in COD removal were observed. This indicates that effluent quality from the HPB system can be guaranteed, since little fluctuations in COD removal indicates stable reactor operation. The COD maximum loading rate achievable was 28 kgCOD removed/m^3.d. This figure is comparable to high rate anaerobic loading rates (Mergaerth *et al.*, 1992; Heijen *et al.*, 1991).

At this high COD loading rate neither oxygen nor toxicity became limiting but reactor foaming stopped further increases in feed rates. Foaming was a problem during start-up. Modifications to deliver the return sludge (retentate) below the reactor liquid level was implemented and mechanical foam breakers installed, which reduced foaming considerably during most of the test period.

It was concluded that the foaming encountered during the high COD loadings was due to the HPB not having reached its steady operating state yet. The ASP also encountered foaming problems during upsets and high loading conditions, which could be treated using silicone antifoam. The foaming could be caused by compounds, which can be degraded biologically. The compound is however difficult to degrade and is not degraded when there is an upset or during low hydraulic residence times (high loads).

Figure 4.7 shows that after the initial start-up period the COD removal remained constant at 90%, except for two occasions where the reactor nearly failed. At COD loadings above 15 kg/m^3.d oxygen transfer to the liquid became limiting with dissolved oxygen (DO) levels below 1 mg/*l*. Excessive foaming also occurred during high COD loadings necessitating the use of antifoam.

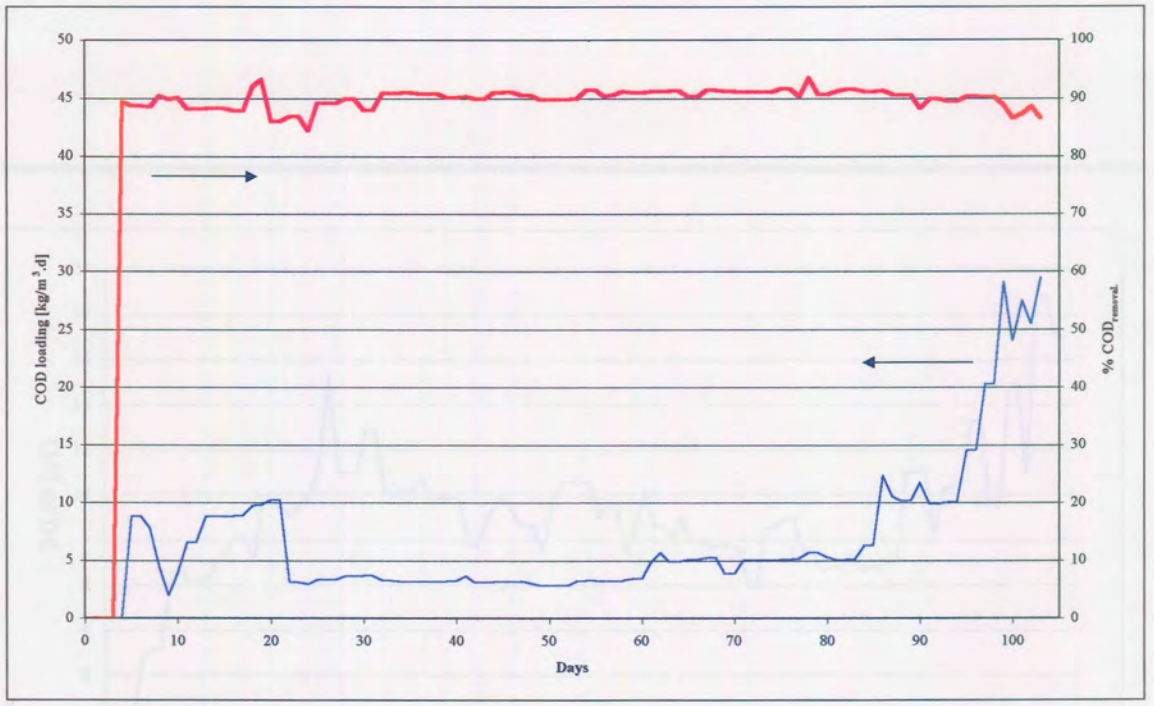

Figure 4.4: The COD loading and COD reduction over the 100-day period for the HPB.

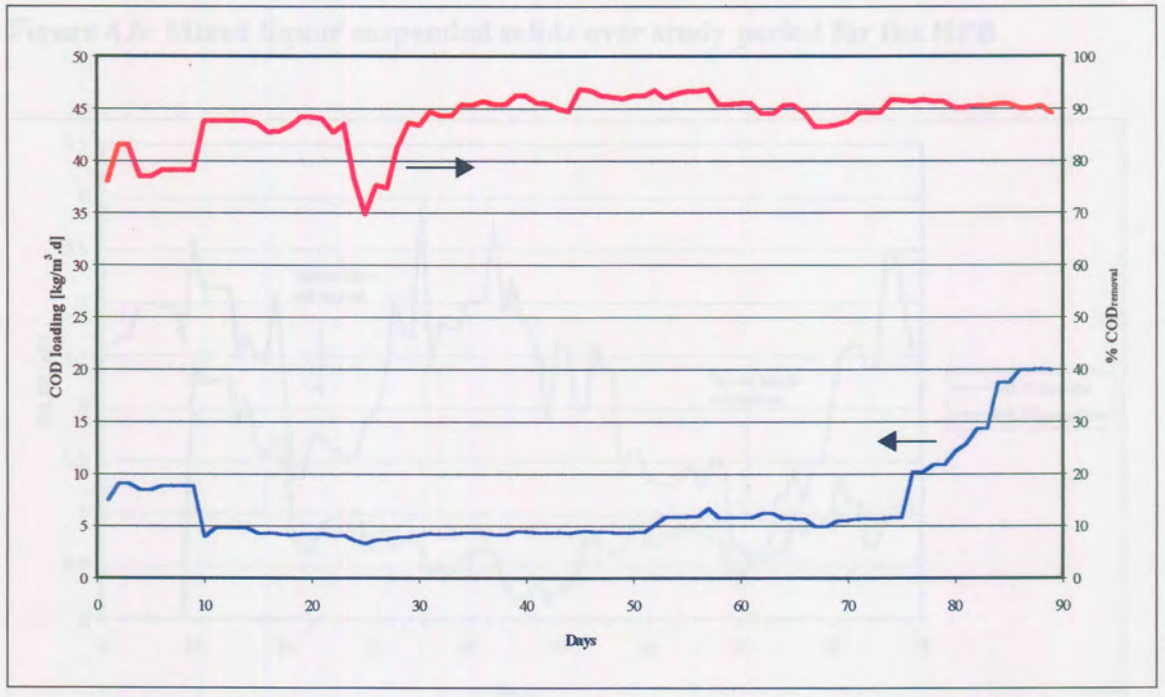

Figure 4.5: The COD reduction achieved by the ASP at different COD loading over the 100-day period.

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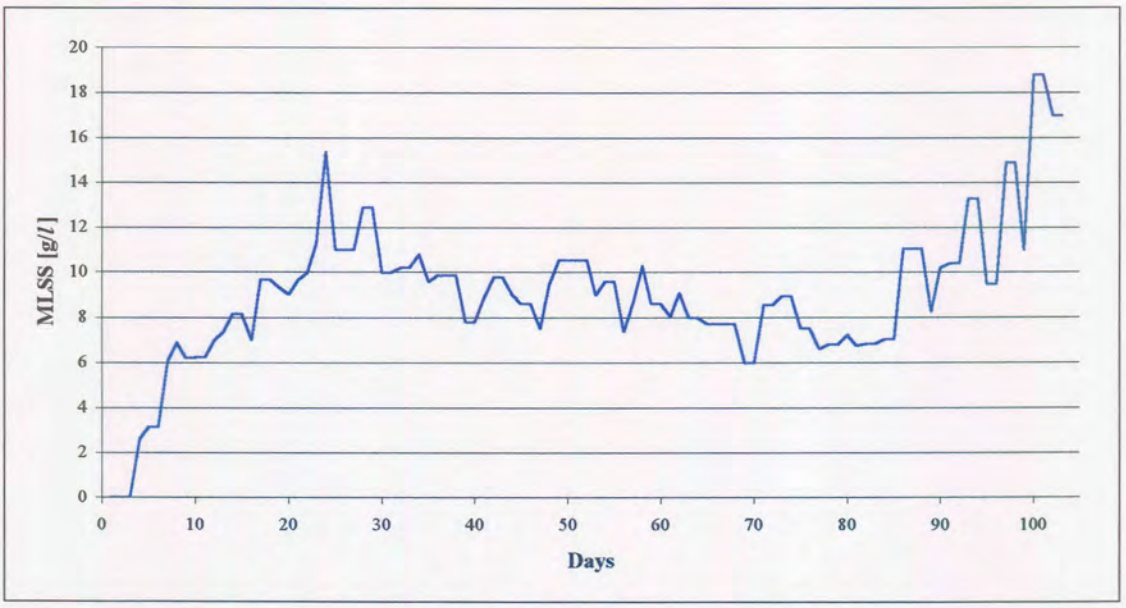

Figure 4.6: Mixed liquor suspended solids over study period for the HPB.

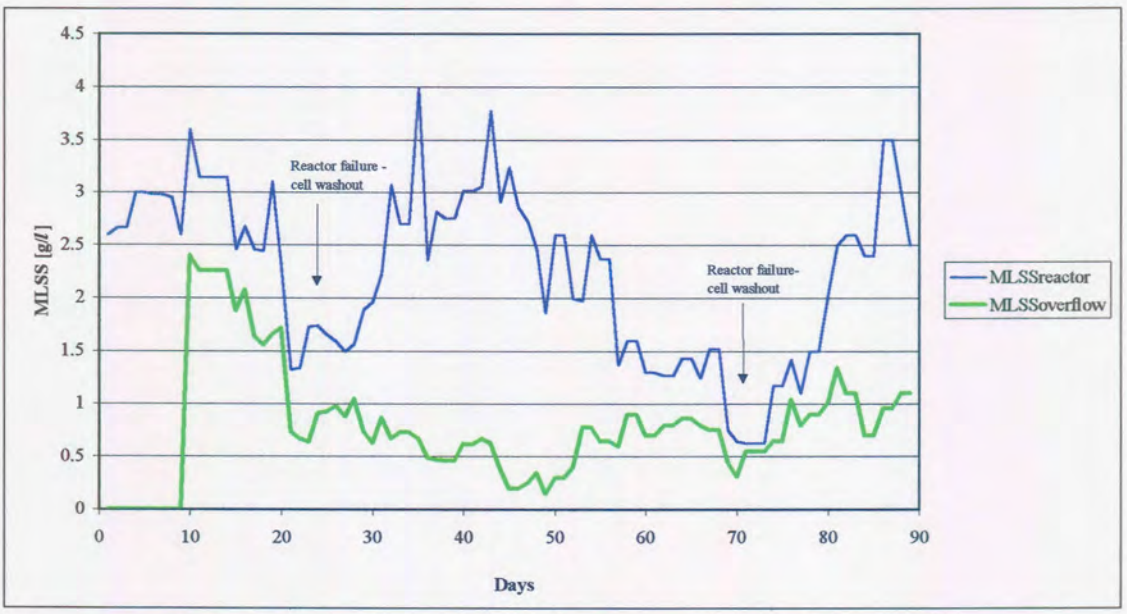

Figure 4.7: MLSS in the ASP reactor and the overflow MLSS concentration during the study period.

Figure 4.6 shows that the average operating MLSS for the HPB is 10g/*l* for a sludge age of 20 days. At high COD loadings the MLSS increased to 18-20 g/*l*, even for low sludge ages. The MLVSS remained a constant 85±5 % of the MLSS throughout the test. The cell mass could be controlled effectively throughout the test period and reactor washout never occurred, which is often a concern during activated sludge operations (Gaudy *et al*, 1986).

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By decreasing the WAS flow rate one can increase the MLSS and consequently reduce the cost of WAS solids treatment. This is done at the expense of oxygen transfer, since oxygen transfer decreases at higher MLSS concentration (Kühn, 1985). This is seen when comparing Figure 4.12 to Figure 4.6 and noticing that the amount of aeration dropped as the MLSS concentration dropped. An analysis, which compares the cost of aeration to the cost of sludge treatment, must be performed to determine the most economic optimum mode of operation.

The MLSS of the ASP varied considerably between values of 0,6-3,5 *g/l* as seen in Figure 4.7. Twice the reactor became unstable with a loss of cell mass and a decrease in the COD removal, i.e. reactor failure. To prevent total reactor failure cell wastage was stopped and the reactor feed was decreased. Rozich *et al.* (1985) and Bertucco *et al.* (1990) reported on the unstable behavior of ASPs treating inhibitory wastewater. The reactor failure can be explained using the Haldane inhibition growth curve Figure 2.1. From the curve it is evident that if the COD concentration were to exceed the value where maximum growth occurred (maximum on the curves) the cell growth would decrease, leading to decreased COD removal. This in turns would lead to higher COD concentration and to lower cell growth, etc. This is of great concern for the removal of inhibitory chemicals, since full-scale reactor failure could have serious or significant environmental and financial impacts.

The sludge volume index could not be determined since the top water layer still contained more that 15-30% of the solids yielding a false SVI. This fact also meant that the sludge could not be retained effectively and that the effluent quality was poor due to cells in the overflow. Rozich *et al.* (1983) found that they were not able to obtain an effluent cell concentration below 200 mg*/l* for an ASP system treating a synthetic waste high in phenol. It was concluded that the toxic compounds influence the sludge settlability negatively. The high salt concentration might also contribute to the SS in the effluent (Eckenfelder & Englande, 1998). The sludge age depended on the amount sludge that could be retained and is shown in Figure 4.9.

The upflow velocity in the 2*l* settler was 1-2 m/d, which is low compared to the Water Research Commission (1984) recommendation of 15-30 m/d. It was thought that the low upflow velocity was the cause of the poor sludge settleability, since the poor settling sludge (mostly motile and filamentous bacteria) are not washed out of the system. A smaller settler with diameter of 4,5 cm was installed on day 65, which increased the upflow velocity to 2-5 m/d. The settler diameter could not be decreased further because the settler scraper would not fit a smaller diameter settler. In addition the recycle ratio was increased to 6 (1 is the more economical recommendation). This resulted in 50-75% of the sludge having good settling characteristics (SVI 85±15 ml/mg), but 50-25% of the biomass did not settle and was lost in the overflow.

The settling problem arises when an ASP is used to treat a high strength waste. The maximum recommended influent COD concentration that an ASP can treat is roughly 1500 mg/*l*, while average values are in the order of 300-700 mg/*l* (Tchobanoglous & Burton, 1991). If an influent with 11500mg/*l* COD is treated the hydraulic residence times become long since a low feed rate must be employed. The feed rate is determined by the amount of oxygen that can be delivered to an ASP to treat the organic loading. The low feed rate results in a longer hydraulic residence time in the reactor and slower upflow velocity in the settler leading to the growth of non settling bacteria with doubling times shorter than the hydraulic residence time. These bacteria do not form settling flocs and are therefore much more susceptible to toxic and system upsets, both leading to unstable operating conditions (Rozich *et al.*, 1985). From the discussion it can be concluded that an ASP should not be used to treat high strength inhibitory wastes.

4.2.2. Sludge Age

During the first 15 days the HPB was operated with long sludge ages to obtain a stable biomass culture during the transient start-up period as seen in Figure 4.8. The sludge age was reduced (day 15-20) when it was seen that the reactor removed COD effectively and produced cell mass. Through the sludge age reduction, MLSS concentration could effectively be controlled.

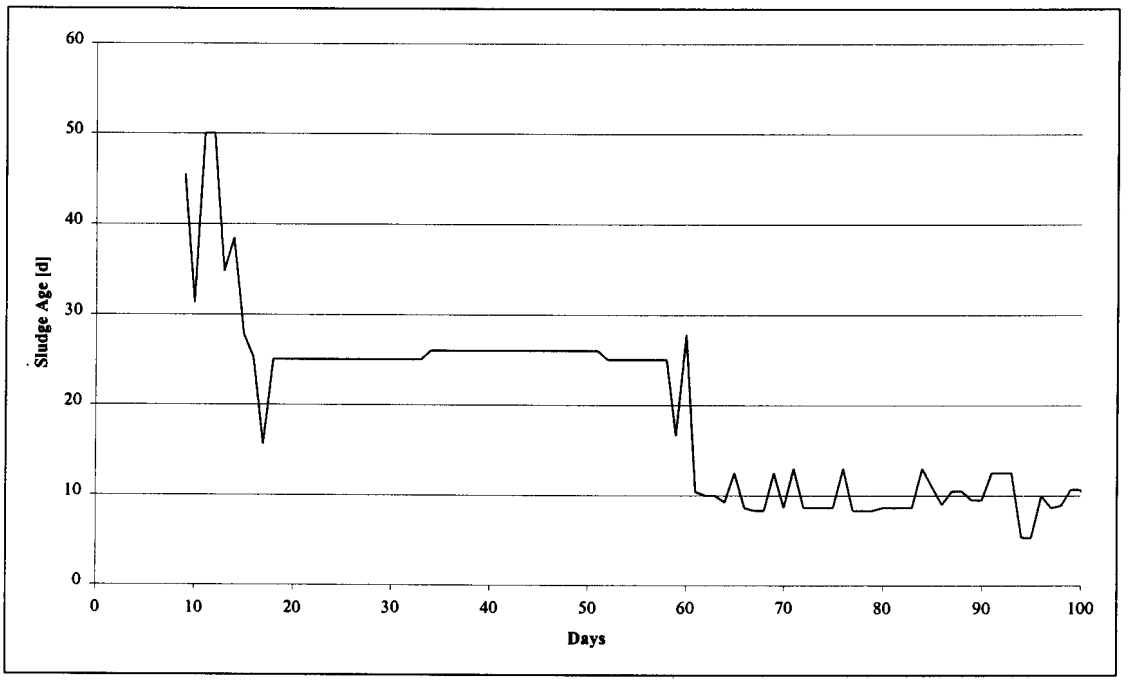

Figure 4.8: The sludge age during the 100-day test period in the HPB.

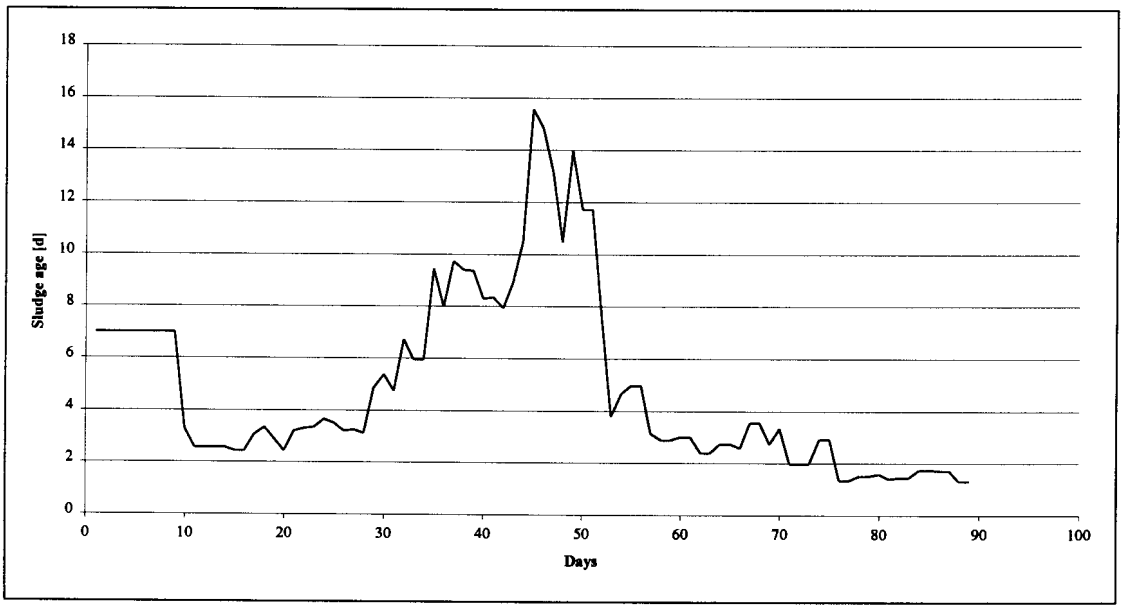

Figure 4.9: The ASP sludge age during the study period.

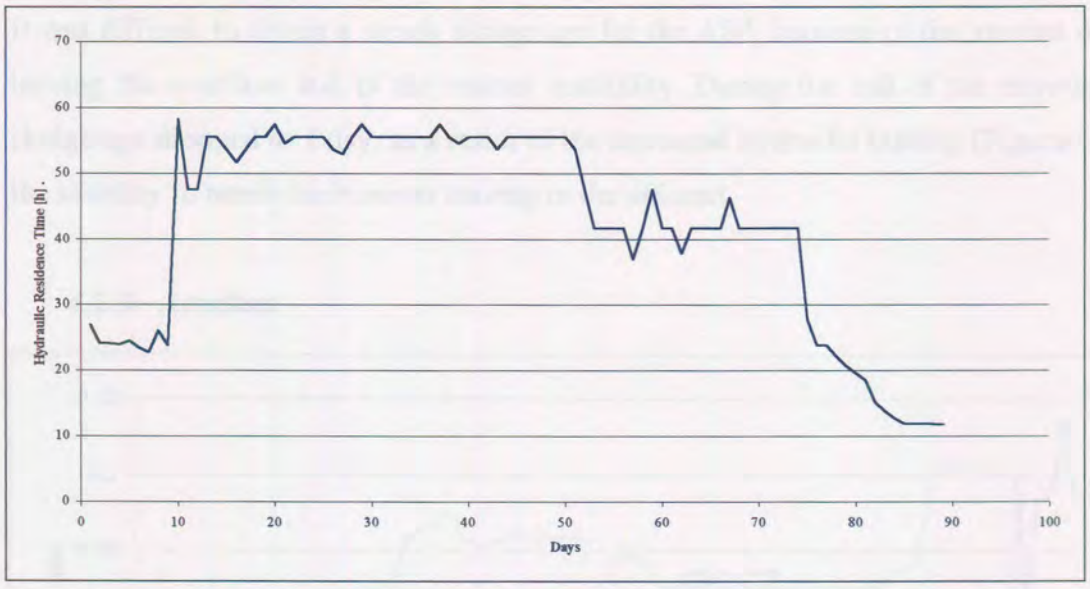

Figure 4.10: The hydraulic residence time of the ASP reactor over time.

Cell growth showing healthy microorganisms were observed under the microscope (seen in Figure 4.11). Protozoan Ciliates can be seen in the biomass, leading to the conclusion that a biomass capable of removing the toxins has developed. The sludge age was decreased substantially after 23 days to reduce the increasing MLSS concentration. This was done to increase the biologically active fraction of the biomass (WRC, 1984), and increase oxygen transfer to the wastewater at lower MLSS concentrations (Kühn, 1985).

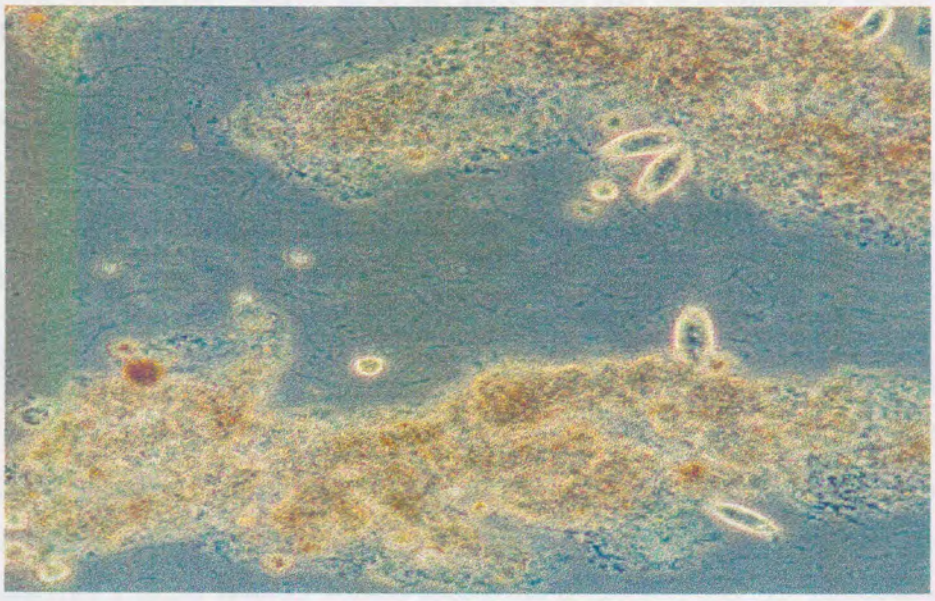

Figure 4.11: Biomass at 150x magnification phase contrast, showing a healthy HPB biomass for a 10 day sludge age.

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It was difficult to obtain a steady sludge age for the ASP, because of the amount of sludge leaving the overflow and of the reactor instability. During the end of the experiment the sludge age dropped to 1 day, as a result of the increased hydraulic loading (Figure 4.10) and the inability to retain the biomass leaving in the effluent.

4.2.3. Aeration

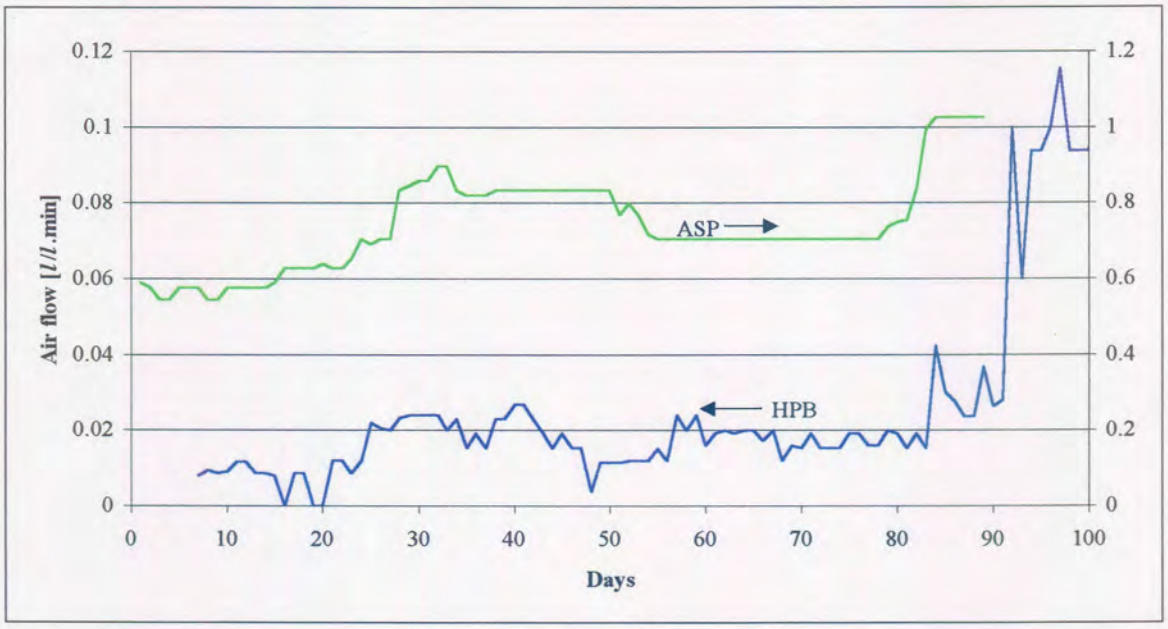

Figure 4.12: Airflow required to the HPB and ASP to maintain a DO concentration higher than 2mg/l.

The required airflow to the HPB and ASP is shown in Figure 4.12 giving an indication of the amount of aeration required for a full-scale system at different COD loading rates. The airflow rate is given per reactor volume to evaluate comparative aeration figures for different size reactors.

If the amount of aeration required is compared between the two reactors, it is clear that the HPB achieved better oxygen transfer than the ASP by a factor of 16-35. This is attributed mainly to the higher operating pressure (3 bar) of the HPB and to the method of aeration which uses a mechanical mixer in addition to the coarse bubble aerators. This in effect meant that a much smaller reactor compared to an ASP can be designed to treat the same volume of wastewater or that much less air will be required to treat the same amount of wastewater.

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4.2.4. pH

The pH of the HPB required acid addition to maintain a pH below 8,5 (where aerobic activity declines) only during start-up. After 2-3 days of operation the amount of CO_2 evolved from microbial action buffered the system to a stable value of pH 7,8-8,0 eliminating the need for further acid dosing. During high aeration, and consequent biological activity, this value dropped to 7,5-7,6. The pH remained constant never moving outside 7,5-8,0 for the whole test period. This gives an indication of the stability of the HPB system. It should be noted that if the wastewater being treated biologically produced as byproduct an acid (i.e. glucose biodegradation), pH control difficulties might occur. The ASP required acid dosing to prevent the pH rising to 9 during aerobic activity.

4.2.5. Membrane

The ultrafitration membrane removed 100% of the microbial cells, giving a clear permeate stream. Wastewater was fed directly to the membrane to determine what fraction of the organic removal could be attributed to membrane processes. It was found that the membrane removed 3-5% of the COD content of the wastewater. It is concluded that 96% of the COD removal can be attributed to microbial breakdown.

The membrane was oversized to provide separation over a wide range of operations (total clean water flux rate equals 1500 l/m^2.min at 25°C, while only 10 l/m^2.min permeate flow was required). It is recommended that microfiltration be used to increase the flux rate available without compromising biomass filtration.

The permeate was controlled using a Saunders valve to maintain the transmembrane pressure. The transmembrane pressure is shown in Figure 4.13, while the flux rate is shown in Figure 4.14.

Krauth & Staab (1993) recommended that a membrane cross flow velocity of 2-5 m/s be used, while Ghyoot & Verstraete (1997) used 2,3-6 m/s. In the experimental setup the cross flow membrane velocity was kept above 1,5 m/s for the first 60 days, but was reduced to 1 m/s at the end of the test period when it was found that little fouling occurred.

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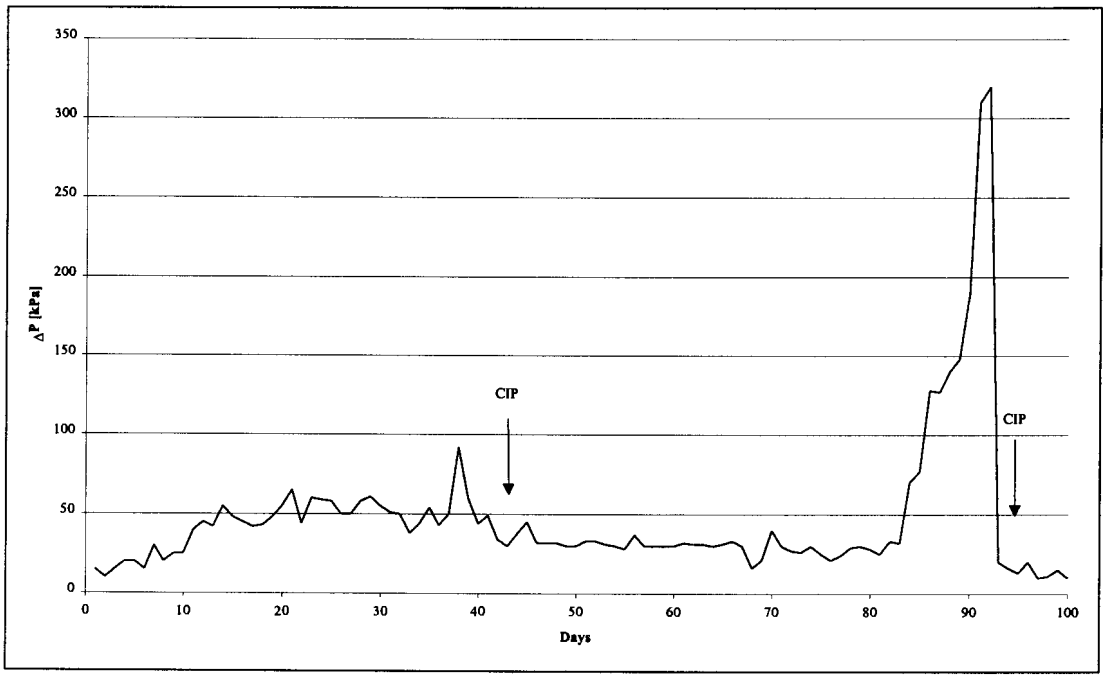

Figure 4.13: Transmembrane pressure of the UF membrane.

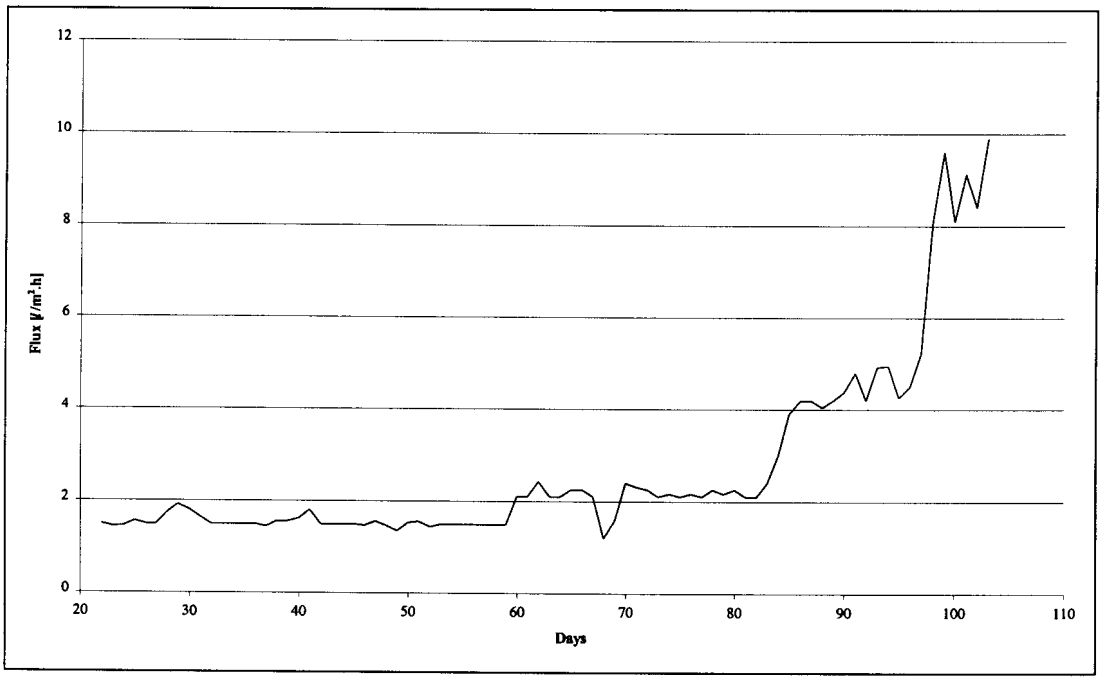

Figure 4.14: Flux rate through the ceramic UF membrane.

Twice in 100 days the membrane became fouled and was cleaned using a back pulse of pressure and water-flush, which returned a near clean flux rate to the membrane. No chemicals were used for membrane cleaning. It is important to note that the back flush method of cleaning could not be used if a tubular polymeric membrane was employed in the system. Only ceramic and capillary polymer membranes can be back washed. The ceramic membrane is expensive when compared to polymeric membranes. It is expected that the capillary polymer membrane might be the most cost effective in terms of price and mode of cleaning.

From Figure 4.13 and the discussion it is clear that the membrane performed well as a technique to separate biomass and reactor content. This is crucial in the effective operation of the HPB where loss of biomass can lead to reactor failures and poor effluent qualities.

4.3. Reactor model

A reactor model was setup as discussed in Chapter 3. To evaluate this steady state model it was necessary to achieve steady states with the HPB. At each of the steady states a COD or oxygen balance was calculated to assess the accuracy of the steady state assumption and the test methods as shown in Table 4.2.

Table 4.2: The organic carbon balances as COD for the different steady states achieved.

COD loading [kg/m^3.d]			**3.3**		**5.3**		**10.2**		**28.08**
COD influent @ 11.5 g/*l*			94.3		150.42		245.18		499.1
Effluent rate	[*l*/d]	7.2		10.08		19.32		41.4	
Waste activated sludge	[*l*/d]	1		3		2		2	
COD in @ 11.5 g/*l*	**[g O/d]**		**94.3**		**150.4**		**245.2**		**499.1**
COD in effluent	[g O/d]		7.954		12.295		22.898		54.25
	[g O/*l*]	970		940		1074		1250	
COD Cells wasted	[g O/d]		11.588		27.04		26.602		48.414
MLSS	[g/*l*]	9		7		10.33		18.8	
WAS	[*l*/d]	1		3		2		2	
Volatile cell mass fraction		0.87		0.87		0.87		0.87	
COD value of cells	[g/gVSS]	1.48		1.48		1.48		1.48	
COD OUR	[g O/d]		73.224		99.144		179.4		346.8
OUR	[mg/*l*.h]	113		153		325		850	
Reactor volume	[*l*]	27		27		23		17	
COD out	**[g O/d]**		**92.77**		**138.5**		**228.9**		**449.5**
C-balance%			101.63		92.06		93.36		90.05
Yield observed	[gVSS/gCOD]		0.0907		0.1323		0.0809		0.0735

COD of a wastewater can be split into biodegradable and non-biodegradable (inert) COD. From biodegradation batch tests run for several days on the wastewater it was determined that 7±1% of the influent organic material remained after biodegradation. This included inert COD and COD converted to inert COD through biological means. This fraction does not take part during growth of microorganisms. The influent COD was consequently split into two fractions; readily biodegradable and inert, with the inert COD excluded from the model.

The first three steady states were achieved at a COD loading of 3,3, 5,3 and 10,2 kg/m^3.d. The forth condition at a COD loading 28,1 kg/m^3.d was not a true steady state, since the reactor did not operate for two sludge ages before the balance was made. It is still included since a satisfactory balance could be draw up for the operational point. For all four operating conditions, good mass balances within 90% could be achieved.

Table 4.3 shows the comparison between the predicted cell mass and COD concentration in the reactor system, versus the observed values at the four steady states. The growth kinetic parameters determined using COD and OUR methods in Appendix C were used as input to the model.

Table 4.3: Observed values vs. predicted cell and COD concentrations in the reactor system using different growth kinetic equations.

	X MLSS [mg/l]	S_e [mg/l]
Steady state 1		
Observed	9000	970
Eq2.3 COD	8723	949
Eq2.7 COD	8908	929
Eq2.3 OUR	8774	944
Eq2.7 OUR	8803	940
Steady state 2		
Observed	7000	940
Eq2.3 COD	6806	959
Eq2.7 COD	6933	932
Eq2.3 OUR	6841	952
Eq2.7 OUR	6860	947
Steady state 3		
Observed	10330	1074
Eq2.3 COD	10321	956
Eq2.7 COD	10423	931
Eq2.3 OUR	10349	950
Eq2.7 OUR	10365	945

Steady state 4		
Observed	18800	1250
Eq2.3 COD	19009	960
Eq2.7 COD	19114	935
Eq2.3 OUR	19038	953
Eq2.7 OUR	19053	949

Table 4.4 compares the cell mass predictions of the model for the two kinetic equation data, showing a correlation coefficient of 0,999. The outlet COD prediction differed from the expected value by more than 13,3% for the first three steady states. This model can consequently be used if an error of 13% is acceptable.

Table 4.4: Comparison (r^2) between the observed cell mass and predicted cell mass in the reactor as well as COD in the outlet using both Eq. 2.3 and 2.7 growth kinetics as determined using the COD and OUR kinetic data.

	Eq. 2.3: COD	Eq. 2.7: COD	Eq. 2.3: OUR	Eq. 2.7: OUR
% difference between observed and expected COD effluent concentration	11,0%	13,3%	11,5%	12,0%
r^2 Cell mass	0,9997	0,9999	0,9998	0,9998

It is noticed that all four carbon mass balances conducted over the reactor system achieved 1-10 % accuracy compared to the acceptable error, which is 10% (Ekama *et al.*, 1986). The first three steady states are therefore assumed to be correct and can be used in correlation with the model.

The yield coefficients calculated in Table 4.2 are low compared to normal ASP values of 0,45 mgVSS/mgCOD (WRC, 1984). Close correlation was observed between the literature values for the observed yields for similar membrane reactors:

Krauth (1996) Y_{obs}= 0,05-0,186 mgVSS/mgCOD,

Knoblock *et al.* (1994) Y_{obs} = 0,06 mgVSS/mgCOD and

Krauth & Staab (1993) Y_{obs} = 0,14 mgVSS/mgCOD.

Waste activated sludge disposal is one of the major cost components of wastewater treatment (Tchobanoglous & Burton, 1991). However, this study and literature indicates that a membrane reactor with high oxygen transfer efficiencies has a lower cell mass yields compared to the ASP values. This is advantageous since a smaller waste activated sludge

stream will be generated, by the HPB. The cell mass will already be concentrated in the WAS of the HPB due to the fact that the reactor operates at high MLSS concentrations. This can facilitate WAS treatment by skipping the sludge thickening step.

Table 4.3 indicates that a good correlation between the observed cell mass and the predicted cell mass existed. Table 4.4 shows that this correlation was $r^2 = 0,999$ for all the microbial kinetics. This indicates that the model including the assumptions used were correct for the calculation of the cell mass. Although there is little to choose between the different kinetic constants used to determine the MLSS concentrations (<1%), Eq. 2.3 and 2.7 COD determined values are slightly better than the OUR determined values (there is however no significant difference between the two). If the figures of the kinetic constants are inspected; Figure C.2 and C.3, one sees that the initial slope (up to about 1000 mgCOD/*l*) for both the kinetic models are the same. This is the region for stable reactor operation and of most concern during design. The rest of the graph should however not be ignored, since it gives an indication when the reactor will become unstable and what to do to correct it.

Biodegradation batch test done on the wastewater indicated a 92% biodegradability of the COD concentration of the wastewater. This equates to a minimum effluent concentration of 920 mgCOD/*l*. The observed concentration of 950 mgCOD/*l* show that 30 mgCOD/*l* of biodegradable material is not removed in the reactor. This value remains constant over the entire test period indicated in Figure 4.4. The reactor model also predicted a constant removal with 30 mgCOD/*l* remaining unbiodegraded. It is accepted that during long sludge ages an ASP removes almost all of the COD fed to it (WRC, 1984).

As the sludge age approaches the hydraulic residence time an increase in the effluent COD concentration is observed for ASP treating non-inhibitory wastewater (Grady & Lim, 1980). Reactors treating inhibitory substrates show a slight increase in COD concentration followed by a sudden reactor failure as the sludge age approaches the hydraulic residence time (Rozich *et al.*, 1983; Gaudy *et al.*, 1986).

This behavior was not observed in the HPB, but the model predicts such system failure at sludge ages of 9,5h. A HPB can therefore treat inhibitory wastes more effectively (higher throughput with less risk of washout) than an ASP.

The only deviation from the model is for the COD value of the fourth steady state. The COD concentration increased to 1250 mgCOD/*l* for the fourth steady state during the last few days of testing, after an increase in reactor loading (28,1 $kg/m^3.d$). At the fourth steady state the cell concentration also showed its biggest deviation from the model. It should be noted that this was not a true steady state, since the reactor did not operate for more than two sludge ages.

The effect of volatile stripping in the reactor on cell mass was 1% according to the model. This was attributed to low levels of biodegradable COD (10-20mg/*l*) observed in the CSTR reactor, little stripping was observed or expected. Namkung & Rittmann (1987) found that 1-3% biodegradable non-chloriated organics in ASP were removed through volatilasation, while Parker *et al.* (1993) observed values raging from 1% for 4-Ethyltoluene to 15% for toluene. It can be accepted that if a compound is biodegradable it will be removed from the wastewater through a biodegradation mechanism to a much greater extent than through a volatilisation mechanism. Taking this into account it was decided that corrections to the volatilisation constant for reactor operation (air:liquid ratio, pH, Temperature and agitation) would not be made, since its effects will be negligible.

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5. CONCLUSIONS

The HPB produced a consistent effluent quality at a COD removal rate comparable to anaerobic high rate reactors. The HPB was more stable than the ASP since reactor failure or cell washout never occurred, while the ASP failed twice. This stability was attributed to more effective biomass separation and retention when using the membrane. The HPB achieved much higher MLSS concentrations than the activated sludge reactor, also leading to more stable operation.

The HPB has higher oxygen transfer efficiency leading to the fact that the HPB effectively treated the wastewater at twice the COD loading (28 $kg/m^3.d$) than the activated sludge reactor (15 $kg/m^3.d$) could. The oxygen transfer of the HPB was 16 to 35 times more efficient compared to the ASP, but that mechanical energy was needed in addition to the bubble aeration to achieve this.

The ASP can effectively remove COD at half the rate of the HPB. The ASP operation is however inherently unstable and MLSS loss can be expected in the effluent, with possible reactor failure.

The reactor model proposed can be used to predict the effluent COD to 87% and cell mass concentration to 99% accuracy in the HPB. This model can be used to determine operation conditions for any wastewater, which is characterised i.e. kinetic parameters and biodegradability known.

The most significant removal mechanisms, if a compound is biodegradable is through biodegradation and not volatilisation. Volatilisation accounted for only 1% removal of the organic content of the wastewater.

The membrane can be used as an effective method in the removal of cell mass from the treated wastewater. Membranes that can be backwashed/pulsed should be employed when separating cell mass.

6. RECOMMENDATIONS

The compounds in the feed that cause foaming should be identified and eliminated. If that cannot be done the operating and physical condition to minimize foaming should be investigated. When the foaming can be controlled the reactor loads should be increased further to determine the maximum amount of COD that can be removed.

An economic optimum of operation should be carried out to determine the MLSS concentration at which the HPB should operate. The economic analysis should be carried out to determine the optimum between membrane area, recirculation required and WAS treatment.

The reactor should be operated near the point of unstable operation to evaluate the maxima on the growth curves.

Capillary membranes should be tested as a more cost effective method of MLSS removal, both in terms of efficiency as well as ease of cleaning.

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APPENDICES

Appendix A: TOXICITY OF WASTE WATER

Many organics exhibit toxic threshold concentrations where microbial growth is inhibited. This can be represented by a LC_{50} or EC_{50} value (van der Hoeven, 1991; Larson & Schaeffer, 1982). This value represents the concentration, which causes a decrease of 50% of the normal respiration rate of active microbes (EC_{50}) or death of 50% of the microbial population (LC_{50}).

When a particular wastewater inhibits microbial growth, it impacts directly on the design of a treatment system and the operation of that system (Rozich, 1992). This is because the activity of the microbes is affected, which impacts on the rate of substrate removal and oxygen uptake. The high-strength petrochemical wastewater used in this study was expected to inhibit normal microbiological growth, due to the high concentrations of phenols (950mg/*l*) in the wastewater. This assumption consequently needed to be verified before a treatment system could be designed or operated.

Toxicity of a wastewater to microbes can be measured using respirometry (Spanjers *et al.*, 1994; Kilroy & Gray, 1992). Other methods exist such as glucose [C^{14}] uptake rate and Adenosine Triphosphate (ATP) measurment (Larson & Schaeffer, 1982; van der Hoeven, 1991). All these methods evaluate the decrease in a microbial population's *activity* as an inhibitory compound's concentration is increased. Respirometry is a simple method and does not require expensive compounds for analysis, unlike ATP measurement and glucose [C^{14}] measurement. Respirometry was therefore chosen to evaluate the toxic effects of the wastewater.

Certain chemicals inhibit microbial growth by uncoupling oxidative phosphorylation resulting in uncontrolled respiration. This mode of inhibition can not be measured by respirometry and other methods have to be employed if the petrochemical wastewater exhibited this kind of inhibition (Larson & Schaeffer, 1982).

A.1. Materials and Methods

The toxicology method "Activated Sludge, Respiration Inhibition Tests", OECD (1996), was used to determine the concentration of wastewater that inhibit 50% of the respiration rate (EC_{50}) of a typical activated sludge population.

Activated sludge from a domestic activated sludge process was fed a nutrient broth, prepared according to OECD (1996). Feeding of readily degradable nutrient broth ensured that the sludge was active.

5 ml of this active mixture of sludge was then exposed to different concentrations of the high strength wastewater. The initial respiration rate for each concentration was measured using a Dissolved Oxygen probe.

The respiration rate of activated sludge grown in a range of wastewater concentrations was plotted on a logarithmic scale. This usually exhibit a linear relationship from which the plot of the logarithmic relationship can be determined and the concentration at 50% inhibition be read of, thus yielding the EC_{50} value.

The OECD (1996) method was also employed to determine when 50% inhibition occurred for the phenol degrading organism *Pseudomonas putida*. *P. putida* was selected, since the major organic contaminant of the wastewater was phenol (950 mg/*l*). The test was carried out in the same manner as for the activated sludge sample except that *P. putida* was used.

A.2. Results and discussion

The results of the tests are shown in Figure A.1. It can be seen that 50% inhibition of activated sludge occurs at 98% concentration of the wastewater. While *P putida* is inhibited at 9,1% concentration.

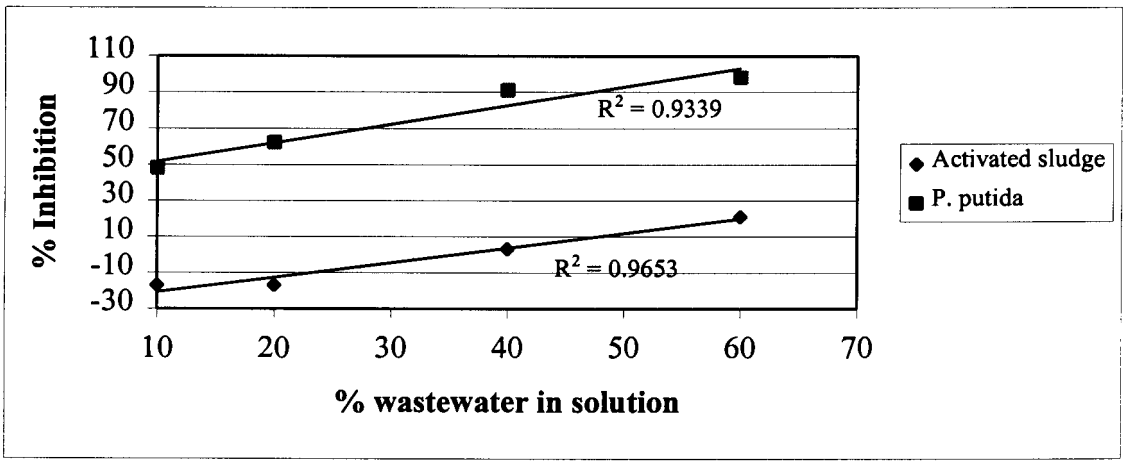

Figure A.1: Toxicity of untreated wastewater to activated sludge and *Pseudomonas putida*. EC_{50} for Activated sludge is 98% and 9,1% for *P. putida*.

Figure A.1 shows that the phenol degrading bacterial *P. putida* is almost totally inhibited by the wastewater and would not be able to treat the wastewater. The consortium of organisms found in activated sludge, could however degrade the wastewater showing growth (negative inhibition) for dilute samples.

A.3. Conclusions

It can be concluded that unacclimated activated sludge is inhibited by the high strength wastewater, but that growth does occur at low dilutions. From the observation, it is clear that the activated sludge does contain a population of organisms capable of metabolising the wastewater. Acclimation of the activated sludge should increase this fraction with selection pressures, as discussed in Section 2. The next step was therefore to acclimatise a microbial population and determine the kinetics of the organic removal efficiency of the acclimated population.

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Appendix B: VOLATILE ORGANIC COMPOUND STRIPPING

The volatile organic compounds (VOC) in the petrochemical wastewater will be included in the COD measurement of the influent water. During the biological treatment the air supplied to the reactors will strip some of the VOC, thereby decreasing the availability of organics for biodegradations. Effluent COD tests will attribute the COD reduction of the stripped VOC to biological efficiency. The VOC stripped, as a percentage of the influent COD load, needed to be determined as a function of time before biological processes were employed. After the kinetics of the volatilisation process was determined, it could be included in the reactor model.

B.1. Experimental setup

The amount of VOC stripped from the petrochemical wastewater before biodegradation needed to be determined. This was done by enumerating the K_v value in Equation 2.12.

B.1.1. Method

The method consisted of aerating 1,2 *l* of wastewater with a 1,5 *l*/min airflow rate using a porous diffuser. At a constant temperature of 30°C three runs at pH 6,5; 7,5; 8,5 were done.

The wastewater was kept at a constant temperature, while all biological activity was inhibited by the addition of 0,5 mg/*l* $HgCl_2$. Samples were taken over a 24-hour period and stored at 4°C for analysis. The COD was determined for each sample using the open reflux method (5220-B) of the Standard methods (1989).

From the linear logarithmic relationship of COD and time K_v was determined as the slope of the plot (Equation 2.8).

The COD test measures all oxidisable compounds and is not a specific test. It is therefore necessary to eliminate as much interference as possible such as adsorption of oxidisable organics and loss of VOC during testing. To avoid adsorption of organic compounds on materials, only glass came into contact with the wastewater (Standard Methods, 1989).

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The experimental setup consisting of the 1,2*l* sample is shown in Figure B.1.

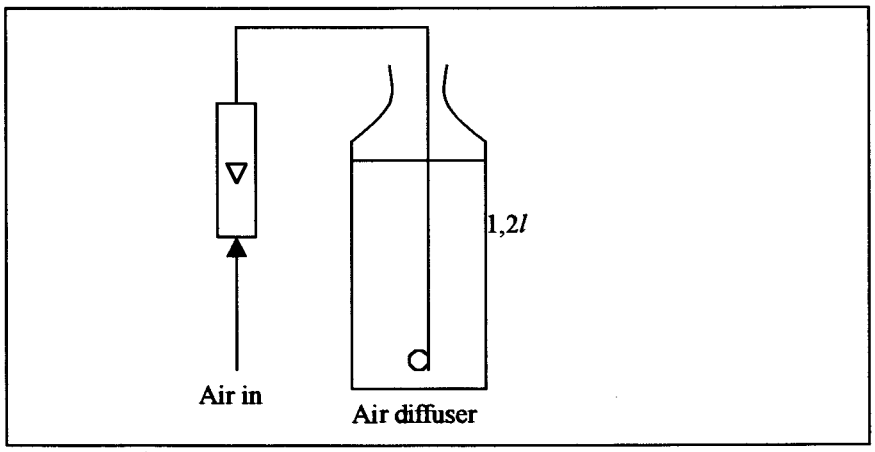

Figure B.1: Experimental setup to determine VOC stripping.

B.2. Results and discussion

The reduction of COD because of aeration at 30°C is shown in Figure B.2.

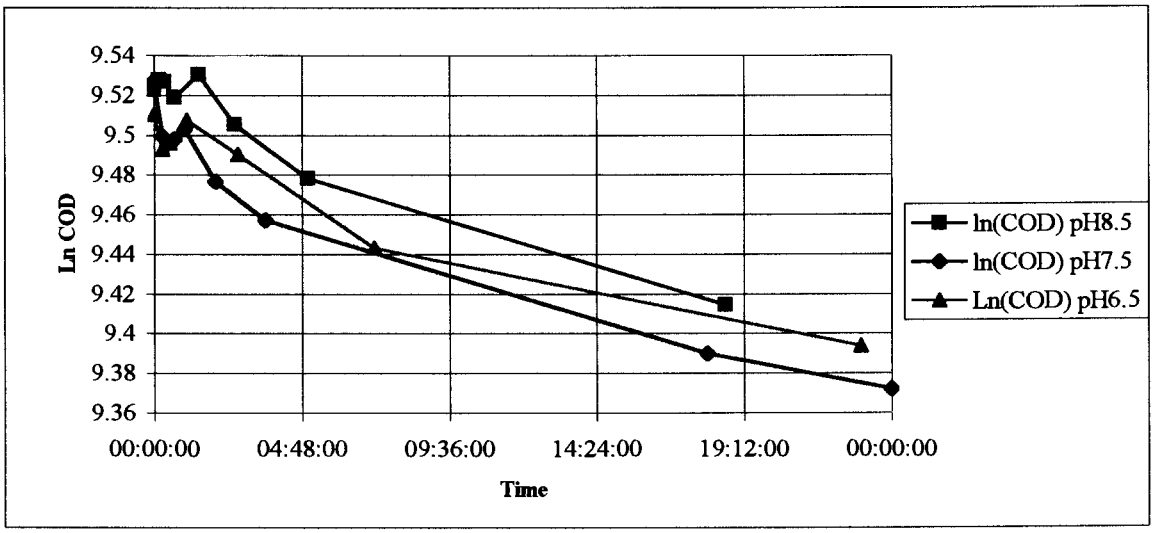

Figure B.2: COD as a logarithmic function of time for different pH's at 30°C.

The values for K_v at 30°C with statistical analysis are shown in Table B.1.

Table B.1: The values of K_v determined at different pH values and temperatures.

Temperature [°C]	pH	K_v [h^{-1}]	% COD reduction in 24 hours [%]	Pearson correlation, r
30	8,5	-0,1481	11	0,975
30	7,5	-0,1387	14	0,962
30	6,5	-0,1779	11	0,961

For this setup the gas holdup is 1,2 /1,5 = 0,8 min

Bubble size determined form photographic analysis were 12±3mm.

B.3. Discussion

The tests were carried out at 30°C because it is expected that this will be the temperature at which the reactors will treat the wastewater. This temperature was also selected as the base for comparison between the two reactors. The amount of VOC stripped was between 11-14%, comparable to the findings of Namkung & Rittmann (1987) which observed 16% volatilisation of Benzene and Toluene; Parker *et al.* (1993) 15% for Toluene and Eckenfelder & Musterman (1995) 14-17% for Toluene and Benzene.

Values of K_v varies between 0,106-0,177 h^{-1}. The average value of 0,139 h^{-1} obtained for 30°C and pH 7,5 was be used in further models.

The K_v values for reactor models employing diffusers with different gas holdup size or K_La, than for the experimental setup, must be adjusted for to obtain a new K_v value using Equation 2.9. K_La values are expected to remain fairly constant if the same wastewater at the same temperature (30°C) is used.

Appendix C: KINETIC CONSTANTS

In appendix A it was shown that the petrochemical wastewater inhibits microbial growth at high concentrations. A microbial population can however be acclimated to degrade the specific compounds through a method of adaptation and selection as discussed in chapter 2 (Daigger & Grady, 1982; Pretorius, 1987). This population can then be used to treat the inhibitory wastewater at a dilution, which inhibits unacclimated activated sludge (Edwards, 1970; Kilroy & Gray, 1992).

Kinetic parameters are determined to explicate the dynamic response of the microbes to the wastewater. This is done by measuring the growth rate or organic removal rate of the organisms at various concentration of the wastewater.

C.1.1. Growth rate measurement

Using Equations 2.8 to 2.11 all of the kinetic parameters (growth and decay rate) of microbial growth on a specific wastewater can be determined using either COD measurement or OUR measurement.

C.2. Experimental setup

COD removal rate and OUR were used to determine the growth rate (μ-k_b term). In both studies acclimated seed activated sludge was needed. This was obtained from an ASP as discussed in section 3.1.

C.2.1. Growth rate determination using COD removal rate

Kinetic determination using COD removal rate was discussed in section 3.1. The results are repeated in Figure C.1.

C.2.2. Growth rate determination using OUR data

To evaluate Equation 2.10 several batch reactors each with a different initial COD concentration was again needed. The batch reactors were made up and operated as described for the COD removal rate method in section 3.1.

Initial samples were taken to determine the starting suspended solid and COD concentration. Dissolved oxygen was measured using a DO probe connected to an oxygen utilisation rate (OUR) controller/recorded. The OUR controller aerated the batch reactor until a DO concentration of 5 mg/*l* was reached. Air to the reactor was switched off and the DO decrease (attributed to microbial activity) recorded versus time until a DO of 1 mg/*l* was reached in which case the reactor was re-aerated. The slope of the DO vs time curve therefore yielded the OUR of the microbes. This analysis was done automatically over a 24 hour period recording the OUR.

The logarithm of the OUR data was then plotted as a function of time. The slope of the initial linear region was determined using a least squares fit which equaled the growth rate term (μ-k_b). The decay term k_b was determined in section 4.1 and added to the term to determine the growth rate μ.
Datafit® was again used to fit the three inhibition equations using non-linear regression.

C.3. Results

Equation 2.8 was plotted for different initial COD concentrations as shown in Figure 4.1. The slope of the initial linear region (exponential growth) is then plotted against initial COD concentration (results repeated in Figure C.1).

The result of the OUR method to determine the growth rate is shown in Figure C.2.

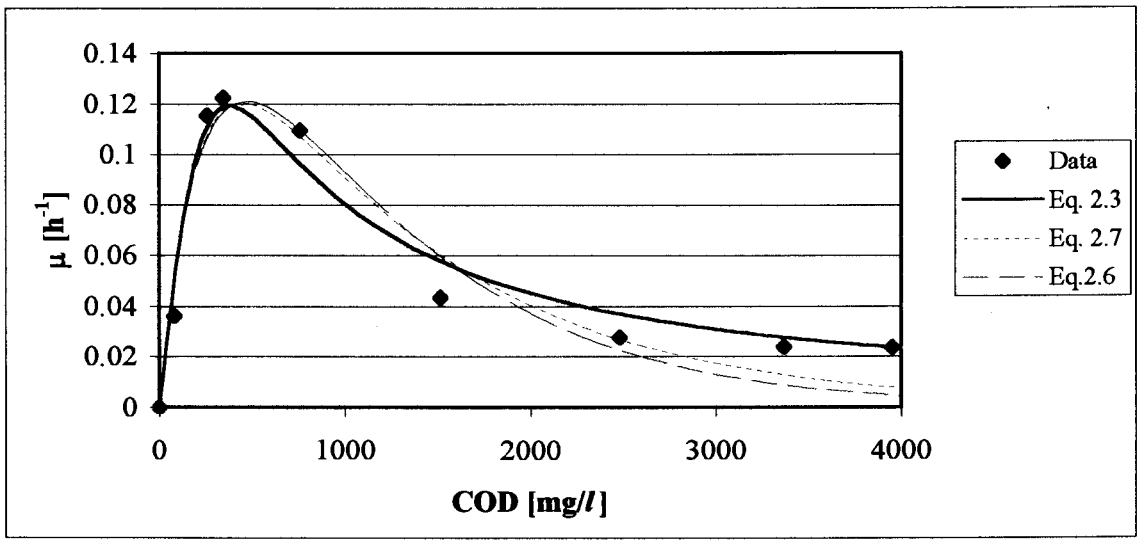

Figure C.1: Growth rate data fitted to the inhibition Equations 2.3, 2.6 and 2.7 using COD reduction rate.

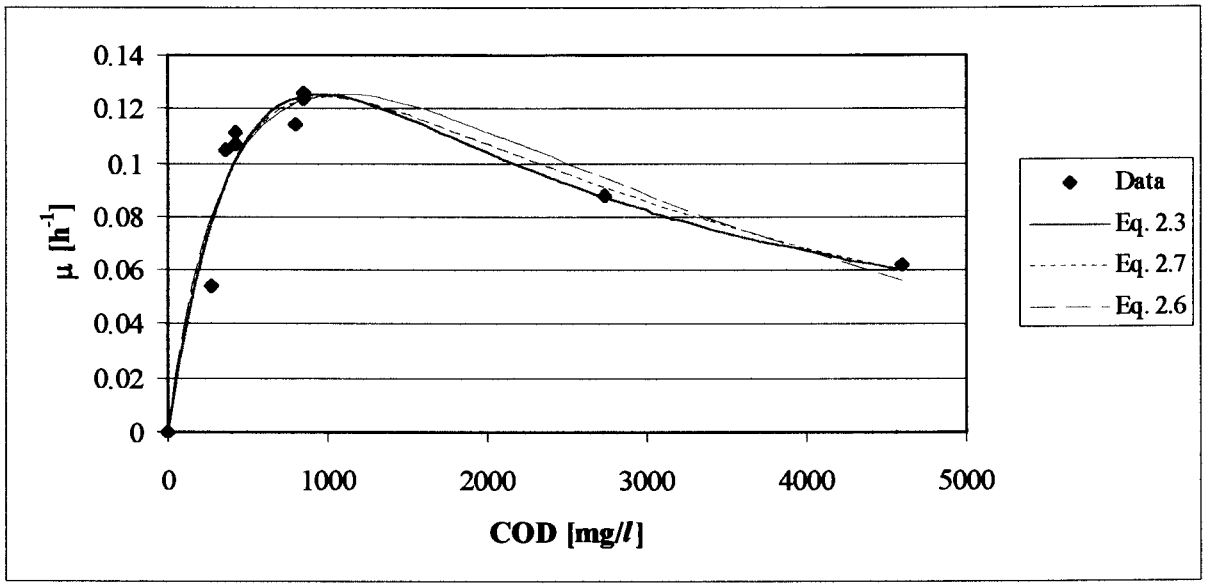

Figure C.2: Growth rate data fitted to the inhibition Equations 2.3, 2.6 and 2.7 using OUR reduction rate.

Table C.1 shows the parameters determined by the regression for both the COD growth rate data and the OUR growth rate data.

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Table C.1: Statistical analysis of inhibition models to COD and OUR growth rate data and comparative literature values.

		μ_{max} [h^{-1}]	K_s [mg/l]	K_i [mg/l]	R^2	Sum of squared errors
COD fitted data	Eq. 2.3	2,39	7779,9	18,8	0,944	$0,725.10^{-3}$
	Eq. 2.6	0,429	519,9	901,62	0,927	$1,260.10^{-3}$
	Eq. 2.7	0,214	215,69	1198,5	0,940	$0,8760.10^{-3}$
OUR fitted data	Eq. 2.3	0,4278	1141,69	786,01	0,936	$0,9064.10^{-3}$
	Eq. 2.6	0,2679	566,36	3199,41	0,923	$1,085.10^{-3}$
	Eq. 2.7	0,1695	363,55	4413,16	0,932	$0,9693.10^{-3}$
Rozich *et al.* (1985) Phenol	Eq. 2.3	0,16-0,36	5-266	200-1200		$0,8\text{-}1,6.e^{-3}$
	Eq. 2.6	0,16-0,35	30-247	281-1300		$0,7\text{-}12.e^{-3}$
	Eq. 2.7	0,16-0,24	24-272	350-1440		$0,6\text{-}4,4.e^{-3}$
Palowsky & Howell (1973) Phenol	Eq. 2.3	0,223	5,86	934,5		$11,4.e^{-3}$
	Eq. 2.6	0,205	2,00	1564		$12,5.e^{-3}$
	Eq. 2.7	0,205	16,07	1550		$11,4.e^{-3}$

C.4. Discussion

Figures C.1 and C.2 showed a characteristic inhibition shape indicating that microbial inhibition took place at higher organic concentrations. The Monod equation would not describe the growth kinetics and inhibition models would have to be employed. It was decided that Equation 2.3, 2.6 and 2.7 would be used to fit the experimental data. Equation 2.4 and 2.5 was not used, since researchers (Rozich *et al.*, 1983; D'Adamo *et al.*, 1984, Edwards, 1970) showed that the use of a forth parameter (K_{i2}) did not improve the quality of fit compared to the three parameter equation (2.3,2.6 and 2.7). The use of additional parameters (such as K_{i2}) leads to less general models as discussed in Chapter 2.

C.4.1. Statistical fit

Equations 2.3, 2.6 and 2.7 were fitted to both the COD and OUR data sets as shown in Figure C.1 and C.2. From Figure C.1 it is seen that Eq. 2.6 and 2.7 fit the experimental data well near the maximum tuning point, but that they differed at high COD concentrations. Eq. 2.3 fitted the data well at high COD concentration, but did not represent the turning point

well. Looking at Figure C.2 all equations fitted the data well. From Table C.1 it is seen that Eq. 2.3 and 2.7 gave the best fits with Eq 2.3 slightly better than 2.7, while Eq 2.6 gave the worst fit. This agrees with inhibition data on phenol presented by Rozich *et al.* (1985) and Palowsky & Howell (1973).

When comparing the different kinetic equation one should not only look at the best fit achieved (R^2 or sum of the squared errors), but also at the ease with which the equation could be fitted. The values of Eq 2.3 for μ_{max} and K_s are unrealistically large and K_i unrealistically small compared to the other equations and to results from other researches (D'Adamo *et al.*, 1984; Rozich *et al.*, 1985). During the nonlinear regression fitting procedure a matrix of starting values were used for the kinetic parameters. Using this starting value matrix Eq. 2.3 almost never achieved the same end values for the kinetic parameters in the number of iteration used (1500), while Eq. 2.6 and 2.7 almost always converged to the same end values within 20 to 30 iterations. One concludes that Eq. 2.6 and 2.7 are sensitive to the data, converging quickly to new values of μ_{max}, K_s and K_i if new data are used, while Eq 2.3 is insensitive to the data.

Gaudy *et al.* (1986) reported that the fitting procedure (for Eq 2.3-2.7) is sensitive to starting values. Rozich *et al.* (1985) and Palowsky & Howell (1973) concluded that Equations 2.3 and 2.7 both represented phenol inhibition data the best of the five equations, but that statistically there was no difference between the two equations.

C.4.2. Characteristic of graph

Comparing Figures C.1 and C.2 it is noticed that the maximum growth rate was 0,121 h^{-1} for both the COD and OUR data, but that the maximum occurred at a COD value of 500 mg/*l* for the COD data and 800 mg/*l* for the OUR data. It is also observed that the COD data decreases much more in the high COD range than does the OUR data. Although the microbes are active (respiring) their ability to take up organic matter is might be inhibited. The OUR determination will then register microbes able to transport some organic content for organic processes but not enough for significant COD reduction.

C.5. Conclusions

It is concluded that any of the Equations 2.3, 2.6 or 2.7 can be used to represent the inhibition data adequately. For the inhibition data of this study Eq 2.3 or 2.7 gave the best results. Eq. 2.7 is the model of choice, since it gave a good fit and was easily fitted yielding unique parameters for each set of data. Respirometry can be employed to measure the inhibition kinetics of microbes degrading an inhibitory substrate. Respirometry might be preferred above COD determination since it is less time consuming (automatic) and cheaper, generating more data thereby increasing the statistical significance of the generated data.