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Immersed Membrane Bioreactors for Produced Water Treatment

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Abstract

The performance of a submerged membrane bioreactor for the duty of gas field produced water treatment was appraised. The system was operated under steady state conditions at a range of mixed liquor suspended solids (MLSS) concentrations and treatment and membrane performance examined. Organics removal (COD and TOC) display removal rates between 90 and 97%. Removal of specific target compounds Benzene, Toulene, Ethylbenzene and Xylene were removed to above 99% in liquid phase with loss to atmosphere between 0.3 and 1%. Comparison of fouling rates at a number of imposed fluxes has been made between long term filtration trials and short term tests using the flux step method. Produced water fed biomass displays a greater fouling propensity than municipal wastewater fed biomass from previous studies. Results indicate an exponential relationship between fouling rate and flux for both long and short term trials, although the value was an order of magnitude lower during long term tests. Moreover, operation during long term trials is characterised by a period of pseudo stable operation followed by a catastrophic rise in TMP at a given critical filtration time (t_{filt}) during trials at 6 $g.L^{-1}$. This time of stable operation, t_{filt}, is characterised by a linear relationship between fouling rate and flux. Results have been compared with the literature. Data for membrane fouling prior to the end of t_{filt} yielded a poor fit with a recently proposed model. Trends recorded at $t > t_{filt}$ revealed the fouling rate to follow no definable trend with flux. The system showed resilience to free oil shocking up to an oil concentration of 200ppmv. Following an increase in oil concentration to 500 ppmv, rapid and exponential fouling ensued.

Key words: MBR. Produced water, BTEX, oil, membrane fouling, sustainable flux

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Abbreviations and Notations

CFV	Cross flow velocity	
CST	Capillarity suction time	(s)
CSTn	Normalised capillarity suction time	($s.L.g^{-1}$)
DO	Dissolved oxygen	($mg.L^{-1}$)
DOC	Dissolved organic carbon	($mgC.L^{-1}$)
EPS	Extracellular polymer substances	($mg.L^{-1}/mg.gSS^{-1}$)
EPSc	Fraction of carbohydrate contained in extracted solution from sludge	($mg.L^{-1}/mg.gSS^{-1}$)
EPSp	Fraction of protein contained in extracted solution from sludge	($mg.L^{-1}/mg.gSS^{-1}$)
FP	Flat plate	
H	Hydrophobicity	(%)
HF	Hollow fibre	
HRT	Hydraulic retention time	(hours)
MBR	Membrane bioreactor	
MF	Microfiltration	
MLSS	Mixed liquor suspended solids	($g.L^{-1}$)
MLVSS	Mixed liquor volatile suspended solids	($g.L^{-1}$)
OLR	Organic loading rate	($kg.m^{-3}.d^{-1}$)
PSD	Paricle size distribution	
SMP	Soluble microbial products	($mg.L^{-1}$)
SMPc	Fraction of carbohydrate contained in the sludge Solution	($mg.L^{-1}$)

SMPp	Fraction of protein contained in the sludge solution	($mg.L^{-1}$)
SRT	Solids/sludge retention time	(d)
SS	Sidestream	
TMP	Transmembrane pressure	(mbar)
TOC	Total organic carbon	($mgC.L^{-1}$)
UF	Ultrafiltration	
ΔP_0	Initial TMP increase	(mbar)
dP/dt	Rate of TMP increase	($mbar.min^{-1}$)
dK/dt	Rate of permeability decline	($mbar.min^{-1}$)
J	Flux	($L.m^{-2}.h^{-1}$)
J_{trans}	Transitional flux	($L.m^{-2}.h^{-1}$)
K	Permeability	($L.m^{-2}.h^{-1}.bar^{-1}$)
P_{ave}	Average TMP	(mbar)
T_{filt}	Period of stable membrane operation	(days)

1 Introduction

1.1 Background

Wastewater containing oil encompasses a variety of matrices from metal cutting fluids to ship ballast water (Table 1.1). Current technologies employed in dealing with oily waste include physical, chemical and biological processes or a combination of these.

Table 1.1 Sources of oil wastewater in industry (Modified from Cheryan *et al.* 1998).

Source of oily wastes	***Industries***	***Nature***
Alkaline/acidic cleaners	Metal fabrication, iron and steel, metal finishing, industrial laundries	Normally highly emulsified due to surfactants; Difficult to treat; Mixture of various types of oils from spills of hydraulic and cutting fluids
Floor washes	All industries	Mixture of various types of oils from spills of hydraulic and cutting fluids, oil mists from spraying/coating; Can be present in both free and emulsified forms stabilised by dirt, debris and solvents
Machine coolants	Metals and metal manufacturing, machining	Normally emulsified and difficult to treat
Vegetable and animal fats splitting, refining, rendering	Edible oil, detergent manufacture, rendering, fish processing, textile (wool scouring), leather (hide processing)	Both free and emulsified oils present; difficulty of treatment varies
Petroleum oils from tanker washes, spills, drilling, various production processing steps	Petroleum refining, oil drilling, processing	Both free and emulsified oils; difficulty of treatment varies

Oil in wastewater may be present in several forms; free, dispersed and emulsified and the distinction is primarily due to size. Free oil typically has droplet sizes greater than 150 μm in size, dispersed oil has a size range of 20-150 μm, and emulsified oil has droplets less than 20 μm in size (Cheryan *et al.* 1998). Different treatment strategies are required to reduce or remove oil in different forms.

Oil and gas reservoirs have a natural water layer (called formation water) that, being denser, lies under the hydrocarbons. Oil reservoirs frequently contain large volumes of water, while gas reservoirs tend to produce only small quantities (UKOAA, 1998). To achieve maximum oil recovery, additional water is usually injected into the reservoirs to help force the oil to the surface. Both formation and injected water are eventually co-produced along with the hydrocarbons and, as an oil or gas field becomes depleted, the amount of produced water increases as the reservoir fills with injected seawater.

At the surface, produced water is separated from the hydrocarbons, treated to remove as much oil as possible, and then either discharged to sea or injected back into the wells. In addition, some installations are able to inject produced water into other suitable geological formations. The nature and quantity of produced water generated varies from each application depending on the nature of formation and recovery (Tellez *et al.* 1995). After treatment, produced water still contains traces of oil and discharge into the sea is strictly controlled by legislation.

1.2 Motivation for work

The work described in this thesis focussed on the efficacy of using MBRs to treat produced water.

The quantities of water discharged from offshore installations over the last four years along with the amounts of oil discharged with the produced water are shown in Table 1.2. The progressive increase in produced water results from a combination of an increasing number of installations and increasingly aging fields. Improvements in

technology have resulted in the gradual decrease of the concentration of oil associated compounds in water.

Table 1.2 Oil discharge from offshore oil installations (Modified UKOOA, 1999 & 2000)

Year	*Number of installations*	*Water quantity (millions of tonnes)*	*Oil levels (ppm)*	*Oil quantity (tonnes)*
1996	59	210	27	5,706
1997	64	234	25	5,764
1998	67	253	22.45	5,690
1999	67	260	21.67	5,643

The small quantities of water that arise from gas reservoirs may contain traces of natural gas liquids, called condensate. Table 1.3 shows discharges from offshore gas platforms. A considerably lower volume of wastewater is produced from gas installations.

Table 1.3 Condensate discharge from offshore gas installations (Modified UKOOA, 1999 & 2000)

Year	*Number of Installations*	*Water quantity (tonnes)*	*Average condensate content (ppm)*	*Total condensate discharged (tonnes)*
1996	3	617,939	20	12
1997	24	328,394	65	21
1998	32	450,769	66	30
1999	33	~ 1,000,000	32	32

The UK offshore industry has voluntarily accepted a target of 30 $mg.L^{-1}$ on a company annual average basis from January 1999 and over a number of years, legislation is likely to become tighter, restricting the discharges to perhaps only 15 $mg.L^{-1}$. In the long term,

there is likely to be a requirement for the removal of the dissolved component, something that cannot be achieved by conventional intensive physical separation technologies such as hydrocyclones.

Organic components present in produced water may be divided into four main groups:

1. Aliphatic compounds (lighter compounds $<C_5$ are most soluble)
2. Aromatic components (inc. benzene toluene, ethyl-benzene, xylene [BTEX] and polycyclic aromatic hydrocarbons [PAHs])
3. Polar compounds – primary compound is phenol
4. Fatty acid components – dominant species acetic acid

The aliphatic and aromatic collectively represent the hydrocarbon content with polar compounds and fatty acid components usually termed 'other organics' (Hansen and Davies, 1994).

1.3 Scope of study

The main aim of this study was to assess the viability of MBR technology for the treatment of dissolved aromatic and aliphatic hydrocarbons in gas field produced water. Optimisation of operating parameters and conditions for both biological and membrane performance is required to maximise treatment performance of the system whilst minimising membrane fouling, impacting on environmental impact and operating costs respectively. The study performed involved pilot scale study of produced water treatment employing a range of analytical techniques, biomass characterisation and membrane fouling tests.

1.4 Thesis plan and publications

A brief review of the state of the art of MBR treatment has been conducted to characterise the current market and variations of technology used (Chapter 2.2). Pertinent literature for oil derived wastewater treatment has been reviewed (Chapter 2.3) to help identify the most appropriate operating conditions for biological treatment.

The membrane performance and fouling propensity of the produced water fed to the bioreactor was determined experimentally and compared with that of a municipal fed bioreactor, with the properties of the biomass from different sources also being compared. The findings presented as two papers at the Fifth International Membrane Science and Technology Conference, 10-14th November 2003, Sydney, Australia: Brookes, A., Jefferson, B., Le-Clech, P., Judd, S. J. (2003). Fouling of membrane bioreactors during treatment of produced water. In: *Proc. 5th International Membrane Science & Technology Conference.* 10-14th November 2003, Sydney, Australia. And: Brookes, A., Judd, S. J., Reid, E., Germain, E., Smith, S., Alvarez, H., Le-Clech, P., Stephenson, T., Turra, E., Jefferson, B., (2003). Characterisation and impact of biomass foulants in membrane bioreactors. *Proc. 5th International Membrane Science & Technology Conference.* 10-14th November 2003, Sydney, Australia.

Further results comparing short term fouling trials to long term trends were presented at IWA conference on Scaling and Corrosion in Water and Wastewater Systems. 25-26th March 2003, Cranfield, UK (Brookes, A., Jefferson, B., Le-Clech, P., Judd, S. J. (2003). Methods for understanding organic fouling in MBRs In: *Proc. 1st IWA Conference on Scaling and Corrosion in Water and Wastewater Systems.* 25-26th March 2003, Cranfield, UK) and later published: B. Jefferson, A. Brookes, P. Le-Clech, and Judd, S.

J. (2004). Methods for understanding organic fouling in MBRs *Water Science and Technology.* **49** (2)

A characteristic pattern appeared to be common for long term membrane fouling trials during sub-critical flux operation. A review of literature describing this phenomenon has been carried out (Chapter 2.3) and subsequently published (Pollice, A., Brookes, A., Jefferson, B. and Judd, S. Sub-critical flux fouling in membrane bioreactors - a review of recent literature. *Desalination*, **174**), and results from all trials were collated and presented at the IWA World Water Congress and Exhibition, 19-24th September 2004 Marrakech, Morocco: Judd, S. (2004). Fouling in Submerged MBRs. In: *Proceedings of the IWA World Water Congress and Exhibition.* Marrakech, Morocco, 19-24th September 2004. Trends in sub-critical fouling determined experimentally in the current study have been compared with those found in the literature and an attempt made to fit data to an existing model describing sub-critical fouling (Brookes, A., Jefferson, B., Guglielmi, G., Judd, S. J. Sub-critical flux operation in membrane bioreactors. *Water Research* [submitted]). All the published results and further treatment results are reported and discussed in the appropriate results chapters (Chapter 5, 6 and 7).

Finally any conclusions made from the research were discussed and suggestions for further work made in Chapter 7.

2 Literature Review

2.1 Introduction

The benefits offered by membrane bioreactors (MBRs) over conventional technologies for wastewater treatment duties are well documented (Stephenson *et al.* 2000). These include enhanced clarification and disinfection, obviating of bulking problems, smaller footprint and reduced sludge volumes. However, their performance is limited by membrane fouling, and it is the efficacy of the strategies adopted to ameliorate this problem that generally dictate the viability of the process for a given duty. This is especially the case for higher strength and potentially more highly fouling matrices such as produced water, which present a high loading. A brief comparison of available systems is detailed in Section 2.2 with respect to design and operating conditions together with their market share.

A review of produced water treatment by MBRs is made in Section 2.3 with respect to available information on the treatment of representative feedwaters. The latter may not necessarily be limited to produced water, since there are a limited number of full-scale examples of these globally. Industrial effluent treatment by MBRs for feedwaters having similar characteristics to produced water are included so as to allow a comparison of performance of process types and operating conditions.

Finally all pertinent studies are appraised in Section 2.4 so as to provide an insight into membrane fouling and long term operation in the membrane bioreactor process, mainly with reference to municipal and industrial wastewaters. Experimental evidence of fouling under sub-critical conditions are scattered in a number of research publications,

which this part of the review aims to collate. The main operational parameters for the identification of pseudo-constant flux operation are considered, along with levels of key biomass components of soluble microbial products (SMP) and extracted extracellular polymeric substances (EPS).

2.2 Membrane bioreactor systems for wastewater treatment – state of the art

Much debate exists as to the relative merits offered by the various commercially available systems. However the central issues are the membrane cost, the system robustness and, perhaps most important of all, the control of fouling and the related cleaning efficiency. Membrane production costs continue to decrease, albeit only slightly of late, and system robustness seems now beyond question given the length of time some of the early installations have been running without substantial operational problems. Since fouling impacts directly upon pumping and/or aeration requirements, its control or the amelioration of problems it imposes is critical in determining process cost.

2.2.1 Commercially available membranes and modules

Products are either available as membrane elements/modules, or complete systems hence, some companies are licensees; e.g. the licensee for Kubota products are *Copa*, in the UK and *Enviroquip* in the US. Zenon, on the other hand, are a global company and have licensing agreements on the basis of application, rather than region. So, for example, Filtration Engineering in the US holds the license for dairy effluent treatment.

Licensees provide systems based on membrane technology and design "complete solution" whilst other companies provide patented processes. Thus Wehrle Werk provides the *Biomembrat* process based usually on Norit multitube membrane modules. Some of the currently available membrane systems are listed in Table 2.1.

Table 2.1 Submerged and sidestream proprietary membranes and systems

Submerged	Sidestream
• Huber	• Degremont
• Kubota	• Grontmij
• Millenniumpore	• Orelis
• Mitsubushi Rayon	• Norit/Stork
• Toray	• Wehrle Werk
• USF/Memcor	• Weir Envif (ADUF)
• Zenon	

All submerged systems use polymeric membranes. The base polymers are modified to make them hydrophilic. Only two side-stream systems employ ceramic membranes: Orelis and Degremont which are used for niche applications. Table 2.2 displays various membrane suppliers and properties of their products. Whilst some of the other membrane and process suppliers are increasing their market share, Zenon and Kubota remain the two most significant providers in the MBR marketplace (Cornel and Crause, 2003). Current installed capacity for Zenon is around 1.5 Mm^3/day, whilst there are currently around 1500 Kubota plants in the world representing a high proportion of the approximately 2200 total MBR installations worldwide (Yang *et al.* 2005).

Table 2.2 Membrane supplier and properties

Supplier	Material	Pore size or MWCO, μm or kDa	Geometry (orientation)	Membrane dimensions or area	Area/module volume, $m^2 m^{-3}$
Degremont	ceramic	-	tube	-	-
Kubota	chlorinated polythene	0.1 μm	flat plate	0.8 m^2/panel	46
Memcor	hydrophilic PVDF	0.2 μm	HF	0.8 mm dia.	-
Millennium-pore	polyethyl sulphone	0.1 μm	tube (*wide-bore HF*)	5-10 mm dia	73
Mitsibushi Rayon	hydrophilic polyethylene	0.1-0.4 μm	HF	64 m^2 (for *UMF 6424*)	79
Orelis	polysulphone Al_2O_3 - TiO_2	3-50 kDa 15-300 kDa	plate-&-frame tube	1.5 m^2/plate 2.5-6 mm dia	28 270
Wehrle Werk	polymer	"UF and MF"	tube (vertical)	8-12 mm dia.	280
X-flow (Norit)	Hydrophilic PVDF	0.03 μm	tube	4-8mm dia	-
Zenon	hydrophilic PVDF	0.04 μm	HF	1.9mm 2x0.7x0.2m (for *ZW-500A*)	146

2.3 Treatment of Oil in Wastewater

The selection of the most appropriate technology or combination of technologies for oil containing wastewater treatment is dependent on a number of factors including: wastewater flowrate, composition and loading patterns, site characteristics including operation and treatment capabilities, and treatment objectives. Factors contributing to the toxicity of produced water are (API, 1995):

- very small particles,
- salinity,
- volatile compounds,

- extractable organics (acidic, basic, neutral),
- ammonia and hydrogen sulphide.

It stands to reason that treatment of produced water should be capable or removing some or all of the above.

2.3.1 Treatment options

Gravity separation is the most common primary treatment of oily wastewater to remove the free oil component, utilising the difference in the specific gravity of oil and water. If the resulting effluent is not of a sufficiently high standard to meet discharge consents, secondary treatment of the waste is used to lower the levels of dissolved, emulsified and dispersed oils.

Enhanced gravity separation technologies such as hydrocyclones and centrifuges have become more common over the last decade (OGP, 2002) enabling further improvements in effluent quality. However such systems are used to remove dispersed oil and usually cannot remove soluble oil or dissolved aromatic compounds.

Six water treatment technologies already proven onshore were evaluated and their cost has been estimated for offshore use in a report by the API (1995). Although each method presented technical problems, none of these were considered insuperable by the authors. The report made it clear that, by using combinations of different technologies, it is possible to reduce the pollutants in produced waster to almost undetectable levels. The accompanying table shows the technologies assessed by the API group (Table 2.3).

Table 2.3 Available technology to treat produced water (modified from API, 1995)

Technology	***Processes***	***Advantages***	***Disadvantages***	***Costs***
Carbon adsorption	Modular granular activated carbon systems.	Removes hydrocarbons and acid, base and neutral compounds; low energy requirements; higher throughput than other treatments (except biological); treats a broad range of contaminants; very efficient at removing high molecular weight (HMW) organics.	Fouling of carbon granules is a problem; produces waste stream of carbon and backwash; requires some pre-treatment of produced water stream.	"Middle range" of costs.
Air stripping	Packed tower with air bubbling through the produced water stream.	Can remove 95% of volatile compounds as well as benzene, toluene, naphthalene, phenanthrene, anthracene, pyrene and phenols; higher temperature improves removal of semi-volatiles; small size, low weight and low energy requirements; simple to operate; well-known technology.	Can be fouled by oil; risk of iron and calcium scales forming; generates an off-gas waste stream that may require treatment; requires some pre-treatment of produced water stream.	Low capital and operating costs; overall treatment cost US$0.02 to $0.10/1,000 gallons
Filtration	Membranes.	Effective removal of particles and dispersed and emulsified oil; small size, low weight and low energy requirements; high throughput rates.	Does not remove volatiles or dissolved compounds. Does not affect salinity; oil, sulfides or bacteria may foul membrane, which requires daily cleaning; waste streams may contain radioactive material; requires some pre-treatment of produced water stream.	Low capital and operating costs (similar to air stripping).
Ultra-violet light	Irradiation by UV lamps	Destroys dissolved organics and both volatile and non-volatile organic compounds, including organic biocides; does not generate additional waste stream; handles upset or high-loading conditions.	Will not treat ammonia, dispersed oil droplets, heavy metals or salinity; relatively high energy requirements; UV lamps may become fouled; requires some pre-treatment of produced water stream.	Similar capital costs to chem. oxidation with ozone but operating costs lower because no waste stream.
Chemical oxidation	Ozone and/or hydrogen peroxide oxidation	Removes H_2S and particulates; treats hydrocarbons, acid, base and neutral organics, volatiles and non-volatiles; low energy requirements if peroxide system used; straightforward to operate.	High energy inputs for ozone system; oil may foul catalyst; may produce sludge and toxic residues; requires some pre-treatment of produced water stream.	"Middle range" of costs.
Biological treatment	Aerobic system with fixed film biotower or suspended growth (e.g. deep shaft)	Treats biodegradable hydrocarbons and organic compounds, H_2S, some metals and, in some conditions, ammonia; "fairly low" energy requirements; handles variable loadings, if acclimated.	Large, heavy plant required for long residence times; build-up of oil and/or iron may hinder biological activity; may produce gas and sludge requiring treatment; requires some pre-treatment of produced water stream.	No costs estimated.

Currently most offshore water treatment facilities are able to achieve oil levels of <40 $mg.L^{-1}$ in the treated water using hydrocyclones and a polishing stage such as a degasser vessel. Such systems may be able to remove oil to 15-30 $mg.L^{-1}$ if optimised. In order to further remove dispersed oil, mechanical coalescing and chemical coagulation and flocculation systems have been employed to modify the oil droplet upstream of the primary treatment (OGP, 2002).

Conventional hydro-cyclones enable large volumes of water to be processed at short residence times, providing a significant reduction in the size and weight of the treatment system. This is critical, since key factors for offshore operations are weight and space limitations. Thus supplementary processes must be similarly low in footprint and weight to be commercially and practically viable. Thus, although biotreatment of produced waters represents an alternative to physicochemical conventional processes, due to the size of these installations they have to date generally been confined to land based treatment at refineries or where produced water is shipped ashore for treatment after storage on a platform (API, 1995).

The high salt concentration often associated with this type of waste poses a difficulty when using biological processes (Campos *et al.* 2002). In the conventional activated sludge process, a high salinity usually results in sludge washout and hence an increased concentration of suspended matter in the clarifier (Bakx *et al.* 2000). Dalmacija *et al.* (1996) investigated the enhancement of the activated sludge process by the addition of powdered activated carbon (PAC) to the bioreactor in treating oil-field brine. The addition of PAC to the bioreactor and the dilution of the wastewater with surface water resulted in an increase in performance and sludge quality.

Membrane processing of oily wastewater has become a commercial success with more than 3000 polymeric ultrafiltration/microfiltration installations and over 75 inorganic/ceramic units worldwide (Cheryan, 1998). Campos *et al.* (2002) examined the use of a combined membrane and biological system to treat offshore oilfield wastewater. The membrane stage resulted in removal efficiencies of COD, TOC, oils and grease, and phenols of 35%, 25%, 92% and 35% respectively. Permeate from the microfiltration treatment was fed to an air-lift reactor.

The use of membranes in an oilfield type application specifically, however, is unproven (OGP, 2002). Depending on the type of membrane used, it would be possible to remove the majority of aromatics (BTEX, NPD and PAH) and also dispersed oil. Inevitably membrane fouling is a limitation. In addition the process is only suitable to be used as an additional water treatment stage for upgrading plants as a polishing stage.

Zaloum *et al.* (1994) conducted toxicity tests on an oily waste from a metal rolling mill. The treatment consisted of a pre-filter, followed by an API separator and finally through a process tank to an ultrafiltration unit. Toxicity tests using the microtox test revealed a 130 fold reduction in toxicity due to the ultrafiltration step. Trials using a membrane bioreactor showed the waste underwent a further 10 fold reduction in toxicity due to this step (Zaloum *et al.* 1994).

In summary, it can be stated that conventional processes may be constrained by one or more of the following:

- intolerance to changing feedwater conditions (especially biological processes and chemical coagulation)
- fouling (in particular physical membrane separation processes or clogging)
- high cost and/or high risk (especially advanced oxidation processes such as UV/ozonation or supercritical water oxidation)
- toxicity
- unreliable product water quality, and
- generation of a problematic waste stream

The latter two limitations apply to most conventional non-barrier-processes. Membrane bioreactors are less constrained by these factors than conventional processes. Moreover, currently available conventional biological processes are mostly incapable of complete removal of hydrocarbons (Scholz and Fuchs, 2000): it is not known whether an enhanced biological process such as an MBR can offer improved hydrocarbon removal.

2.3.2 Membrane bioreactors for oil wastewater treatment

An indication of the comparative performance of a membrane bioreactor and the activated sludge process specifically for the treatment of oily water is shown in Table 2.4. In addition to the full retention of biomass achieved by these systems, the use of a membrane allows a higher concentration to be maintained, up to around 30g MLSS L^{-1} resulting in the reduction in the size of the bioreactor compared to a conventional process.

Table 2.4 Comparison of operating parameters and performance between activated sludge and the membrane bioreactor systems treating refinery waste (Scholz and Fuchs, 2000)

	Membrane bioreactor	***Conventional activated sludge system***
SLR (kg COD kg^{-1} d^{-1})	0.6-0.8	0.15-0.30
VLR (kg COD m^{-3} d^{-1})	8.6-12.9	0.75-1
Sludge concentration (kg m^{-3})	15-25	3-5
Ratio COD/N/P	100/0.75/0.09	100/1.7/0.3
Excessive sludge (kg kg^{-1} COD)	0.09-0.11	0.3-0.5
pH	7-7.8	7.3-7.8
COD removal efficiency (%)	97	82
Oil (ppm)	0.036-0.35	0.75-2
Oil removal efficiency (%)	99.9	82

A number of limitations of the process also exist including both technical and economic. Fouling is the principal limitation of the process that restricts the widespread application of MBRs, this being the deposition of a fouling layer which limits the permeate flux (Chang *et al.* 2002). Fouling is often described as being reversible (removable by physical washing), or irreversible (requiring chemical cleaning) and takes place on the surface of the membrane or in the membrane pores (Chang *et al.* 2002). The nature and severity of the fouling is controlled by three principal factors: biomass characteristics, membrane characteristics and operating conditions (Section 2.4).

A second limitation is that of aeration efficiency at high biomass concentrations. At increasing biomass concentrations the oxygen transfer efficiency decreases, elevating the operating costs.

Membrane capital costs have fallen rapidly during the last decade and are now substantially cheaper. Combined with operational experience suggesting a lifespan of up to 10 years, cost is less prohibitive that it was 5-6 years ago but remains higher than conventional biological processing.

2.3.2.1 Case Studies

One of the main applications of MBR systems in treating oily water has been to automotive metal working wastewater. Several full-scale installations have been implemented in the US following large pilot studies at these sites (Mishra *et al.* 1997). Treatment of oil wastewater specifically produced from gas condensate platforms, on the other hand, are not frequently reported in the literature. The suitability of the process to treat this waste may be considered with respect to the similarity of these two wastewaters, both characterised by high COD, aromatics, amines and dissolved oil often measured as fats, oils, and greases (FOG).

Data for both biological and membrane performance from several studies reported in the literature are presented in Table 2.5 and Table 2.6 respectively.

2.3.3 Performance

Overall the literature indicates that various sources of oil containing wastewater are readily treated in terms of organic load (BOD, COD, TOC). COD removal efficiencies between 90 and 97% have been obtained, with associated organic loading rates between 0.36 and 9.82 kg COD m-3 d-1 (Table 1.6). These are substantially higher than in municipal applications that are typically within 0.3 and 2 kg COD m^{-3} d^{-1} (Stephenson

et al. 2000). This is the result of the higher strength of the waste, with typical feed concentration being 29,400 mg l-1 COD (Zaloum *et al.* 1994).

Oil removals of up to 99.9 % are reported (Scholz and Fuchs, 2000) with effluent concentrations typically between 0.13 and 14 mg l^{-1}. Significant degradation has been shown in all cases, even during shock loading. After a microbial acclimation period oil biodegradation rates of up to 0.82 g hydrocarbons per g MLVSS per day were found (Scholz and Fuchs, 2000).

Table 2.5 Biological performance of MBRs treating oil wastewater

Wastewater	Type	V (m^3)	HRT (h)	SRT (d)	Sludge load (kg COD kg MLSS d^{-1})	Organic load (kg COD m^3 d)	BOD[a], COD[b] (mg. L^{-1})		MLSS (kg m^{-3})	Sludge yield (kg MLSS kg COD^{-1} d^{-1})	DO (mg.L^{-1})	Reference
							Influent	Permeate				
Oil, Metal working fluid	T/SS	1.9	144-240	50-75	1.36-2.72	2.45-4.91	5105[a]	<20[a]	1.8	1.3-2%		Zaloum *et al.* 1994
							29430[b]	<2943[b]				
Oil, Car Plant	T/SS	1.325	69.6	65	0.13	0.39[a]	1147[a]	15[a]	28.9	0.126	1.3-6.7	Sutton *et al.* 1994
						3.84[b]	11133[b]	1043[b]				
	T/SS	3.78	44.8	50	0.2	0.61 2.97	1145 5543	7 540	14.95	0.112	0.3-7.5	
	T/SS	3.78	47.2	74	0.036	0.07 0.71	134 1406	6 249	19.6		0.3-7.5	
Oil, Car Plant	T/SS	1.325	72	36	0.21	0.57[a]	1711[a]	17[a]	26.2	0.141	1.3-6.7	Knoblock *et al.* 1994
						5.54[b]	16609[b]	1190[b]				
	T/SS	3.78	89.7	50	0.29	0.25[a] 1.16[b]	919 4345	3 183	4.03	0.074	0.3-7.5	
	T/SS	3.78	44.8	50	0.57	0.64[a]	1206	34	6.5	0.039		
Oil	T/SS	287	54	31	0.012	6.3[b]	14180[b]	799[b]	28.7	0.16		Mishra *et al.* 1996
Oil	HF/SS	-	88	300	0.18	0.36[b]	1333[b]	40.8[b]	2	0.348		Seo *et al.* 1997
Oil	T/SS	0.011	13.3	-	0.6-0.8	1.64-9.82	4384[b]	188[b]	30	0.09-0.11	2-3	Scolz and Fuchs, 2000
Petroleum wash-water	HF/S	0.19	12-48	-	-	-	774[a] 1294[b]	29[a] 173[b]	-	-	>2	Olmstead *et al.* 2004

Table 2.6 Membrane performance of MBRs treating oil wastewater

Wastewater	Type	Pore Size (μm)	x-flow velocity ($m\ s^{-2}$)	Pressure (bar)	Initial flux ($l\ m^{-2}\ h^{-1}$)	Final/mean flux ($l\ m^{-2}\ h^{-1}$)	Area (m^2)	Reference
Oily, Metal	T/SS	0.03	-	2.44	70	37	-	Zaloum *et al.* 1994
Oily, Car (GM)	T/SS	0.03	-	-	90	63.6	195	Sutton *et al.* 1994
					90	63.6	195	
Oily, Car (GM)	T/SS	0.03	-	-	-	-	-	Knoblock *et al.* 1994
Oily	HF/SS	0.08	-	1 kg cm^{-2}	10.2	-	0.086	Seo *et al.* 1997
Oily	T/SS	0.03	2.2	1.5	90	60	0.23	Scholz and Fuchs, 2000

2.3.4 Operating parameters and system variables

A long hydraulic retention time (HRT) is required for treatment of this type of wastewater in any biological system. As shown in Table 2.6 these range from 13 to 240 hours, a typical value being around 80 hours. Reported sludge ages range from 30 to 300 days. Results from a trial conducted by Sutton *et al.* (1994) reveal there to be no benefits in operating the system at increased HRTs. Hydraulic retention time was varied between 1.87 and 3.74 days and sludge age between 50 and 100 days, with a similar result of over 90% COD removal in most cases.

In an experiment to examine the response of the system to organic overloading Zaloum *et al.* (1994) decreased the HRT from 10 to 6 days, nearly doubling the organic load. The reactor coped well with the change both during the transition and during the period at equilibrium, with BOD removal efficiency remaining at 99% and FOG removal only falling slightly from 99 to 98%. In contrast, Seo *et al.* (1997) showed that a longer HRT and sludge age from 5 to 30 days resulted in an increase in COD removal from 89 to 97%. Zaloum *et al.* (1994) also noted that the biomass required two months to acclimate to the oily waste since the bioreactor was first seeded with activated sludge from a municipal plant.

When operating at long SRTs the high selectivity of membrane filtration results in the retention of high-molecular-weight soluble compounds as well as suspended material. When combined with a biological step the result may be a build up of non-reactive compounds (inerts) in the reactor. The biological activity of the reactor can be inhibited by the build up of these recalcitrant compounds (Knoblock *et al.* 1994).

Reported biomass concentrations range between 2,000 and 29,000 mg l^{-1} depending on the feed strength and operating conditions of the system (Table 2.6). Zaloum *et al.* (1994) found that as the BOD of the influent increased from 3,000 mg l^{-1} to a peak of around 25,000, the concentration of the mixed liquor increased very quickly in response to this change from 6,000 to almost 24,000 mg l^{-1}. MBR systems are capable of low or zero sludge production (i.e. infinite SRT). As discussed earlier the penalty of operating at high biomass concentrations, which inevitably result from long SRTs, is the loss in aeration efficiency.

Sludge production rates reported in the literature vary between 0.04 to 0.45 kg MLSS kg COD^{-1} d^{-1} (Table 2.6). Scholz and Fuchs (2000) reported a difference in sludge production when treating fuel oil or lubricating oil. During fuel oil stages of the experiment, the excess sludge production was 0.09 – 0.11 kg sludge kg COD^{-1}. With lubricant oil higher sludge yields occurred, between 0.26 and 0.51 kg sludge per kg COD^{-1}. The yield will also be composition dependent. Wastes with a higher extractable-hydrocarbon fats oils and greases (FOG) to total FOG ratio, such as those with a high fraction of petroleum based metal working fluids, have been found to have higher net yield coefficients (Sutton *et al.* 1994; Stephenson *et al.* 2000). This implies that the overall composition of the compounds making up the total COD have a significant bearing on the net yield coefficient.

Nutrient addition is often required during treatment of industrial wastewater, including phosphorus, nitrogen and trace elements. Sutton *et al.* (1994) found there to be a nitrogen deficiency at two out of three sites in the study, resulting in incomplete BOD removal. The other site in the study received nutrient addition in the form of

diammonium phosphate to provide sources of both nitrogen and phosphorus and appeared to perform better at the same operating conditions.

Scholz and Fuchs (2000) found that a lower concentration of nutrients was required during MBR treatment than that required in activated sludge process for oil degradation. The requirement in conventional systems is around 120 g nitrogen and 20 g phosphorus for 1 kg of oil biodegraded. In the MBR system in comparison only required 6.7 g nitrogen and 0.8 g phosphorus as the nutrient supply for 1 kg oil degraded. The resulting C:N:P ratios are 100/1.7/0.3 for a conventional system and 100/0.75/0.09 for MBR (Scholz and Fuchs, 2000).

2.3.4.1 Process Configuration

All of the applications shown in Table 2.5 are of a similar configuration; side stream with mainly tubular membranes having a pore size between 0.03 and 0.08 μm, i.e. coarse UF/fine MF. Only one recently reported system (Olmstead *et al.* 2004) is of immersed configuration, highlighting the dominance of sidestream systems for industrial wastewater treatment.

The possibility of stripping of volatile compounds was recognised by Scholz and Fuchs (2000). Off-gas containing hydrocarbons were cleaned by an activated carbon filter and monitored regularly, although no further results were detailed. A submerged system with higher aeration may promote greater stripping during operation and becomes an important consideration in their operation.

2.3.4.2 Flux and fouling

Very little data has been found regarding applied fluxes in systems treating oil wastewater. Flux rates tend to be conservative due to the nature of the feed, with submerged systems operating at fluxes of ~12 $L.m^{-2}.h^{-1}$ and sidestream plants at fluxes up to 60 $L.m^{-2}.h^{-1}$. The exact flux at which a system operates is dependent upon a number of complex inter-related parameters including hydraulic parameters (trans-membrane pressure (TMP) and cross-flow velocity), membrane pore size and biomass characteristics. Most of the sidestream systems operate at a relatively high TMP of 1.5-2.4 bar and cross flow velocities of 2.2 ms^{-2}. Seo *et al.* (1997) reported a flux reduction from 11 $l.m^{-2}.h^{-1}$ to 3 $l.m^{-2}.h^{-1}$ in 7 days operation. Despite periodic manual cleaning restoring the flux to about 80% of the initial value, a gradual decline was observed to a final flux of 2 $l.m^{-2}.h^{-1}$ after 20 days operation.

2.4 Fouling and hydrodynamic control

The control of hydrodynamics, and so fouling, in a submerged system is through membrane aeration, whereas for the sidestream configuration it is generally through pumping so as to increase the crossflow velocity. Since hydrodynamic control by coarse bubble aeration is limited, submerged MBRs necessarily operate at lower fluxes than sidestream systems. This then means that the permeability is much higher since fouling follows a roughly exponential trend with flux (Le Clech *et al.* 2003a). Hence, debates concerning the relative merits offered by the various commercial systems invariably revolve around (a) the energy demanded to control fouling, and (b) the cleaning efficiency attainable to maintain a sustainable flux.

2.4.1 Sustainable flux fouling

It has been generally understood from membrane filtration studies that there exists a critical flux (J_c) below which a decline in membrane permeability with time does not occur and above which fouling is observed (Field *et al.* 1995). J_c is most conveniently determined by the classical flux-step method in which the flux is incrementally increased and the impact recorded on fouling rate, manifested as an increase in pressure or decrease in permeability with time. The resultant data is then used to generate plots of dP/dt and/or K against flux step (Figure 2.1), which then generally suggest no fouling below a certain flux. However, it has recently become evident that fouling arises below the critical flux in some studies of membrane bioreactors (MBRs). Close examination of the flux-step data used to generate Figure 2.1 reveals small positive pressure gradients even at very low fluxes, indicating slight but none-the-less significant sub-critical fouling to take place.

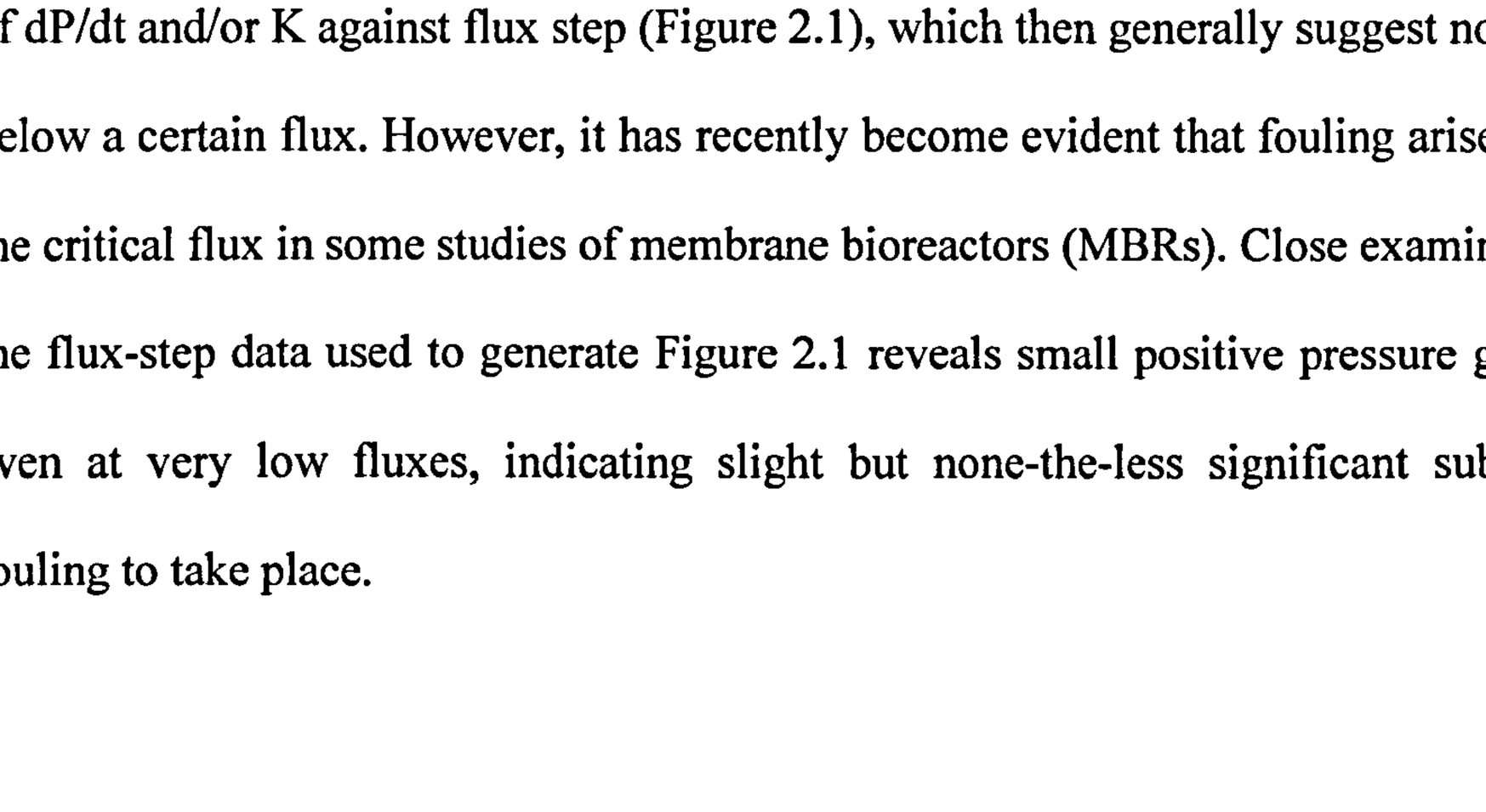

Figure 2.1 Mean permeability and fouling rate vs. flux as determined in short-term flux-step trials for a sewage feed (data from Le Clech *et al.* 2003a).

Further evidence of low-level fouling at low fluxes is provided from long-term studies, where a characteristic pattern of behaviour over time appears to evolve. An initial rapid but small increase in the transmembrane pressure (TMP) takes place followed by a very small TMP rise over an extended time period. In some studies (Ognier *et al.* 2001, Cho and Fane 2002, Ognier *et al.* 2002, Le Clech *et al.* 2003b) a noticeable change in the rate of TMP increase arises after some critical time period. It has subsequently been suggested that the critical flux actually represents the boundary between fouling by the dissolved/colloidal components and suspended matter of the biomass (Cho and Fane 2002).

2.4.2 Operational indicators of sub-critical fouling.

Two parameters may be considered for a comparative evaluation of sustainability of MBR operation under sub-critical conditions: the time over which the rate of fouling is low and stable (t_{filt}), and either the rate of TMP increase – sometimes referred to as the fouling rate - or the permeability decline over the stable period of operation (dP/dt or dK/dt respectively). Values of these parameters calculated from literature data from sub-critical operation (Table 2.7) show broad differences in permeability behaviour between studies, presumably due to the commensurate variation in operating conditions, membrane and process configuration and plant size. These factors all impact upon the shear rate, which is crucial in determining flux and greatly affected by the aeration conditions (Chang *et al.* 2002, Judd and Jefferson 2003).

In Table 2.7, the only anaerobic system reported indicates pronounced permeability decay over time, possibly due to the composition of its colloidal and soluble fractions (Cho and Fane 2002). Among the aerobic plants challenged with real sewage, very low

permeability decline rates (dK/dt = 4-11 x 10^{-5} L/m^{-2} h^{-2} bar^{-1} based on constant flux operation) are obtained at large-pilot plants of several m^3 capacity operated with relaxation, i.e. with intermittent zero permeate flow to allow the aeration to scour the membrane surface.

Table 2.7 Sub-critical long-term data calculated from results of different investigations

System Size and scale	Membrane	Feed	MLSS g/L	Flux L/m² h	J_{crit}(1) L/m² h	T_{filt}(2) H	dP/dt(3) Bar/h	dK/dt(4) (L/m⁻² h⁻² bar⁻¹)	Reference
UASB *Bench*	SS FP MF (0.22 μm)	Syn Mun	0.3-0.5	30	50	360	0.12	3.6	Cho and Fane, 2002
Aerobic 20 L	SS Tub. MF (0.05 μm)	Syn Mun	1.8	10	-	550	0.03	0.33	Ognier *et al.* 2001
Aerobic 40 L	Subm. Tub. MF (0.2 μm)	Mun	3	9	18	240	3.7×10^{-5}	1.08	Le Clech *et al.* 2003b
Aerobic 20 L	Subm. HF MF (0.1 μm)	Syn Mun	17-27	12	-	-	2×10^{-4}	2.4×10^{-3}	Bouhabila *et al.* 2001
Aerobic 6.3 m^3	Subm. HF MF (0.1 μm)	Mun	12-19	12	19	-	9.3×10^{-6}	1.1×10^{-4}	Guglielmi, 2002
Aerobic 4.3 m^3	Subm. FP MF (0.4 μm)	Mun	10-18	9	20	-	1.2×10^{-5} - 9.2×10^{-6}	1.1×10^{-4} - 8.3×10^{-5}	Guglielmi, 2002
Aerobic 15 m^3	Subm. FP MF (0.4 μm)	Mun	8-12	17	-	-	2.4×10^{-6} - 5.9×10^{-6}	1.0×10^{-4} - 4.0×10^{-5}	Churchouse, 2002
Aerobic 50 L	SS. HF MF (0.22 μm)	Syn Mun	5-6	22	-	1220	1.1×10^{-4}	-	Wen *et al.* 2004
Aerobic 50 L	SS. HF MF (0.22 μm)	Syn Mun	5-6	25	-	-	2.4×10^{-3}	-	Wen *et al.* 2004
Aerobic 50 L	SS. HF MF (0.22 μm)	Syn Mun	5-6	30	-	-	7.2×10^{-3}	-	Wen *et al.* 2004

SS - sidestream; Subm – submerged
Syn Mun – synthetic municipal wastewater; Mun – municipal wastewater; Syn Ind – synthetic industrial wastewater
(1) Critical flux, as determined experimentally by flux-step method;
(2) Critical filtration time: duration of stable operation at indicated rate of pressure increase / permeability decrease;
(3) Rate of transmembrane pressure increase during sub-critical operation: $(p_2-p_1)/\Delta t$;

Coincidentally, the submerged flat plate (FP) and hollow fibre (HF) dP/dt values identified in this table are quite similar. Much greater dK/dt values are obtained either at smaller scale or with synthetic feedwaters. Moreover, it is predominantly, though not exclusively, with synthetic feedwaters that critical filtration times are discernable.

It is likely that the lower fouling rates (dP/dt) reflect the ameliorative effects of relaxation, but they could also be attributable to plant size. The impact of scale of operation is predominantly on the system hydrodynamics, specifically via the coarse bubble aeration. Longer vertically-mounted membranes in larger systems are subject to a wider range of transmembrane pressures along the length of the membrane than shorter membranes, and also higher rise velocities of the bubbles. Given the complexities of the shear transient induced by large air bubbles, so called 'slug flow', it is perhaps unsurprising that data from small pilot trials (10's of litres) data do not reflect those at larger scales (several m^3). On the other hand, periods of relatively rapid fouling (1.3×10^{-4} bar/hr; 0.0372 L/m^{-2} h^{-2} bar^{-1}) in large pilot-scale plants have been reported under sub-critical operating conditions even with regular backflushing (Rosenberger *et al.* 2002). There is no pattern of t_{crit} between different studies other than, once again, the large-scale studies tending to show no t_{filt} value thus indicating a lower fouling propensity, as also reflected in the dP/dt and dK/dt values.

Clearly, a number of factors determine sub-critical fouling rates, including membrane characteristics, feedwater and mixed liquor characteristics, and system operation (Chang *et al.* 2002). No cursory analysis can shed light on the relative importance of module design (i.e. membrane material, type and module configuration), process operation (including aeration rate, hydraulic and sludge residence times) and feedwater matrix. Having said this, candidate foulants within the biomass which may contribute to sub-critical fouling can be identified and quantified and their impact on operation assessed.

2.4.3 Mixed liquor characteristics.

Fouling of MBR membranes is normally attributed to the accumulation of organic macromolecules in the pores and/or at the membrane surface leading to progressively

increasing resistance to filtration (Defrance and Jaffrin, 1999). Adsorption is considered to be responsible for the initial rapid and mostly irreversible decline of membrane permeability which is independent of the hydrodynamic conditions and decreases the permeability over that obtained with pure water (Ognier *et al.* 2002). Interpretation of sub-critical fouling as being solely caused by adsorption on the internal walls of the pores leading to progressive pore closure has been recently integrated in a complete model (Cho *et al.* 1999; Cho and Fane, 2002). This considers gradual pore closure and surface deposition of organics as the cause of loss of local permeability, resulting in local fluxes exceeding the critical flux for the dominant foulant (biomass). This heterogeneous distribution of local fluxes under sub-critical conditions justifies the observation of slow pressure growth patterns followed by sudden increase when the critical flux is locally exceeded (Ognier *et al.* 2001; Cho and Fane, 2002).

Fouling in MBRs is mainly caused by organic macromoleules such as soluble microbial products (SMP), extracellular polymeric substances (EPS) and possibly other substances resulting from cell lysis or lost during cell synthesis (Chang *et al.* 2001). Although the precise definition of these groups of compounds is still open to debate, SMP may be identified as cellular components excreted through the cellular membrane due to metabolism under normal or stressed conditions (Barker and Stuckey, 1999). EPS has been defined as a complex mixture of polysaccharides, proteins, lipids and nucleic acids which form highly hydrated gel or fibrillar matrices in the range of a few nanometers, providing the dominant bridging mechanism between cells in activated sludge (Bura *et al.* 1998). These organic compounds are known to provide a substantial barrier to filtration, but quantitative information is very limited and different studies have reported significant differences in the contribution of the soluble fractions to fouling (Table 2.8).

Such differences may be partly attributed to the different methods used for fractionation, but it is also the case that different membranes, process configurations and feedwater matrices were used for the studies cited.

Table 2.8 Contributions to membrane fouling (Bouhabila *et al.* 2001).

Foulant fraction	Case 1	Case 2	Case 3
Soluble	52%	5%	26%
Colloids	25%	30%	50%
Suspended solids	23%	65%	24%

To assess the significance of data such as those presented in Table 2.8, a set of reference data for a single process configuration and/or feedwater matrix is required, along with an evaluation of possible interrelationships among the key parameters. The latter include standard operational parameters, such as hydraulic and sludge retention times (HRT and SRT respectively), filterability - most conveniently quantified as capillary suction time (CST), and concentration of candidate foulants including SMP and EPS.

The specific influence of the sludge age on EPS concentrations and composition is also shown in Figure 2.2, where the results of a series of bench-scale MBRs operated at different SRTs are reported (Judd and Jefferson, 2003). Here, the protein concentrations appear to be relatively stable and independent of the sludge age, whereas the carbohydrate concentrations tend to decrease for increasing SRTs, both in the sludge matrix and in the supernatant (SMP). This suggests that a higher fouling potential may be observed during MBR start-up when the biomass is building-up in the reactor, the MLSS concentration lower than at steady state and the SRT progressively increasing.

Under these conditions the two effects of proportionally higher levels of undegraded feed fractions and higher EPS concentrations from the growing biomass may combine to produce larger loading of potential foulants on the membrane. In other words, the stability of the sludge concentration at a given organic loading rate may be more relevant than the MLSS concentration in defining the mixed liquor fouling potential. This is partially confirmed by previous observations, where SRT and organic load were identified among the key parameters for minimizing SMP production in activated sludge (Barker and Stuckey, 1999). However, the same authors also reported proportionality between biomass concentration and SMP production due to increased release of organic material from cell lysis. This could increase fouling propensity for higher MLSS concentrations also under sub-critical conditions.

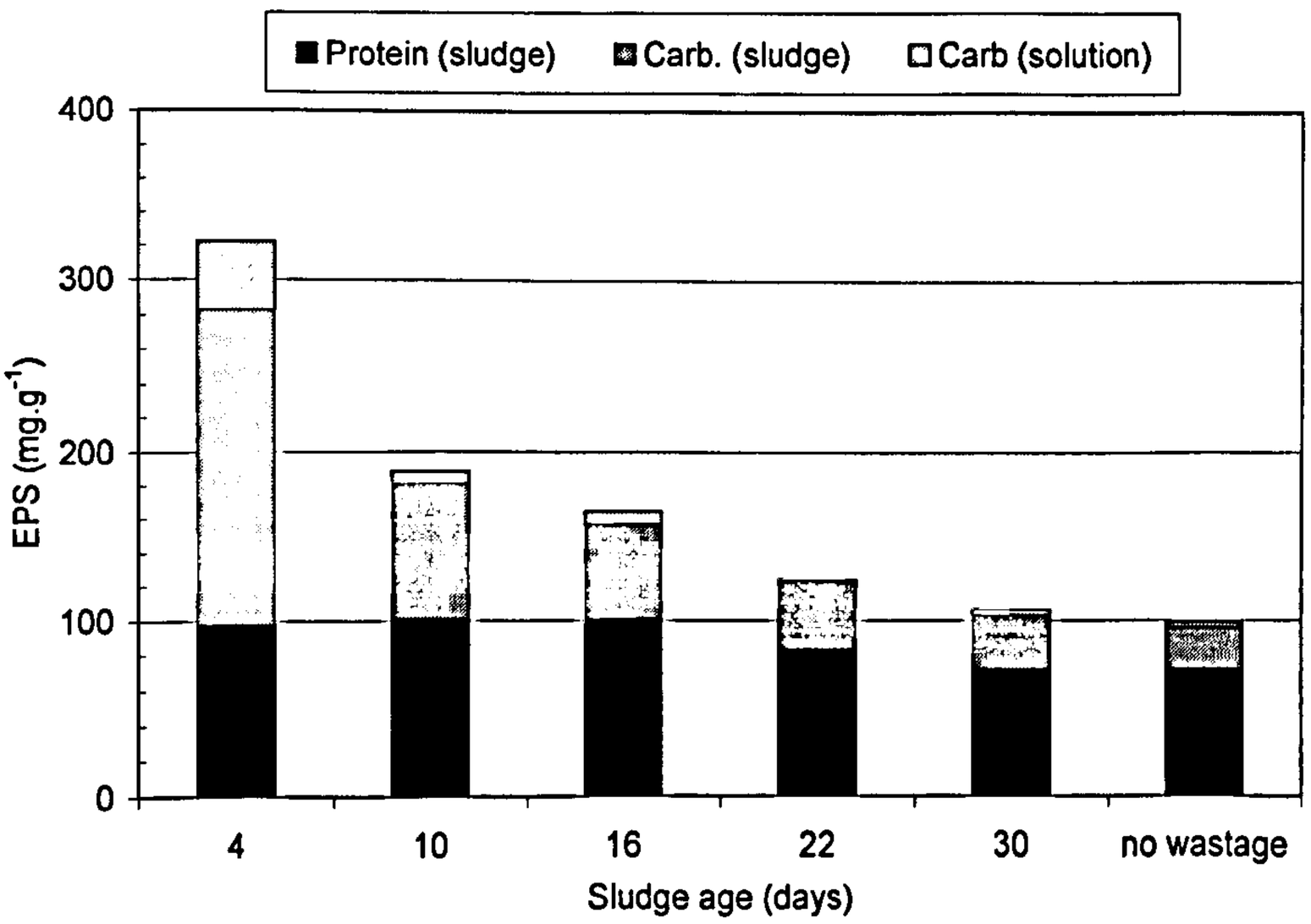

Figure 2.2 EPS and SMP level vs. sludge age (Judd and Jefferson, 2003).

The effects of MLSS concentration on the filtration resistance are mostly related to cake permeability, and thus would be expected to affect super-critical rather than sub-critical operation. The CST values for MBRs were compared with other filterability data drawn

from the literature (Houghton *et al.* 2002, Judd and Jefferson, 2003). Figure 2.3 suggests an exponential trend between CST and MLSS and shows the MBR biomass to have poorer permeability than the other sludge tested and to rapidly decrease between concentrations of 10 and 15 $g.L^{1}$. A similar exponential relationship between filterability and solvent-extracted EPS has been proposed by Rosenberger and Kraume (2002).

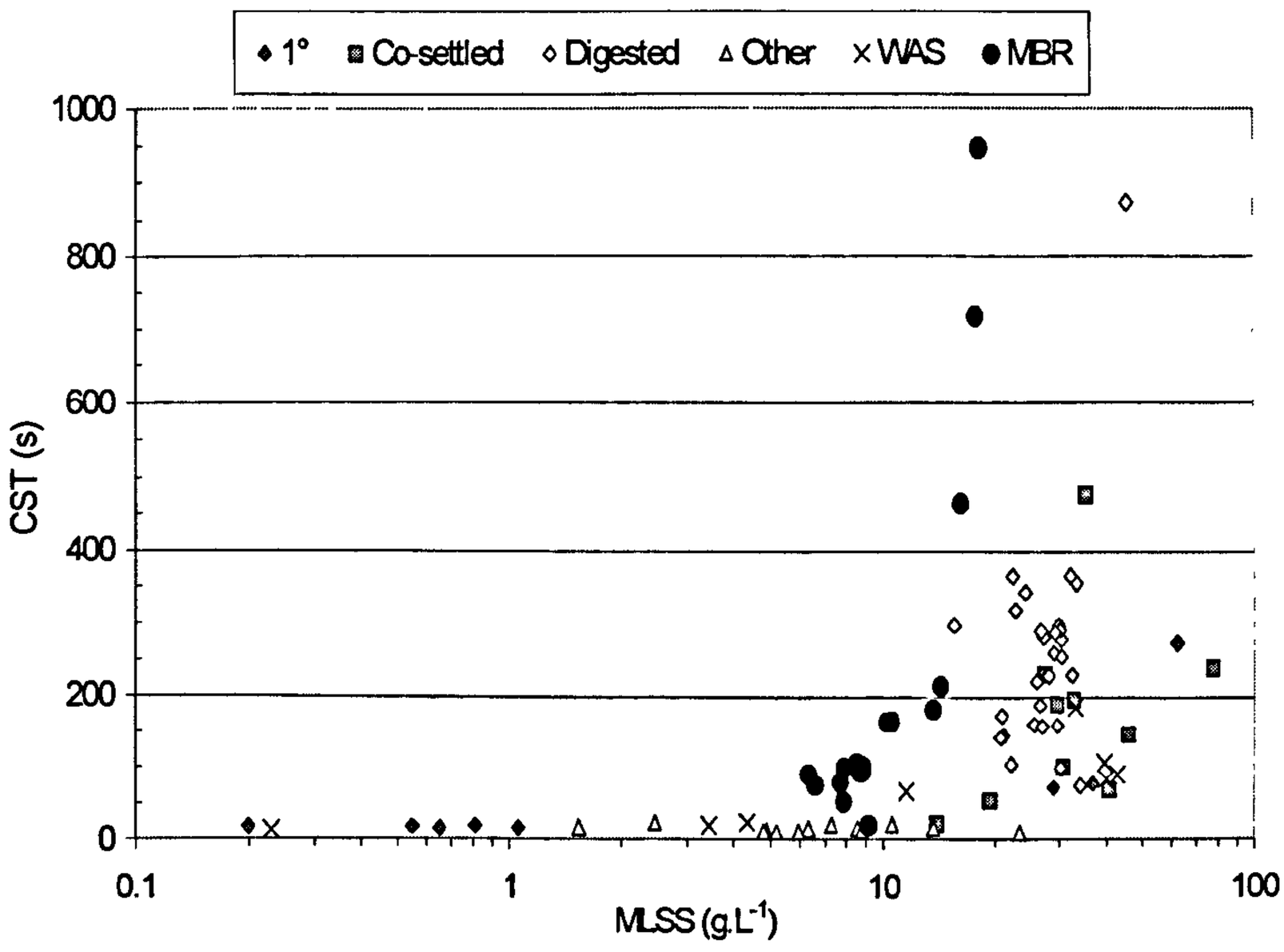

Figure 2.3 CST vs. MLSS for various sludges (Houghton *et al.* 2002).

These observations suggest that while long sludge ages yield decreased EPS levels, and thus presumably reduced sub-critical fouling, the high MLSS concentrations generate increased filtration resistance under super-critical conditions. However, the role of MLSS in sub-critical fouling is unclear, since long-term sub-critical fouling has not been incontrovertibly linked to any one foulants or group of foulants. However, given the generally noted significantly higher fouling propensity of raw sewage over that of

biomass it is evident that start-up without fouling relies on the existence of a suitable biomass inoculum and low-flux operation until the system is fully acclimatised. Start-up strategies based on slow and progressive flux increase have been proposed in theoretical studies, though in this case it is to reduce colloid-colloid interactions and ultimately produce less consolidated deposit layers (Chen *et al.* 1997; Chen, 1998), and such strategies are routinely employed at full scale.

2.4.4 Conclusions

Recent data from sub-critical flux operation of MBRs allow an assessment of relevant parameters affecting the sustainability of long-term operation under these conditions. In terms of operational parameters, the following observations can be made:

- Information on sub-critical behaviour obtained at the laboratory or pilot scale is difficult to transfer to full-scale plants since the plant size probably impacts upon the hydrodynamics in a submerged system.
- Values of permeability decline (dK/dt) and fouling rate (dP/dt) vary widely between studies, with no observable trend across studies other than the tendency towards increased fouling at smaller scales of operation and for analogues.
- Critical filtration time (t_{filt}) has been observed only in small-scale experiments, with the limited data available suggesting that is a function of flux.
- Short-term fouling experiments (step-flux) may be helpful in detecting the occurrence of fouling even at sub-critical fluxes and quantify relative fouling propensity of factors such as feedwater characteristics, but the absolute measured fouling rates do not appear to be applicable to long-term operation.

In terms of mixed liquor characteristics, the main conclusions are the following:

- Sludge concentration is more significant in super-critical than sub-critical operation.
- HRT and SRT impact upon the soluble and colloidal fractions in the MLSS.
- Extractable EPS are the dominant microbial product in the MBR mixed liquor independent of the feed and operating conditions, and are mainly composed of proteins and lower concentrations of carbohydrates.
- Carbohydrate concentrations in SMP and EPS tend to decrease with increasing sludge retention time, whereas proteins appear less affected by the sludge age.
- While long sludge ages may be beneficial in minimizing the EPS carbohydrate levels, thus limiting sub-critical fouling, high MLSS concentrations cause increased filtration resistances under super-critical conditions.
- Higher fouling potentials are more likely to arise during start-up of MBRs due to the combined effects of higher undegraded feed fractions and higher EPS levels from the growing biomass.

2.5 Summary

The MBR technology appears ideally suited to for niche application of dissolved organics removal from produced water due to its inherent benefits as outlined and results from treatment of similar wastewater matrices. However the most significant barrier to its potential use remains membrane fouling. It has become evident recently that even operation at low fluxes reveal membrane fouling to take place.

3 Aims and Objectives

The main aim of this study is to assess the efficacy of MBR technology for the treatment of dissolved aromatic and aliphatic hydrocarbons in produced water. Optimisation of operating parameters and conditions for both biological and membrane performance is required to maximise treatment performance of the system whilst minimising membrane fouling, impacting on environmental impact and operating costs respectively.

This was achieved by carrying out the following objectives:

- Formulate an analogue synthetic feedwater that is representative of gas field produced water
- To undertake pilot scale treatment of produced water in order to assess its biodegradability and treatment performance under a range of operating conditions
- Determine the loss of volatile compounds to the atmosphere during MBR treatment
- Conduct a series of fouling experiments to characterise the fouling propensity of the system under different biomass MLSS concentrations and in comparison to other feedwater matrices.

4 Materials and Methods

4.1 Scope

Two types of pilot plants were set up to treat produced wastewater. The first stage of the study was conducted using Porous Pots (WRc, 1978) as a scoping study to examine the biodegradation potential of the wastewater. Following completion experimentation continued to a pilot scale submerged MBR in order to investigate membrane fouling.

Short term flux step tests and long term sustainable flux operation were carried out to characterise fouling propensity under different operating conditions. In parallel with these trials, several experiments associated with the characterisation of the biomass, and treatment performance in terms of removal through the process by measuring feed and permeate water quality were carried out in the Wastewater Laboratory in the School of Water Sciences, Cranfield University.

4.2 Synthetic wastewater

A synthetic feed-water matrix has been chosen for use rather than real wastewater. Discussion with sponsoring companies and experiments on different matrices in the laboratory resulted in a matrix with the following composition being chosen, to reach a target COD of 2000 $mg.L^{-1}$. The composition representative of a typical North Sea gas-field condensate

Following completion of the first phase of experiments the composition was altered in order to be more challenging to the system as shown in Table 4.1. Concentrations of BTEX, Glycol and Carboxylic acids were doubled and Methanol reduced. Overall COD was reduced from 2000 to 1575 $mg.L^{-1}$.

Table 4.1 Analogue Composition

Compound		***Concentration (mg/L)***	
		First phase	***Second phase***
Benzene		35	70
Toulene		19	40
Ethyl benzene		4	8
Xylene		10	20
Naphthalene		1.7	1.7
Phenol		25	25
PAHs	Acenaphthene	0.3	0.3
	Biphenyl	0.2	0.2
	Phenanthrene	1.4	1.4
Carboxylic acids	acetic acid	28	50
	Propionic acid	7	15
	Valeric acid	2	5
Methanol		1300	500
Ethylene glycol		158	300
Sodium chloride		4.6g	4.6g
Urea		214	41
Orthophosphate		112	11
COD		**2000**	**1575**

Feedwater was prepared in the laboratory at 50 x concentrate solution at weekly intervals.

4.3 Pilot Plant

4.3.1 Porous pot trials

As a scoping study and preliminary investigation into the suitability of biological process for the role of produced water treatment a pilot scale rig was commissioned consisting of six porous pots (WRc, 1978) each 3 litres in volume, enabling a number of operating conditions to be tested simultaneously. The porous pot inner is made from Vyon F, High Density Polyethylene (HDPE), has a surface area 0.167m^2 and mean pore size of 30 μm, the lower end of microfiltration. Aeration is provided to each system by a diffused air sparger positioned at the conical base in order to provide oxygen and promote mixing at a rate of 1.2 $L.min^{-1}$. Feedwater was stored in a 25 L HDPE sealed drum (VWR International Ltd, Dorset, UK) and continuously supplied to the system using a 201 S/D Watson-Marlow pump (Watson-Marlow Ltd, Falmouth).

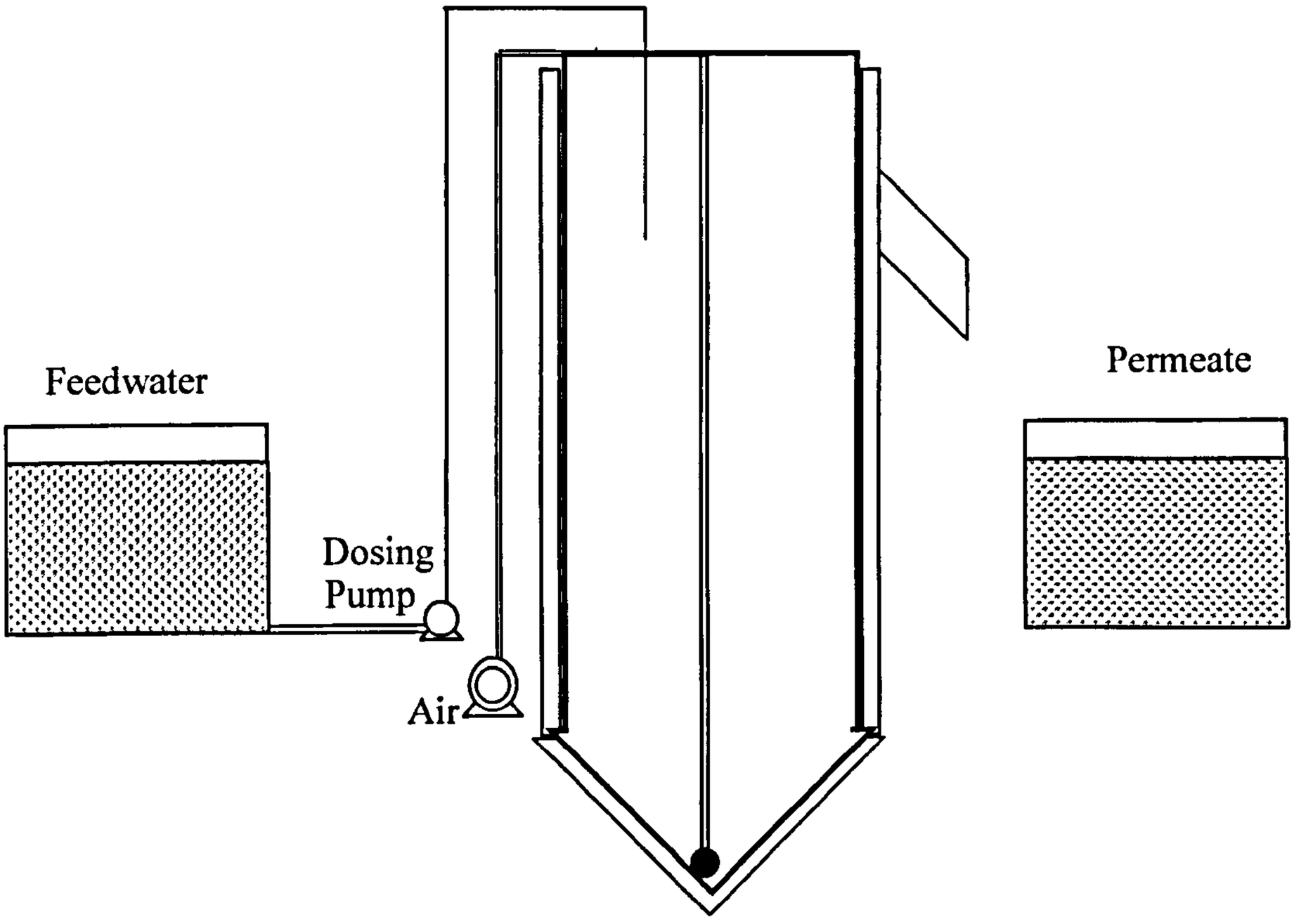

Figure 4.1 Porous Pot rig schematic

Figure 4.2 Porous Pot rig

Due to the nature of the feed-water and the uncertainty regarding the degree of stripping of volatile components the rig was positioned external to the Pilot Hall until health and safety issues were addressed.

4.3.2 Submerged Membrane Bioreactor

The submerged MBR (Model products, Wootton) consisted of a Perspex cylinder chamber with an internal diameter of 0.2 m and a total height of 2 m, corresponding to a working volume of 45 L (Figure 4.3 and 4.4) Sampling points were integrated at the middle and the bottom of the column. An air diffuser providing a minimum constant air flowrate of 7 $L.min^{-1}$ was placed at the bottom of the reactor to provide aeration and

maintain sludge in suspension. Additional air supply was made directly to the base of the membrane module at 6 $L.min^{-1}$. All experiments were conducted at a dissolved oxygen concentration greater than 2 $mg.L^{-1}$.

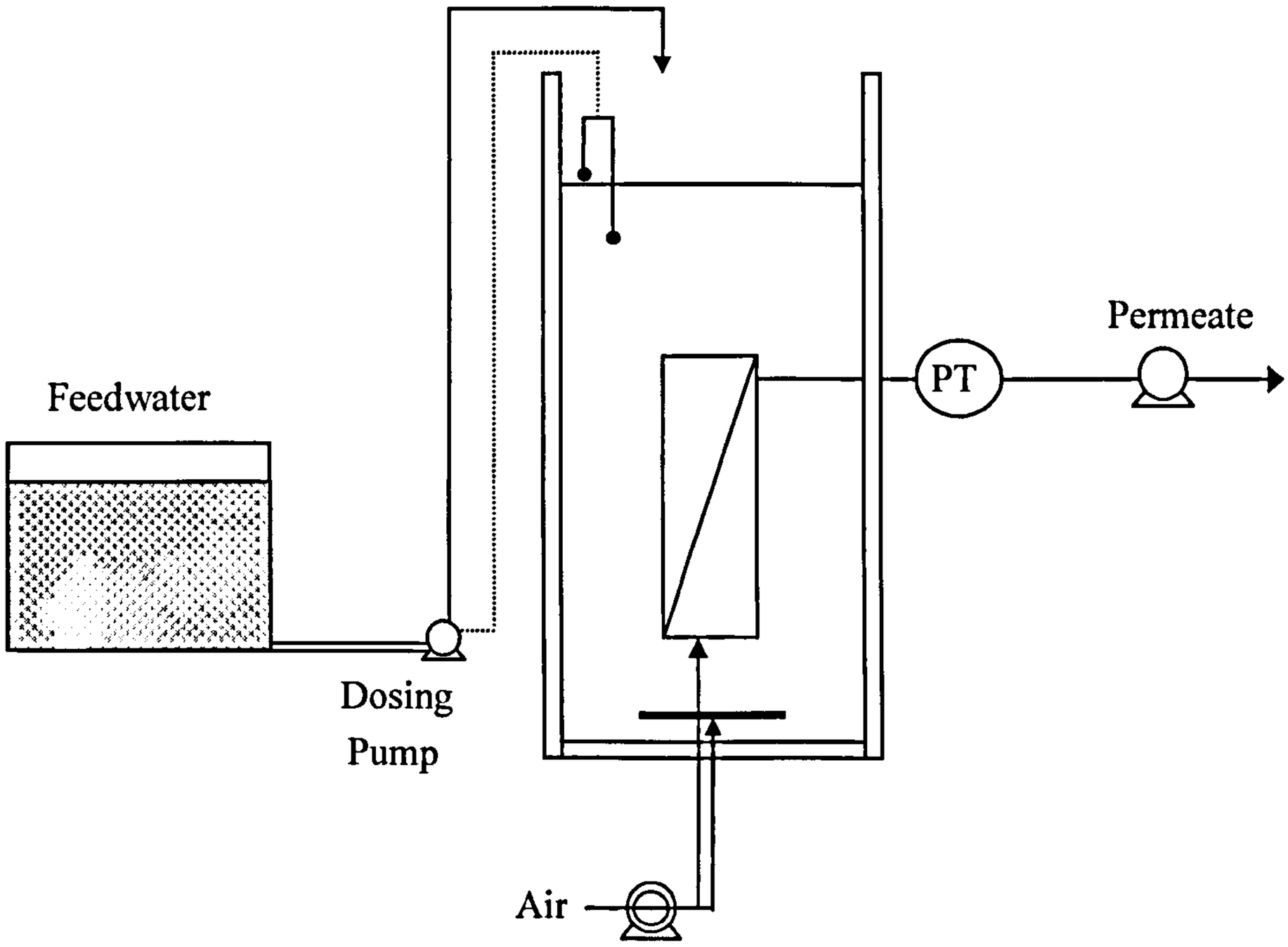

Figure 4.3 MBR rig schematic

During trials the prepared 2 litre 50x concentrate solution was diluted with water into a 100 L holding tank providing sufficient feedwater for 2 days thereby avoiding degradation. The liquid level probe (conductive electrode from RS, Corby) placed at the top of the bioreactor switched the 313 S/D Watson-Marlow pump on (Watson-Marlow Ltd, Falmouth) when required.

Permeate was continuously removed with a peristaltic pump (Watson-Marlow Ltd, model *505 S*, Falmouth) connected to the membrane module. The permeate pressure was measured using a pressure transducer (RS, Corby), and recorded on a PC using specialist data logging system (*Pico* data logging system, Pico technology Ltd., Cambridge).

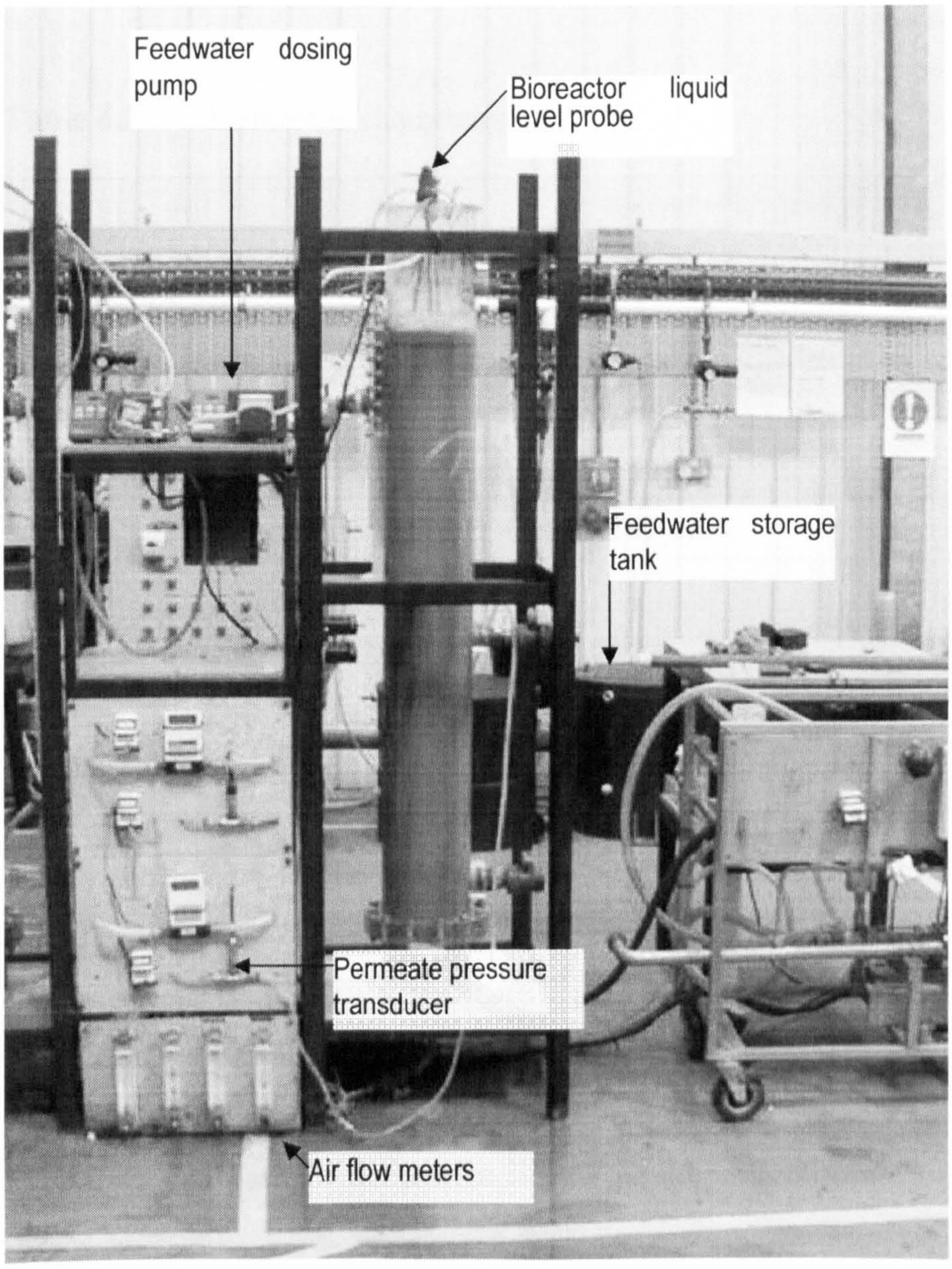

Figure 4.4 MBR Pilot rig

4.3.2.1 Membranes

The membranes used were supplied by X-flow, Norit. The membranes are tubular in geometry and constructed of hydrophilic polyvinylidene fluoride cast on a composite polyester/polyolefine carrier. Each module consists of seven lumen, each with internal diameter of 8mm (Figure 4.5). The membrane structure is asymmetric, the pore size changing across the membrane wall, with nominal pore size of 0.03 μm.

Table 4.2 Membrane characteristics

Type	***X-flow 11PEFr5385***
Material	PVDF
Module length	1 m
Lumen internal diameter	8 mm
Number of lumens	7
Total membrane working area	0.15m^2
Pore size	0.03 μm

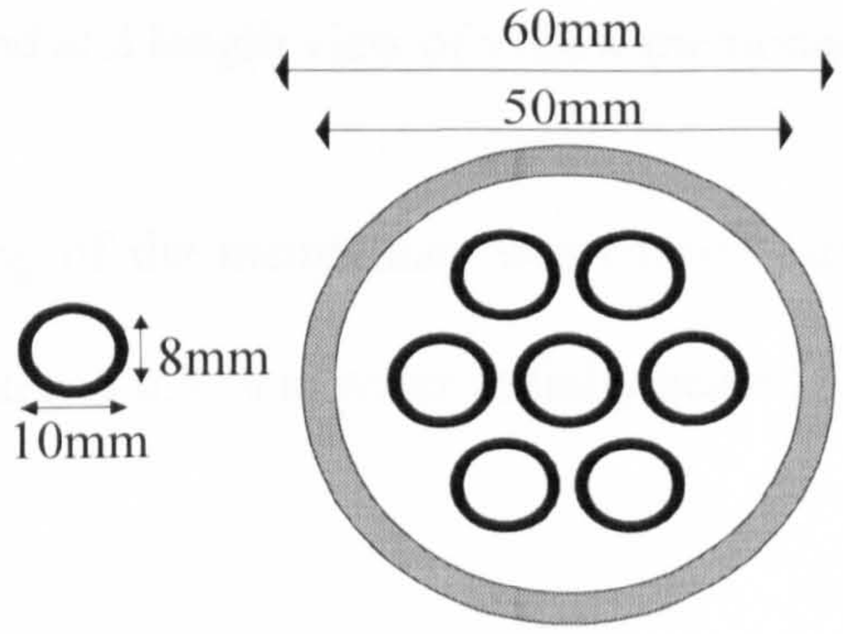

Figure 4.5 Cross sectional representation of the submerged membrane module.

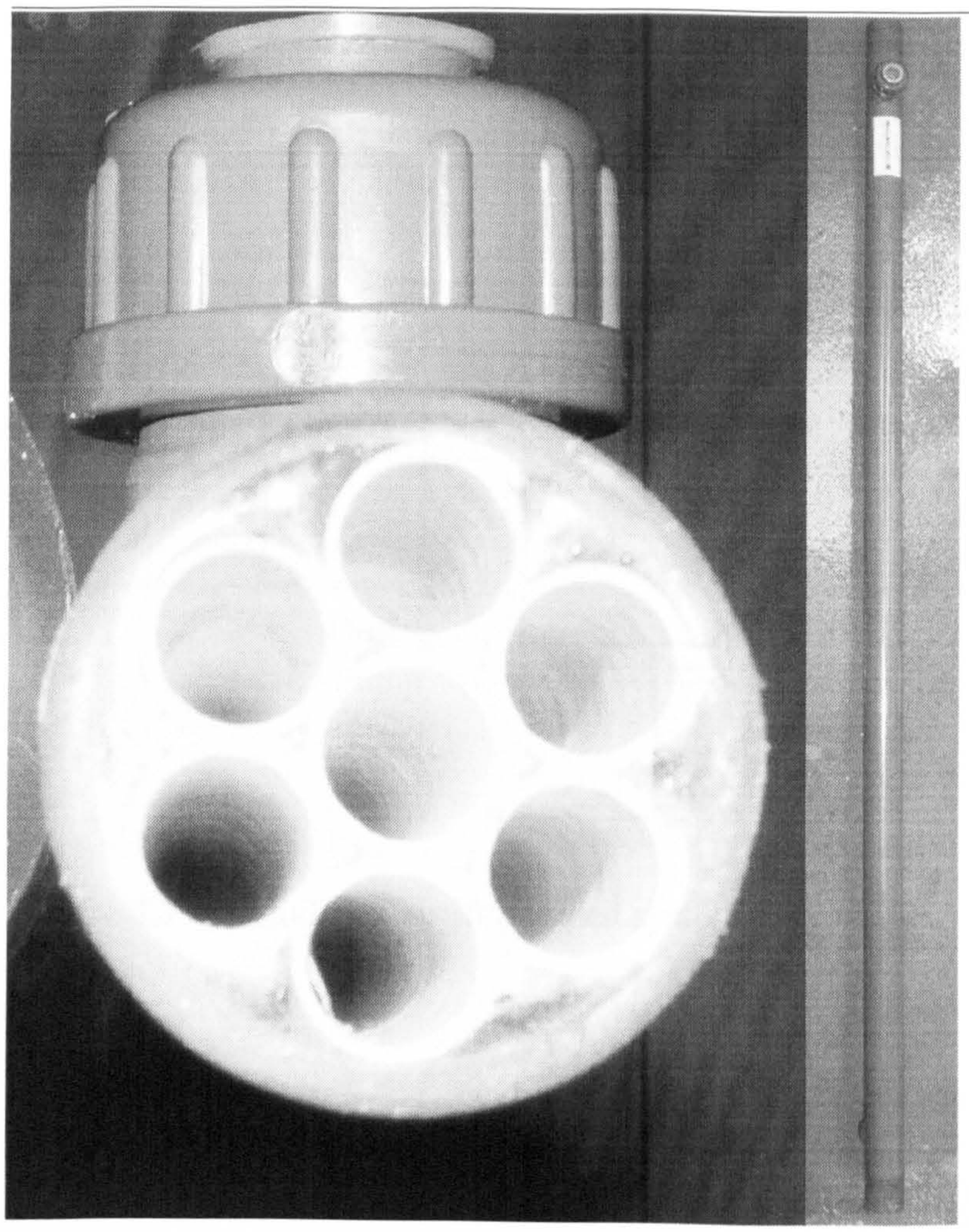

Figure 4.6 End and length view of x-flow membrane module.

Chemical cleaning of the membranes was carried out using a chlorine-based solution (*Ultrasil 75*) diluted at 0.5 % in water initially heated to 50°C for 24 hours.

4.3.3 Side-loop hybrid pumped/airlift system

At the final biomass concentration of 18 $g.L^{-1}$ modifications to the system were made in order to determine behaviour under high shear operating conditions (Figure 4.7).

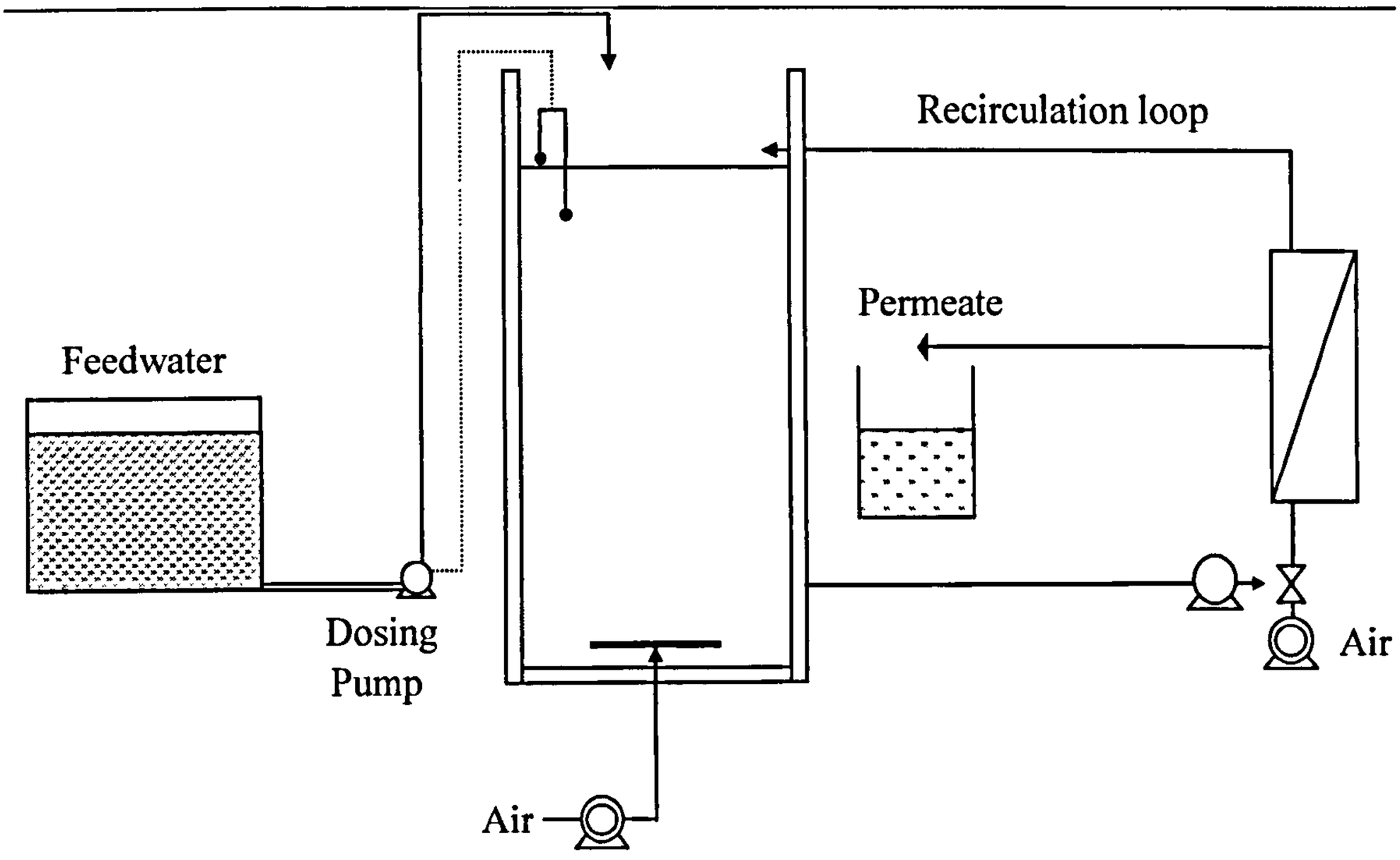

Figure 4.7 Modified airlift/pumped system

A flexible impeller centrifugal pump (*Jabsco 53040 Series* Fisher Scientific Ltd, Loughborough*)* was installed into a side recirculation loop constructed of 1" diameter PVC pipe. Additionally air was provided to the base of the loop in order that the system may be run by airlift alone, pumping alone or a combination of both. Analogue pressure gauges (*RS components)* were fitted each side of the membrane module in order to measure and monitor TMP.

4.4 Analytical techniques

All routine analysis was conducted in the School of Water Sciences Laboratories (Cranfield University, UK). Gas and liquid phase BTEX analysis was outsourced to National Physical Laboratory (Teddington, Middlesex, UK). DGGE and bacterial abundance were carried out by Centre for Ecology and Hydrology (CEH) (Oxford, UK).

4.4.1 MLSS and MLVSS measurement

4.4.1.1 MLSS

The MLSS content was determined using the Standard Method 2540D (APHA *et al.* 1998). A 5 or 10 mL sample (volume dependent on sludge solids content) of well-mixed sludge was filtered, under vacuum (*Speedivac* 2 rotary vaccum pump, D. Benway Ltd, Boreham Wood), using a Buchner flask and filter system fitted with a dried, pre-weighed glass-fibre paper (Whatman *GC/F* 70 mm diameter filter papers, Fisher Scientific Ltd, Loughborough). After the liquid had drained through the filter paper, it was removed and placed in an oven overnight at 105°C (Gallenkamp *Hotbox* oven with fan, OVB 350, Walton on Thames), before being cooled in a desiccator, re-weighed, and the mass of MLSS calculated in $mg.L^{-1}$ from:

$$MLSS = \frac{(A-B)\times 1000}{Samplevolume(mL)} \qquad \textit{Equation 4.1}$$

Where A = weight of filter paper + dried residue (mg) and

B = weight of filter paper (mg)

4.4.1.2 MLVSS

The MLVSS content was determined using the Standard Method 2540E (APHA *et al.* 1998). The SS residue from Method 2540D was ignited in a furnace set at 500 ± 50 °C for 4 h. After cooling, the final stage of which was carried out in a desiccator, the filter paper was re-weighed and the mass of VSS calculated in $mg.L^{-1}$:

$$MLVSS = \frac{(A-B)\times 1000}{Samplevolume(mL)} \qquad \textit{Equation 4.2}$$

Where A = weight of residue + filter paper before ignition (mg)

B = weight of residue + filter paper after ignition (mg)

4.4.2 Sludge dewaterability

Sludge dewaterability was assessed by the capillary suction time (CST) test based on Standard Method 2710 G (APHA, 1998) and conducted using type 200 CST tester (Triton CST filterability tester, model *200*, Triton Electronics Ltd, Essex, UK) using standard filter papers (part No. *815095*) supplied by Triton Electronics. The test provides a quantitative measure of the rate of water release from a sludge and so a relative measure of sludge dewaterability.

A 6.4 mL sample of sludge was placed in the cylindrical sludge reservoir on top of the CST filter paper. The liquid passes outwards through the filter paper by capillary action and as it passes the first electronic contact (E1), the electronic timer was started. The time taken for the water to travel from the first to the second electrode (E2) is monitored as the conductivity change at the electrodes. Once the water reaches the second electrode the timer is stopped. The time taken to travel the distance between E1 and E2 is the water drainage rate .The test was repeated 3 times for each sample (APHA, 1998).

The solids content of the sludge influences the CST determination. At greater solids concentration the thickness of the sludge cake is greater to remove the same volume of water. Consequently it is normal practice to normalise the CST for the sludge MLSS concentration as described in Standard Method 2710 G (APHA, 1998).

4.4.3 Particle size distribution

Sludge particle sizes were measured using a Malvern Mastersizer 2000 particle analyser (Malvern Instruments Ltd, UK). The Mastersizer uses an optical unit to detect the light scattering properties of sludge particles dispersed in deionised water. The dilute sludge suspension is circulated through a measurement cell where the particle fields are exposed to an analysing laser beam. The pattern of light scatter can be used in order to calculate the particle sizes that created the observed scatter by Mie theory, which predicts the way that light is absorbed and scattered by spherical particles.

Sludge samples were analysed using the same standard operating procedure. The optical properties of the material to be analysed (sludge) were set at default properties: Refractive index of 1.52, absorption of 0.1, which are appropriate for the majority of naturally occurring samples. The stirrer pump speed was set at minimum speed of 150 rpm to avoid shear but still allow sample to be well mixed. Sludge samples were introduced to the dispersant tank containing deionised water until laser obscuration was in the range for measurement; between 10 and 20%. Ten measurement cycles were taken with a 5 second delay between cycles and a mean measurement calculated.

The Mastersizer measurement is volume based and according to Mie theory assumes that the particles causing light absorption and scatter are perfect spheres. Consequently the results are volume based and expressed in terms of equivalent spheres. The mass median diameter (d_{50}) that is the particle size at which 50% of the particle size and 50% is larger was used to represent the particle size in this study.

4.4.4 SMP and EPS

Soluble microbial products (SMP) and Extracellular polymeric substances (EPS) were analysed due to their importance in relation to membrane fouling. Procedures proposed by Zhang *et al.* (1999) and modified by Le-Clech *et al.* (2003b) based upon a heating extraction method were used for EPS determination and both SMP and EPS analytical techniques are outlined below:

50 mL of sludge was centrifuged at 5000 rpm for 5 minutes using a Rotanta 96R centrifuge (Hettich Zentrifugen, Tuttlingham, Germany). The supernatant was decanted – representing the SMP or soluble phase of EPS. 50mL of deionised water was added to the centrifuge bottle containing the sludge pellets. The bottle was hand shaken gently to disperse the sludge into liquid. Samples were placed into an oven at 105 °C for one hour (in order for the solution to reach 80 °C for 10 minutes) as the extraction process. The EPS was recovered by further centrifugation at 7500 rpm for 5 minutes and

The carbohydrate content of the SMP or EPS was determined by the phenol – sulphuric acid method of Dubois *et al.* (1956). Filtrate samples (0.4mL) were added to 0.4 mL of 5 % (w/w) phenol solution (Sigma - Aldrich, Gillingham, UK), and then mixed with 2 mL of concentrated sulphuric acid (98%, Fisher Chemicals, Loughborough, UK). Samples were left for 10 minutes before being transferred to a cuvette and the absorbance measured against a blank at 480 nm using a Jenway 6505 UV/Visible Spectrophotometer. Carbohydrate concentration ($mg.L^{-1}$ and $mg.g\ MLSS^{-1}$ for EPS) was calculated against a calibration curve obtained using a glucose standard (Figure 4.8)

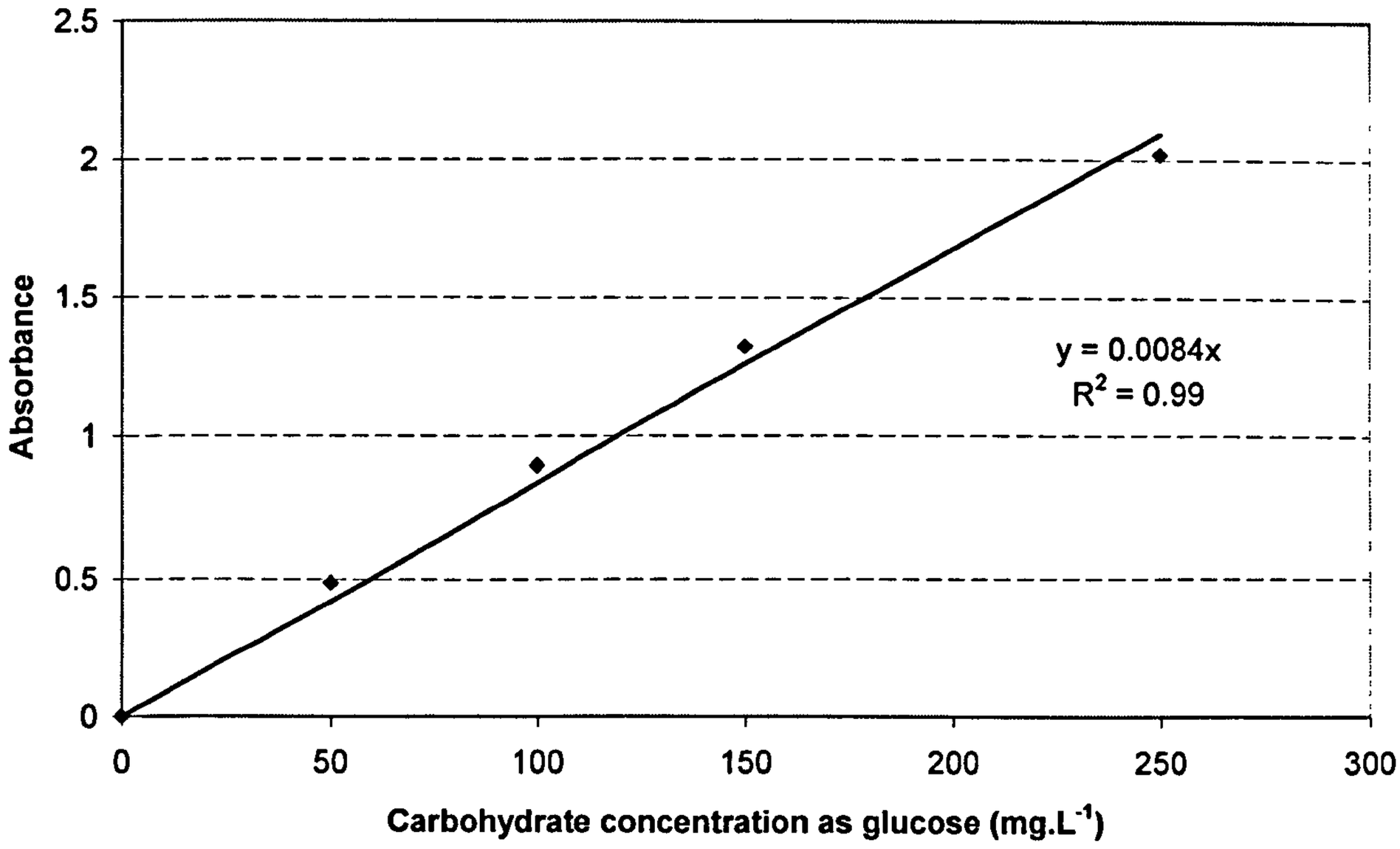

Figure 4.8 Carbohydrate calibration curve for SMP and EPS determination

The protein content of the SMP or EPS was determined using protein diagnostic kit 690A supplied by Sigma - Aldrich, Gillingham, UK. Filtrate samples (0.2mL) were mixed with 2.2 mL of Biuret reagent and kept at room temperature for 10 minutes. 0.1 mL of Folin and Ciocalteu phenol reagent was added. Samples were left for 30 minutes before being transferred to a cuvette and the absorbance measured against a blank at 595 nm using a Jenway 6505 UV/Visible Spectrophotometer. Protein concentration ($mg.L^{-1}$ and $mg.g\ MLSS^{-1}$ for EPS) was calculated against a calibration curve obtained using a protein standard of bovine serum albumin (Sigma - Aldrich, Gillingham, UK) (Figure 4.9).

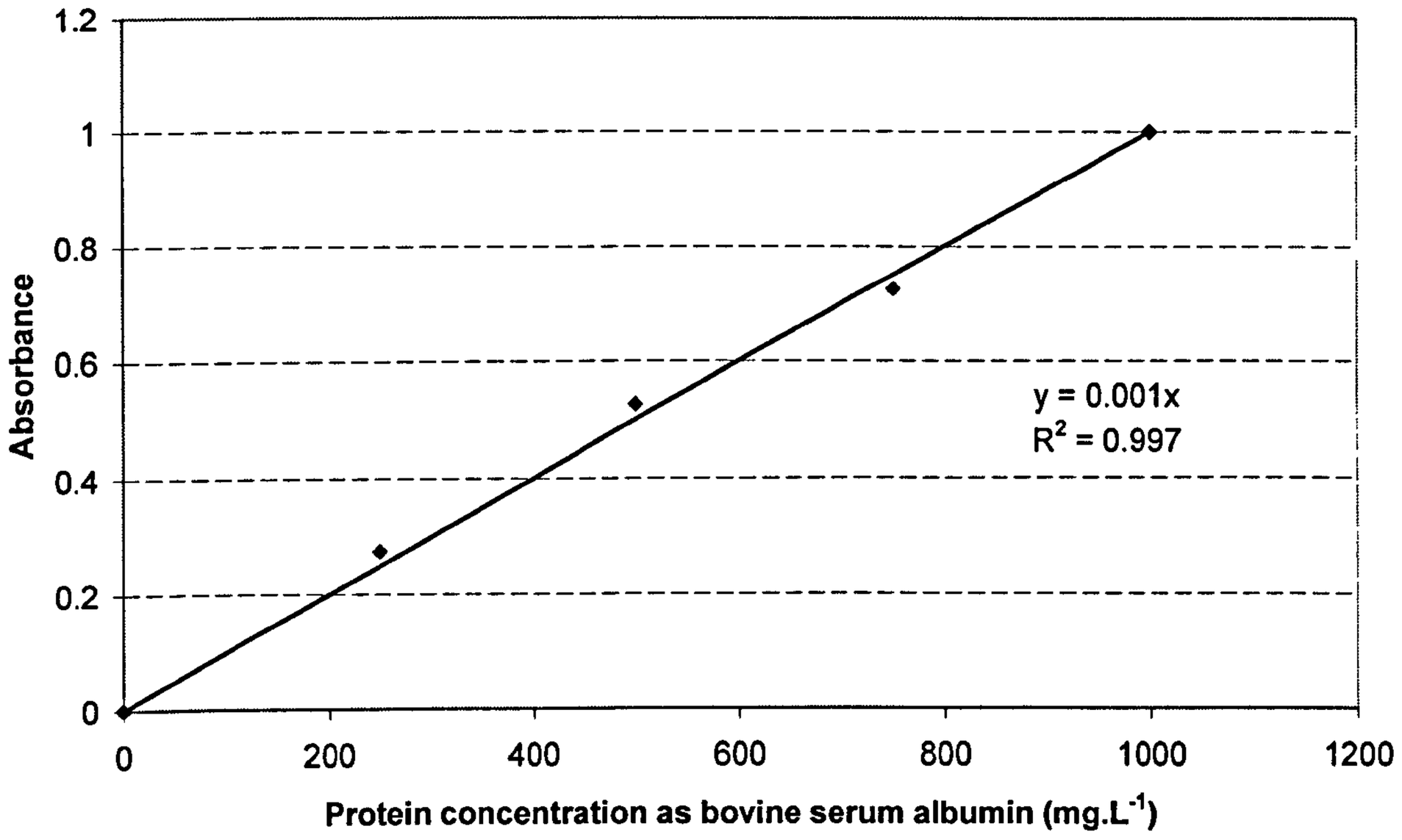

Figure 4.9 Protein calibration curve for SMP and EPS determination

4.4.5 Oxygen uptake rates

A series of respirometric cells were prepared with washed sludge (5 mL) and filtered influent (45 mL) diluted to produce a range of initial substrate concentrations. Oxygen consumption was recorded every 5 minutes for a total run period of 15 hours using a Meritox-20 electrolytic respirometer (Addington Instruments, Richmond, UK) after an initial temperature equalisation of 20 minutes. Cells were continuously stirred and maintained to 20 °C throughout the run period. Oxygen uptake rates (OUR) were converted to standardised oxygen uptake rates (SOUR) by normalising for MLVSS content.

4.4.6 Chemical oxygen demand

COD determination was made using Merck Spectroquant COD cell test 1.14541.0001 (25 – 1500 $mg.L^{-1}$) and COD cell test 1.14550.0001 (350 – 3500 $mg.L^{-1}$). A 2 or 3 mL sample (depending on kit used) was added to the cell test vial and heated at 150 °C for 2 hours. After cooling to room temperature was measuring using Spectroquant Nova 60 Spectrophotometer.

4.4.7 Dissolved organic carbon

Dissolved organic carbon (DOC) was measured using a Shimadzu TOC-5000A analyser (Shimadzu, Milton Keynes, UK). DOC was calculated by measuring the total carbon (TC) and the inorganic carbon (IC) and subtracting the IC from the TC. The TC standard was made by dissolving potassium hydrogen phthalate (2.125 g) in RO water (1 L). The IC standard was made by dissolving sodium hydrogen carbonate (1.750 g) in RO water (500 mL) and adding this to a solution of sodium carbonate (2.205 g) dissolved in RO water (500 mL). The standards produced had a concentration of 1000 $mg.L^{-1}$ and working standards were diluted accordingly with Reverse osmosis water.

4.4.8 BTEX analysis

Measurements of BTEX compounds in were outsourced to the National Physical Laboratory (NPL), Teddington, Middlesex, UK. Air samples for BTEX analysis were taken from the headspace of the reactor using universal sample pump model 224 PC-XR4 (SKC ltd, Blandford, Forum Dorset, UK) calibrated before use and Chromosorb 106 GC sample tubes (SKC ltd, Blandford, Forum Dorset, UK). Sampling was carried

out for 4 hour runs in duplicate for each system, at 20 mL.min-1 giving a total sample volume of 4.8 L.

Air and liquid samples were analysed by the National Physical Laboratory (NPL, Teddington, UK) by GC-MS using a 5972A MSDII (HP ltd, UK) mass spectrophotometer. A summary of the methodology is shown below:

GC tubes were heated to 300 °C and the sample was desorbed for 5 minutes and transferred to cryo-focusing adsorbent. The cryo-focusing trap was cooled to 5 °C in order to collect the sample from primary desorption. After 5 minutes desorption at 300 °C, the sample was released into the GC inlet via a 1 metre long deactivated silica capillary column at 150 °C, before being separated by GC using a fused silica db-1 column. An electronic controller was used to offset peak pressure broadening with increasing GC column temperature. The GC-MS interface was set at 280 °C. Chromatographic retention time and mass spectral matching was used to identify target compounds. Concentrations were reported in $\mu g.m^3$ and later converted to ppmv.

4.4.9 DGGE and microbial abundance

Samples for bacterial community dynamics and abundance were analysed by CEH (Oxford, UK). Samples were stored at -80 °C prior to analysis. Genotypic (denaturing gradient gel electrophoresis {DGGE}) profiling and subsequent cluster analysis was used to monitor bacterial community dynamics described in detail previously by van der Gast, *et al.* (2003), outlined below:

"The variable region of 16S rDNA was enzymatically amplified by Polymerase Chain Reaction (PCR) using primers to conserved regions of the 16S rDNA genes. The primers used were universal bacterial primers GC338F (forward primer with GC clamp) and 530R (reverse primer) (MWG Biotech, Ebersberg, Germany). PCR amplication was performed using a Hybaid-Touchdown Cycler (Hybaid Limited, UK). For each PCR sample tube; 73 μL MilliQ water, 10 μL 10×PCR buffer, 1 μL of each primer (at 10 $pmol.L^{-1}$), 1.5mM of Mg 2+ 200 μM of deoxyribonucleoside triphosphate, 1 μL of BIOTaq DNA polymerase (Bioline, London, UK), and 1 μL of sample were added. The PCR amplification program was set as follows: the first step was 95 ◦C for 5 minutes; the second step was 35 cycles of 95 ◦C for 1 minute, 60 ◦C for 30 seconds, and then 72 ◦C for 30 seconds. The final extension step was 72 ◦C for 30 minutes. Amplification products were checked first by electrophoresis in 1.5% agarose gels and ethidium bromide staining. The gels were photographed with UV transillumination with Bio-Rad Gel Doc 1000 equipment.

DGGE was performed with the Bio-Rad DCode universal mutation detection system which is based on the Bio-Rad Protean II system. PCR samples were applied directly on to 10% (w/v) polyacrylamide gels in 0.5 × TAE (20 mM Tris acetate (pH 7.4), 10mM sodium acetate, 0.5mM Na2-EDTA) with 10% acrylamide, and 30 – 60% denaturing gradient poured according to the manufacturer's instructions.

Electrophoresis was performed at a constant voltage of 160V and a temperature of 60 ◦C for 4 hours. After electrophoresis, the gels were incubated for 15 min in Milli-Q

water containing syber gold (2 mg mL^{-1}, Molecular Probes Ltd., Eugene, Oregon, USA), and photographed with UV transillumination with Bio-Rad Gel Doc 1000 equipment."

Bacterial abundance (total cell counts) was determined by epifluorescence microscopy as previously described (van der Gast, *et al.* 2001). Cells were fixed with fresh 1 % w/v final concentration of paraformaldehyde (Sigma, UK), in phosphate buffer saline solution. DAPI (4', 6' –diamidino–2–phenylindole, Sigma, UK), 2 $\mu g.mL^{-1}$ final concentration, was added to fixed samples and left for 10 minutes at room temperature. Samples were filtered using 0.2 μm pore-size filters (25 mm diameter; Poretics Corp., USA) by applying a slight vacuum. After filtration, filters were mounted in oil and observed immediately by epifluorescence microscopy using a Nikon Eclipse E600 microscope (Nikon, Japan).

4.5 Fouling analysis

4.5.1 Short term flux step trials

Flux step trails were carried out according to methods outlined by Le Clech *et al.* (2003a). A flux step length of 15 minutes was used and step height of 2 $L.m^{-2}.h^{-1}$. Fluxes were incrementally stepped up to maximum flux tested - 16 $L.m^{-2}.h^{-1}$ and then decreased back to the initial flux. The descending phase was used in order to observe if any irreversible fouling had taken place during the test.

Parameters pertaining to membrane behaviour were calculated, namely: membrane fouling rate (dp/dt) the gradient of TMP over the step; initial TMP jump at start of step (ΔPo); average TMP during flux step (P_{ave}).

4.5.2 Long term fouling trials

Long term fouling trials were carried out by setting system to operating flux to studied and observing the behaviour over time. The membrane fouling rate was determined in the same way as during short term trials – gradient of TMP over time. The other parameter recorded was T_{filt} the period of stable filtration before second and more rapid phase of membrane fouling when it was evident

4.5.3 Temperature and flux

The temperature of a liquid will have an effect on membrane filtration and permeability mainly as a result of permeate viscosity with fluid becoming less viscous at increased temperature leading to greater permeability. One method of correcting for temperature is to multiply the permeation rate observed at a given temperature (J_T) by the ratio of the viscosity of the permeate at that temperature to its viscosity at the reference temperature (Equation 4.3). Based on a reference temperature of 25°C, a temperature correction factor can be used to account for temperature deviations (Rautenbach and Albrecht, 1989):

$$\frac{J_t}{J_{25}} = 1.03^{T-25} \qquad \textit{Equation 4.3}$$

Where T is the temperature (°C), and J_{25} is the corrected flux at 25°C.

5 Treatment performance

5.1 Introduction

The primary objective of this work was "to assess the efficacy of MBR technology for the role of produced water treatment" (Section 3). Few examples of MBRs treating produced water were found in the literature (Section 2.2) and thus the biodegradability of the waste is not well proven. An initial experiment using Porous Pot equipment was carried out to ascertain biotreatability (Section 5.2). Studies then proceeded to the pilot scale with an MBR (Section 5.3) challenged with a produced water analogue loaded with TOC/COD, partly comprising key aromatic (BTEX) compounds. The performance under a number of different operating conditions is described (Section 5.2), as well as the assessment of removal of volatile compounds by stripping rather than aerobic degradation, as reported literature suggests is possible (Section 2.3.4). Given the health and safety implications of VOCs and BTEX compounds entering working environment, the degree of stripping was considered of primary importance, and addressed through a mass balance calculation (Section 5.3).

5.2 Organics removal

5.2.1 First phase - Porous pots

The first stage in the investigation of the biodegradability of the wastewater analogue was conducted externally in a well-ventilated area to disperse any potentially harmful off-gas arising (Section 5.3.1). The hydraulic retention time (HRT) during this stage of the trial was 24 hours (equivalent to 0.125 $L.m^{-2}.h^{-1}$). Performance of all systems appeared to be good; greater than 95% COD removal, once the systems had

acclimatised to the wastewater (Table 5.2) for recorded influent chemical oxygen demand (COD) concentration was 2000 ± 100 $mg.L^{-1}$. Consistency of performance is highlighted by the low standard deviation of the effluent COD concentration. Influent dissolved organic carbon (DOC) concentration was 465 ppm and has similar removal efficiency to COD, averaging 97%. DOC removal is marginally better at the longer sludge age. Values for SRT reported in the literature range from 30 - 300 days (Table 2.6, Section 2.3.3) with an average of ~80 days. Values used in the current study are thus towards lower end of the range. From Table 5.1 it appears that an increase in SRT and thus biomass concentration has little effect on treatment performance. This is discussed in more detail in Section 6.3.

Table 5.1 Mean COD and TOC removal at a range of SRTs

SRT (days)	*MLSS ($g.L^{-1}$)*	*Effluent COD ($mg.L^{-1}$)*	*Removal (%)*	*Effluent DOC (ppm)*	*Removal (%)*
10	3.2	81	96	15.9	97
	[0.4]	[20.5]		[1.9]	
30	5.3	112	95	14	97
	[0.7]	[11.3]		[1.6]	
60	6.1	84	96	13	97
	[0.5]	[4.2]		[2]	

[standard deviation]

The impact of feed concentration on effluent quality is depicted in Figure 5.1. It is apparent that the effluent COD concentration changes little with that of the feed, such that apparent removal during initial stages was very poor. This may be attributable to the unaclimitised state of the initial inoculation, which was made with activated sludge from a municipal treatment works. Zaloum *et al.* (1994) found that biomass took 2

months to acclimatise to an oil-containing wastewater when the bioreactor was initially seeded with activated sludge from a municipal plant. Results from the current study indicate that removal efficiency stabilises at around 20 days.

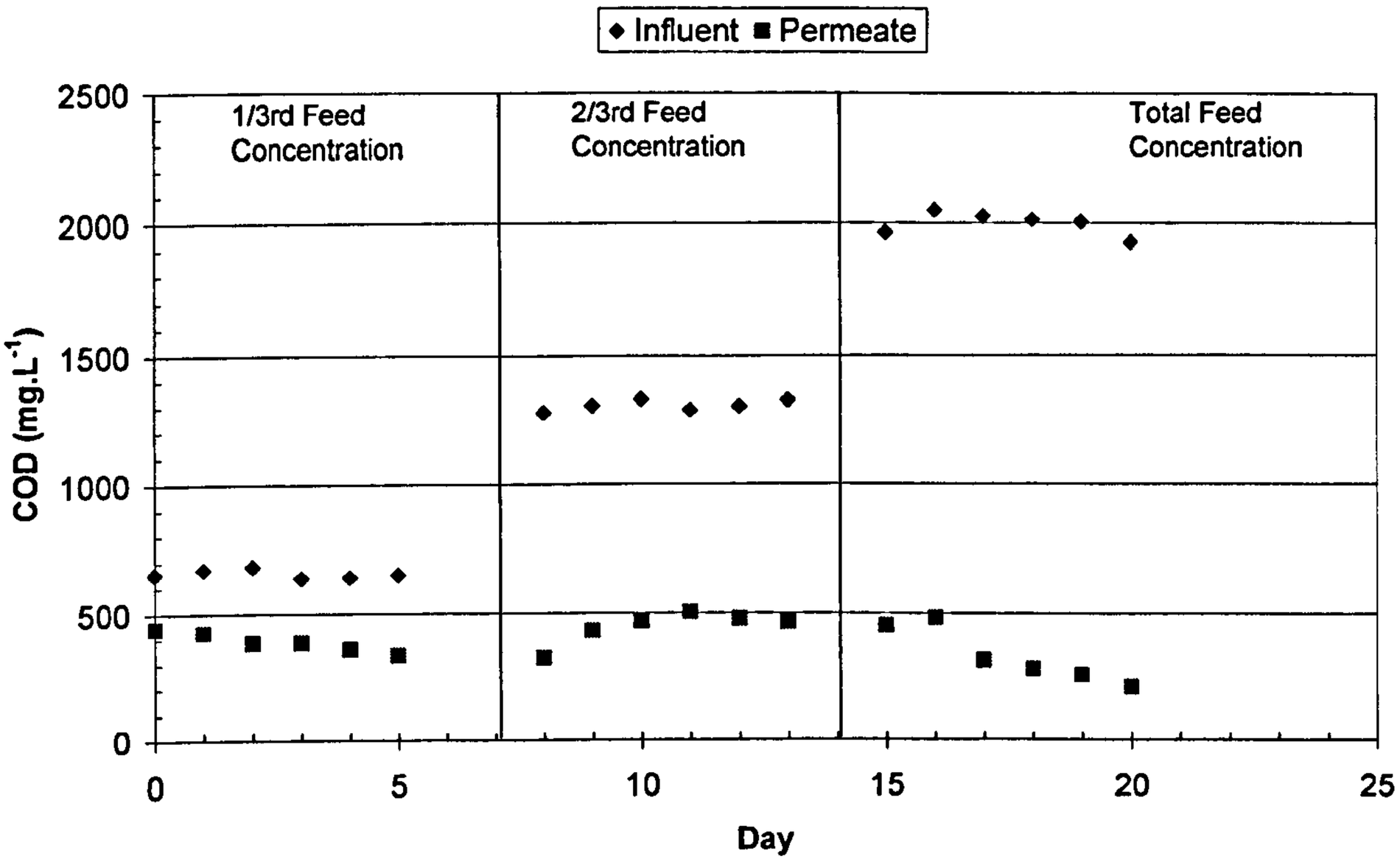

Figure 5.1 COD removal during system start-up

The final stage in the experimentation was a reduction in the HRT to 12 hours (equivalent to 0.25 $L.m^{-2}.h^{-1}$). This was implemented in parallel with operation of a duplicate reactor at the same SRT. It was found that the system was unable to cope with the increased loading, such that operation at this HRT not sustainable. After approximately 12 hours of operation the porous pot liner fouled rapidly, resulting in flooding of the plot and consequent loss of biomass. At 12 hours HRT the organic loading rate was 4 kg $COD.m^{-3}.d^{-1}$, which must be assumed to be too high for the system to function satisfactorily. In contrast, in the study by Zaloum *et al.* (1994) halving the HRT (yielding an OLR of 4.9 kg $COD.m^{-3}.d^{-1}$), led to no discernible deterioration in performance with removal of both COD and BOD remaining at over 99% removed.

During the period of increased loading the PVDF inner of the porous pot fouled considerably more rapidly than that operated at a 24 hour HRT. This was manifested as an increase in the operating level in the reactor, necessitating more regular cleaning. This was not sustainable and operation was ceased after two weeks. Compared with HRT and loading rates reported in the literature (Table 2.6, Section 2.3.3), the system in the current study was operated at a relatively low HRT and high loading rate, reflecting the higher feed organic concentration appropriate to the envisaged duty.

5.2.2 MBR performance

Pilot scale studies of an MBR (Section 4.2.2) followed the porous pot trials; these studies conducted using a modified feedwater composition. Total COD concentration was reduced from 2000 to 1575 $mg.L^{-1}$ and the concentration of primary components doubled (Section 3.2). This represented a more challenging feedwater since the reduced methanol concentration meant that the amount of a readily available carbon source was correspondingly reduced whereas levels of BTEX were increased. As with the porous pot trials, slightly improved effluent quality was evident at increased biomass concentrations, with mean COD values decreasing from 116 to 97 $mg.L^{-1}$ on increasing biomass concentrations from 6 to 17 $g.L^{-1}$.

Table 5.2 Mean COD removal

MLSS ($g.L^{-1}$)	*SRT (days)*	*Effluent COD ($mg.L^{-1}$)*	*Removal (%)*
6.2 [0.8]	~ 12	116 [12.1]	93
12.6 [1.8]	~ 20	100 [10.5]	94
17.4 [1.3]	~ 30	97 [10.8]	94

[standard deviation]

A slightly lower COD removal (92 - 95%) was recorded for the MBR trial than for the porous pot, notwithstanding the greater selectivity (0.03 μm pore size for the membrane cf. nominally 40 μm for the porous pot), and 25% lower loading rate (1.58 cf. 2.00 kg $COD.m^{-3}.d^{-1}$). It would therefore appear that the change in feedwater composition is sufficient to marginally reduce % COD removal.

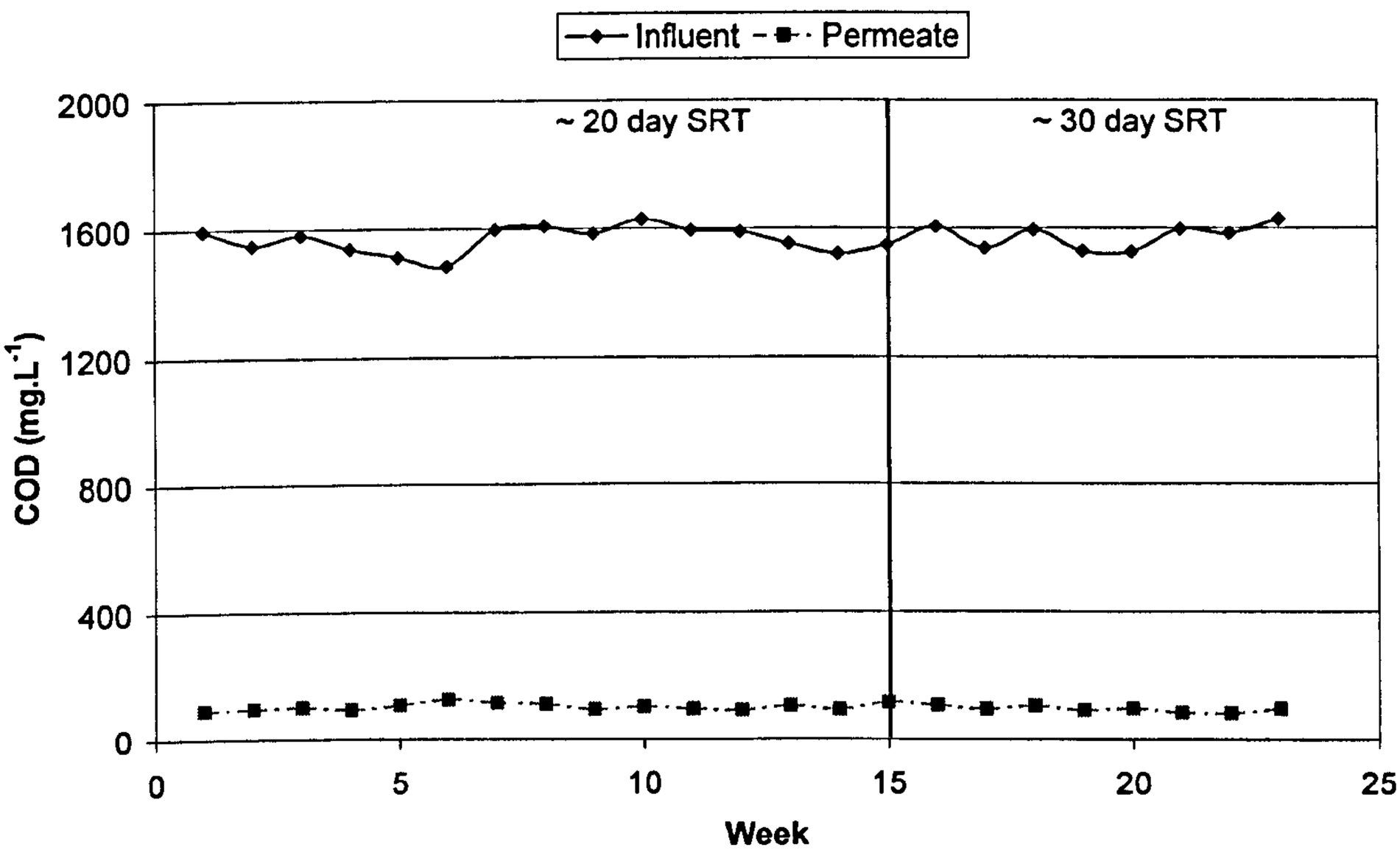

Figure 5.2 COD removal during increase in SRT

The COD removal during transition between 20 and 30 days SRT is shown in Figure 5.2. During the first 15 weeks the system was operating at a biomass concentration of 12 $g.L^{-1} \pm 1.5$, controlled by adjusting volume of sludge wasted daily. The resultant SRT was around 20 days. At week 15 sludge wasting was reduced to allow biomass concentration to increase. During this period there was little increase in the removal of COD, with permeate concentration very stable with mean of 104 $mg.L^{-1}$ during first period shown and reducing slightly to 97 $mg.L^{-1}$ during transition period to higher

biomass concentration, further supporting the previous observation (Section 5.2.1) that little benefit in COD removal is attained by operating at extended SRTs.

COD removal efficiencies between 90 and 97% have been reported for similar wastewaters (Table 2.6, Section 2.3.3); data from the current study fall within the higher end of the range of reported values. Differences may be attributable both to bioreactor configuration and, more reasonably, wastewater biodegradability.

5.3 Species specific off-gas analysis and mass balance

As already stated, the use of an aerobic process to treat wastewater containing volatile organic compounds (VOCs) can lead to the loss of these contaminants through stripping (Scholz *et al.* 1998). Results from the atmospheric analysis from the porous pot trial (Table 5.1) indicate there to be no significant loss to the atmosphere of VOCs. Further liquid and gas phase analysis of BTEX compounds were completed on the MBR to determine the species-specific mass balance and allow the pilot and bench-scale systems to be compared.

5.3.1 Off-gas analysis

Off gas concentrations for the porous pot trials are shown in Table 5.3. The UK time weighted average occupational exposure limit (UK OEL) concentrations for BTEX compounds are 10 ppmv for Benzene and 100 ppmv for Toulene, Ethylbenzene and Xylene. Highest measured concentrations during the porous pot phase were 0.4, 0.14, 0.17 and 0.017 ppmv for Benzene, Toulene, Ethylbenzene and Xylene respectively, 1.5-4 orders of magnitude lower than the OEL values indicating little risk unless the species are allowed to concentrate in the reactor head space.

Table 5.3 BTEX off-gas analysis, porous pot trials

10 day SRT	***Off gas conc (ug/L)***	***MW***	***Conv. Factor***	***Off gas conc (ppmv)***	***Lost in offgas (%)***
Benzene	1.14	78	3.24	0.28	1.9
Toulene	0.48	92	3.83	0.14	1.5
Ethylbenzene	0.039	106.2	4.42	0.01	0.6
Xylene	0.042	106.2	4.42	0.01	0.2
30 day SRT	***Off gas conc (ug/L)***	***MW***	***Conv. Factor***	***Off gas conc (ppmv)***	***Lost in offgas (%)***
Benzene	0.92	78	3.24	0.42	1.5
Toulene	0.39	92	3.83	0.11	1.2
Ethylbenzene	0.058	106.2	4.42	0.01	0.8
Xylene	0.055	106.2	4.42	0.01	0.3
60 day SRT	***Off gas conc (ug/L)***	***MW***	***Conv. Factor***	***Off gas conc (ppmv)***	***Lost in offgas (%)***
Benzene	0.56	78	3.24	0.14	0.9
Toulene	0.31	92	3.83	0.09	0.4
Ethylbenzene	0.075	106.2	4.42	0.017	0.4
Xylene	0.08	106.2	4.42	0.017	0.3

Average biomass concentrations at the three SRTs were: 10 days - 3.2 $g.L^{-1}$, 30 days - 5.3 $g.L^{-1}$ and 60 days - 6.1 $g.L^{-1}$. Greater active biomass concentration has been reported to reduce emission by stripping by promoting biodegradation (Hsieh, 2000). Current results for Benzene and Toulene support this trend, whereas the data for Ethylbenzene and Xylene show no clear trend – a reflection of their lower concentrations in the feedwater. Losses to atmosphere appear to be independent of SRT, and so biomass concentration. The fate and pathways of removal are discussed in more detail in Section 5.3.2.

Results from the MBR trial (Table 5.4), where double the BTEX feedwater concentrations were employed cf. those of the porous pot trials, indicate an almost

negligible corresponding increase in absolute BTEX offgas levels, such that the % lost in the offgas is lower than for the porous pot trials.

Table 5.4 BTEX off-gas analysis, MBR trials (Biomass MLSS concentration 12 $g.L^{-1}$)

	Off gas conc (ug/L)	*MW*	*Conv. Factor*	*Off gas conc (ppmv)*	*Lost in offgas (%)*
Benzene	1.42	78	3.24	0.44	0.86
Toulene	0.85	92	3.83	0.22	0.96
Ethylbenzene	0.055	106.2	4.42	0.01	0.36
Xylene	0.071	106.2	4.42	0.02	0.26

Conversion factor basis:

$$mg/m^3 = \frac{P \times MW \times ppmv \times 1000}{(C \times T)} \qquad \textit{Equation 5.1}$$

Where:

P = Pressure in Atmospheres

MW = Molecular Weight

T = Absolute Temperature in degrees K

C = Molar Gas Constant => 82.05

R = atm x cm3/mole x T (PV=nRT)

As stated earlier the volatility of the compound will have a bearing on the rate at which it is stripped (Hsieh, 2000). Dimensionless Henry's constants *Hc* (air/water) for BTEX compounds are comparable: Benzene - 0.22; Toluene - 0.26; Ethylbenzene - 0.32; Xylenes - 0.29. The higher the *Hc* value the more likely the compound will be released. Comparing removals exhibited by both systems shows that there is little difference between the compounds, the volatility is likely not to be the controlling parameter.

Slightly better off gas results, in general displayed in MBR at higher loading rates, may be attributable to a number of factors. The higher biomass concentration of 12 $g.L^{-1}$ may yield lower emissions due to the promotion of adsorption and biodegradation, but the lower gas to liquid volume ratio in MBR cf. the porous pot, 1.2 $L.min^{-1}$ air flow in 3L liquid volume cf. 12 $L.min^{-1}$ in 45 L liquid in the MBR, is likely to be the greatest contributing factor. Hseih (2002) reported the effect influent air to liquid flow rates and emission factor (proportion of mass of the influent stream) for a range of volatile compounds (Figure 5.3). As expected, stripping increases with higher *Hc* and Q_G/Q_L.

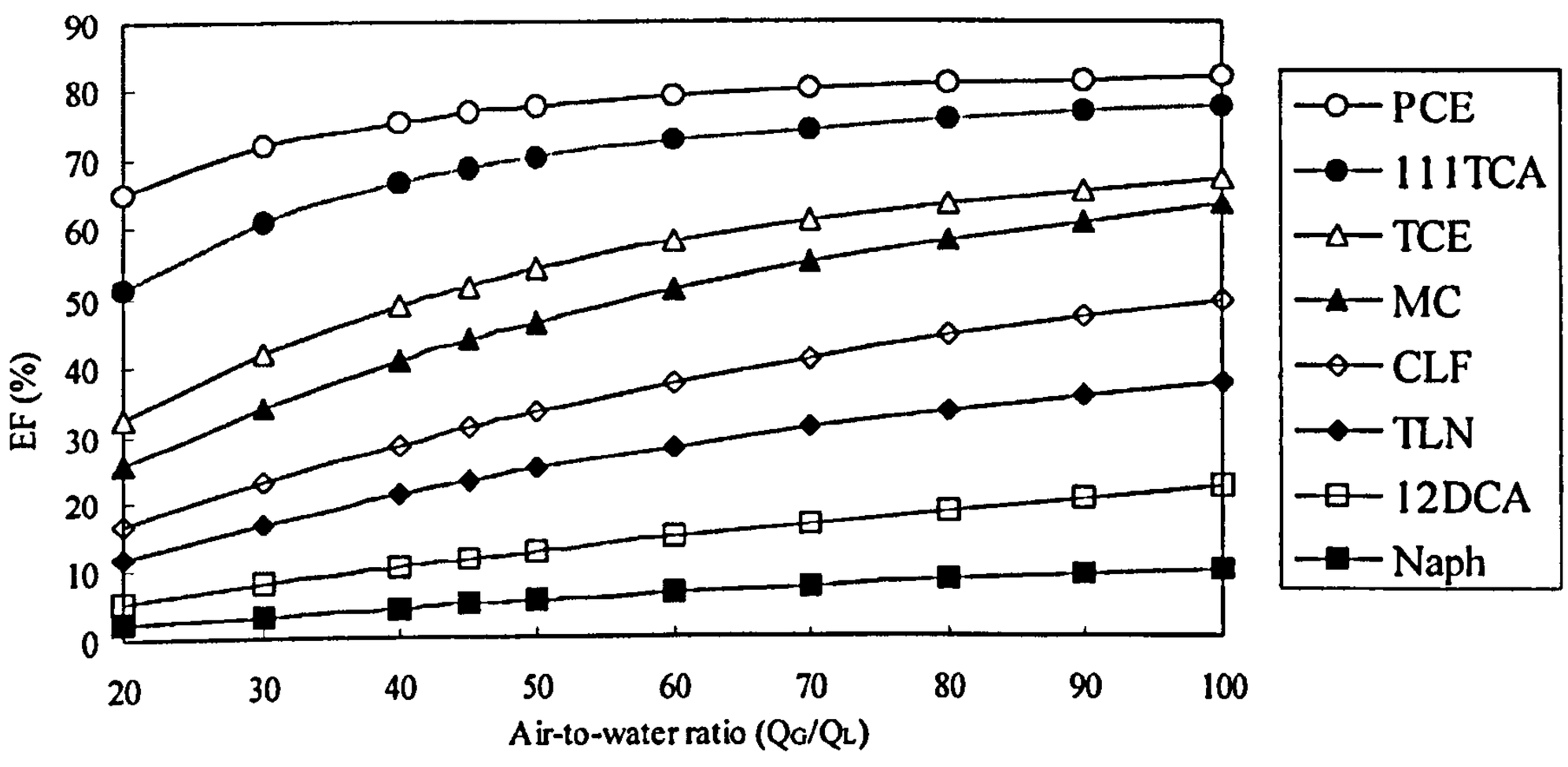

Figure 5.3 The effect of air to water ratio on the emission factor (Hsieh, 2000)

Toulene is reported to be approximately 30% removed by stripping at a Q_G/Q_L ratio of 100. Q_G/Q_L values for both systems in the current study are significantly higher than those reported; 576 for porous pot and 384 for MBR. However loss of toulene in the offgas only accounts for between 1 and 2% of its total loss from the system. The biodegradation rate must thus be more significant in this case.

Relatively high air flow rates were demanded in the current study by the need to maintain biomass in suspension and promote mixing. Ratios reported by Hsieh (2000) are for full scale diffused aeration systems. The results from the current study thus represent the worse case. Larger systems would employ lower Q_G/Q_L values, such that the proportion of stripping and emission could reasonably be expected to decrease.

5.3.2 BTEX mass balance

Liquid and gas phase analysis of BTEX compounds was conducted at the biomass concentration of 12 $g.L^{-1}$ to complete a species-specific balance and determine their fate during treatment. Although VOCs may be removed in the activated sludge process by adsorption, biodegradation and stripping (Namkung and Rittmann, 1987), the adsorption mechanism is not considered to be as significant as biodegradation and stripping since it is merely an intermediate step towards biodegradation (WEF, 1995).

Concentration and flow rates are shown in Table 5.5 for inlet (Table 5.5a) and outlet (Table 5.5b) streams respectively, with mass flow data across the process depicted in Figure 5.4. The BTEX influent concentrations in the gas phase are assumed to be zero in accordance with concentration measured in the blank air sample, which indicated all concentration values to be below the limit of detection (< 1 $\mu g.m^3$). Note that the mass balance ignores the sludge waste stream, since (a) the nature of this matrix makes it extremely difficult to assay for specific VOCs, and (b) trace concentrations of BTEX components in the sludge are of little practical significance, and would tend to zero with increasing sludge age.

Table 5.5a BTEX mass balance data, input

IN – Liquid phase	**Liquid concentration ug/L**	**Flow L/hr**	**Mass flow ug/hr**
Benzene	63470	1.875	118900
Toulene	33810	1.875	63400
Ethylbenzene	5840	1.875	10900
Xylene	10740	1.875	20100
IN – Gas phase	**Concentration ug/L**	**Flow L/hr**	**Mass flow ug/hr**
Benzene	<	720	0*
Toulene	<1	720	0*
Ethylbenzene	<1	720	0*
Xylene	<1	720	0*

*- Concentration in air assumed to be zero

Table 5.5b BTEX mass balance data, outlet

OUT - Liquid phase	**Liquid conc. ug/L**	**Flow L/hr**	**Mass flow ug/hr**	**% lost in permeate**
Benzene	519.4	1.875	974	0.82
Toulene	253.8	1.875	476	0.75
Ethylbenzene	24.9	1.875	46.7	0.43
Xylene	47.5	1.875	89	0.44
OUT – Gas phase	**Off gas conc. ug/L**	**Flow L/hr**	**Mass flow ug/hr**	**% lost in off gas**
Benzene	1.422	720	1023.8	0.86
Toulene	0.846	720	609.1	0.96
Ethylbenzene	0.0547	720	39.4	0.36
Xylene	0.07144	720	51.4	0.26

Results reveal a small loss to the atmosphere as described earlier, together with less than 1% of any BTEX compound lost in the permeate. Losses to atmosphere and in permeate total 1.7% for benzene and toluene, and ~0.8% for both ethylbenzene 0.79% and xylene.

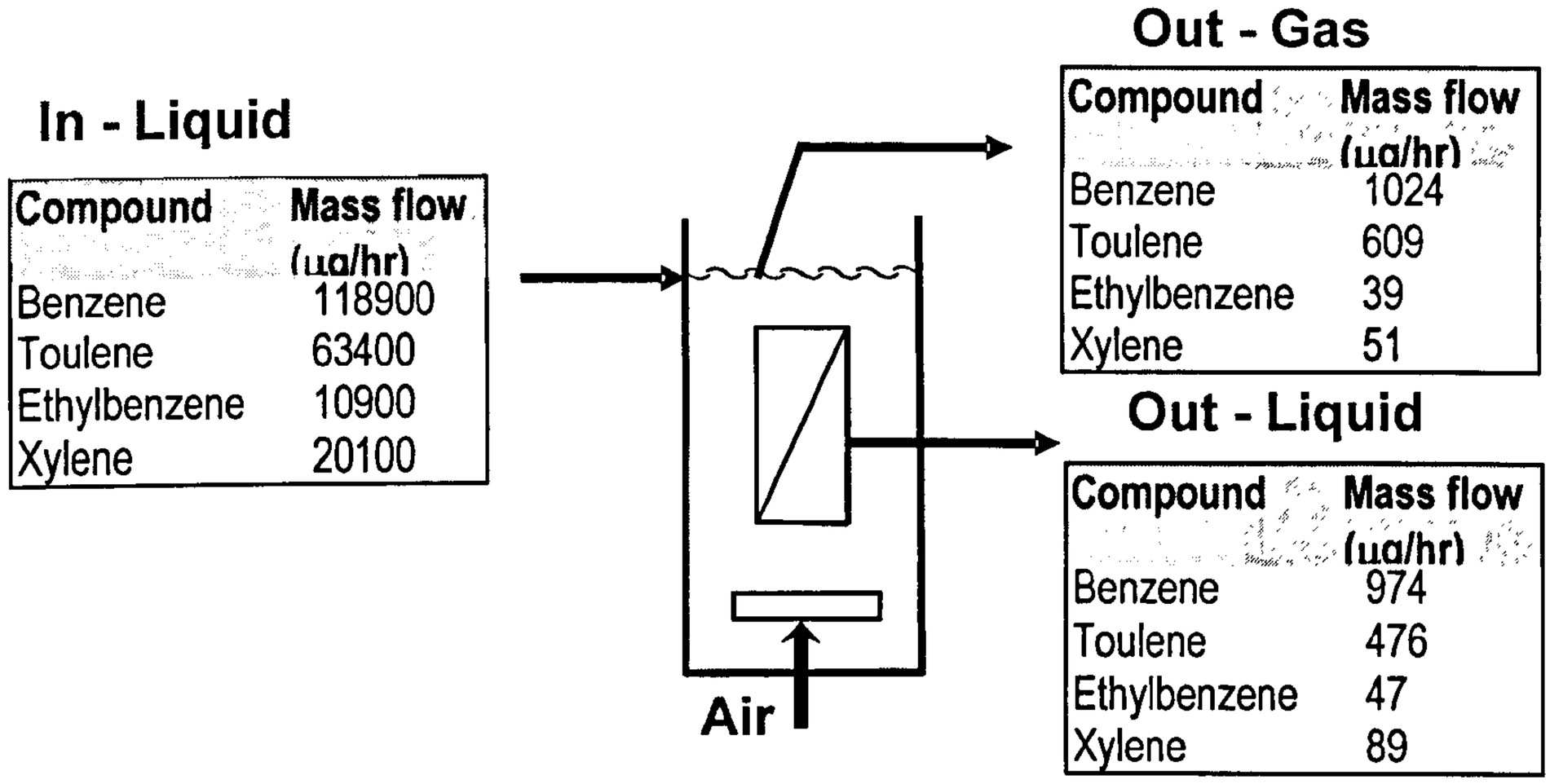

Figure 5.4 BTEX mass flow around MBR system

Figure 5.5 shows the effect of biomass concentration on toulene removal (Hsieh, 2000) at Q_G/Q_L ratio of 35. The effect is greatest at low biomass levels where emission by stripping is the dominant factor and biodegradation is less important. As biomass concentration increases biodegradation becomes the dominant removal mechanism with loss by emission of decreasing importance. At the highest concentration of 4 $g.L^{-1}$ biodegradation represents 85% of the total removal with loss from emission at around 14%. Results from the current study were carried out at a biomass concentration of 12 $g.L^{-1}$ and indicate loss by emission to account for ~1% of the total removal and biodegradation to be ~98%, considerably higher than the proportion predicted by Hsieh (2000) indicating an overestimation of the predicted rate of stripping compared to experimental values found in the present study.

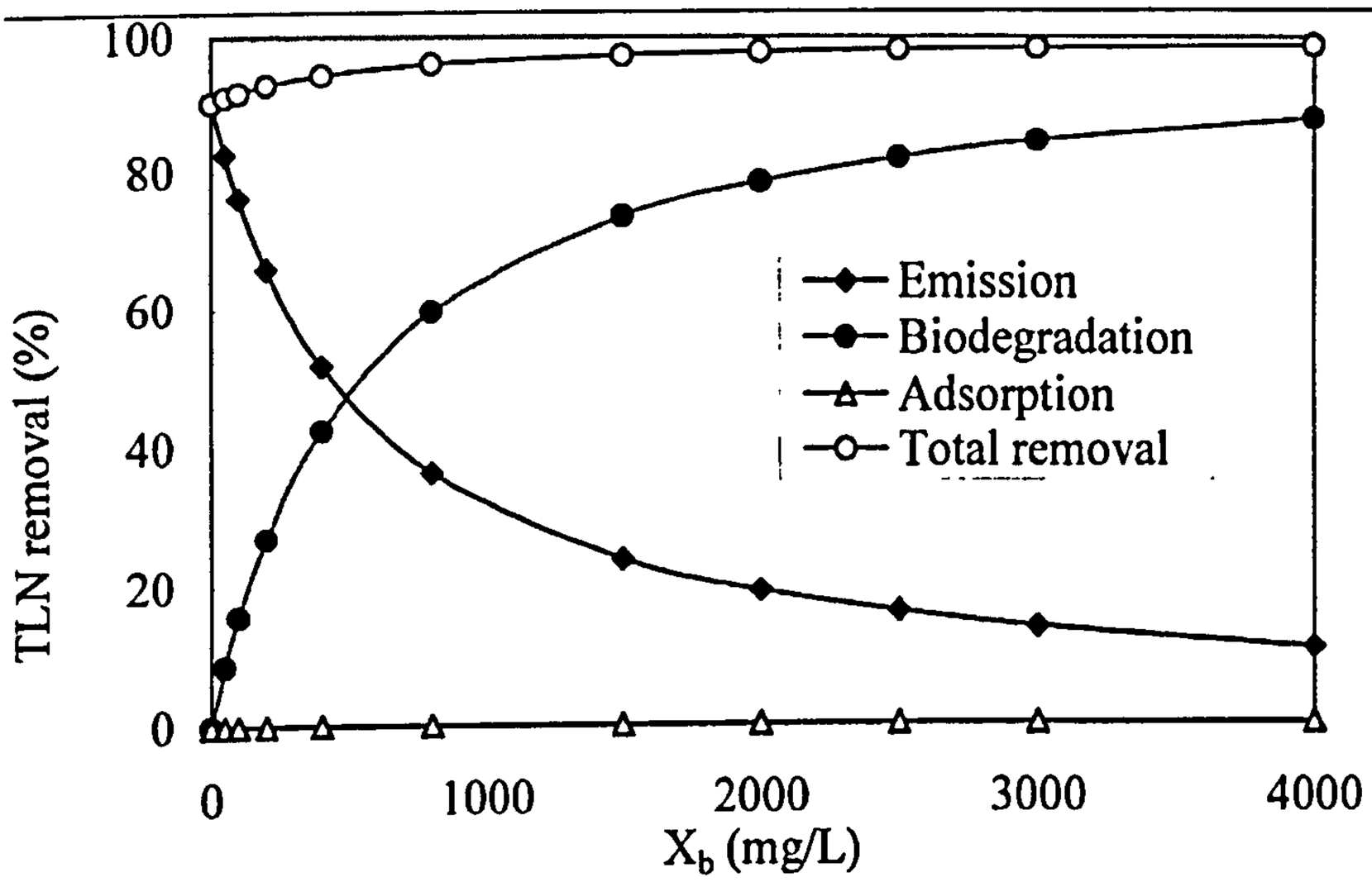

Figure 5.5 The effect of biomass concentration (Xb) on toluene (TLN) removal (Hsieh, 2000)

5.4 Treatment performance results summary

Results from analysis of the treatment performance indicate the following:

1. Both systems displayed excellent removal rates when challenged with two different feedwater matrices, attaining COD and TOC removal rates of between 90 and 97%
2. SRT has little effect on COD and TOC removal
3. Loss of BTEX to the atmosphere by stripping during aerobic treatment was not the dominant removal mechanism for either porous pot or MBR systems despite high air to liquid ratios. Values of emission to atmosphere and permeate for the MBR were similar in magnitude, being between 0.7 and 1.7% with toulene and benzene demonstrating the greatest physical loss and the poorest degradation and ethylbenzene and xylene displaying the lowest physical loss.

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6 Biomass Characterisation

6.1 Introduction

The physical and chemical properties of the biomass that is developed in an MBR during operation will have an effect on both treatment performance and fouling. The concentration and impact on fouling (Chapter 7) will be examined by operating the system under different conditions.

The effect of SRT on biomass characteristics is reported in Section 6.2 including MLSS and MLVSS, CST and particle size analysis and SMP and EPS concentration.

Oxygen uptake rates have been determined by respirometry in order to find the activity of the biomass under different operating conditions and are reported in Section 6.3.

All analysis carried out has been made under steady state conditions defined as twice the sludge age (Smith *et al.* 2002; Rossenberger and Kraume 2002) and at 24hr HRT.

Finally community dynamics and abundance are examined by total cell counts and DGGE and are presented in Section 6.4.

6.2 Physical and chemical properties of the biomass

6.2.1 MLSS and MLVSS

The MLSS concentration of biomass developed at the range of SRTs examined in the porous pot and MBR system are displayed in Tables 6.1 and 6.2.

Table 6.1 Porous Pot biomass MLSS and MLVSS characteristics

Determinant	***Concentration [SD]***		
	10 day SRT	***30 day SRT***	***60 day SRT***
Suspended Solids ($mg.L^{-1}$)	3.2 [0.36]	5.3 [0.68]	6.1 [0.4]
Volatile Suspended Solids ($mg.L^{-1}$)	2.6 [0.4]	4.6 [0.57]	5 [0.73]

Table 6.2 MBR biomass MLSS and MLVSS characteristics

Determinant	***Concentration [SD]***		
	Target 6g.L^{-1}	***Target 12g.L^{-1}***	***Target 18g.L^{-1}***
Suspended Solids ($mg.L^{-1}$)	6.2 [0.8]	12.55 [1.8]	17.4 [1.3]
Volatile Suspended Solids($mg.L^{-1}$)	5.4 [0.7]	11.36 [1.5]	15.9 [1.2]

Operation in the porous pot system at fixed SRTs resulted in higher biomass MLSS concentration at longer sludge age as expected since sludge wastage is lower. The increase in sludge age from 30 to 60 days resulted in only slightly higher MLSS concentration.

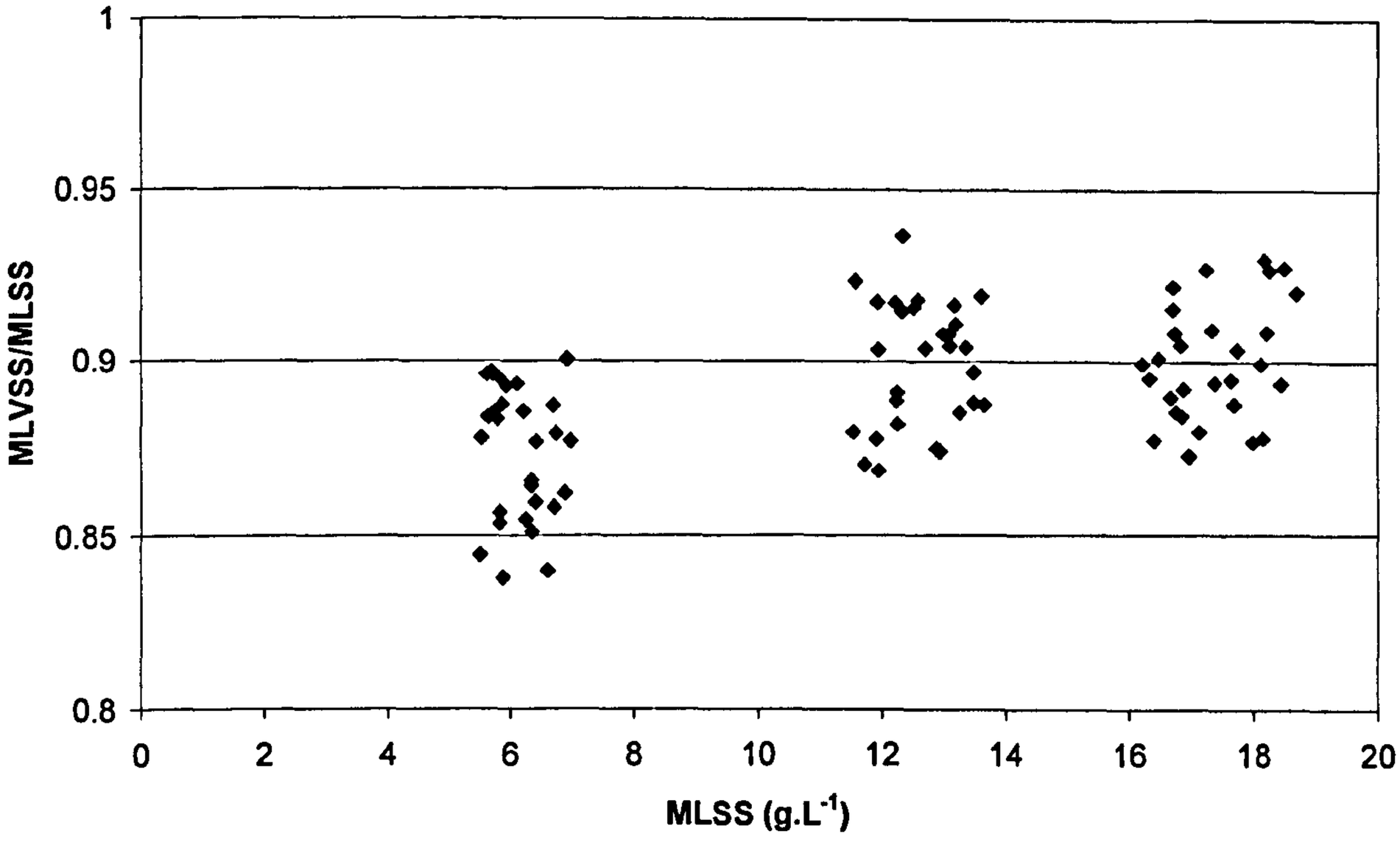

Figure 6.1 MLVSS:MLSS ratio at a range of biomass MLSS concentrations in MBR system

The MLSS:MLVSS ratio defines the organic content of the sludge and ranges between 0.83 and 0.94 (Figure 6.1). Under long sludge ages associated with high biomass MLSS concentrations in the study a build up of non-volatile solids could be expected under low sludge wastage operation. However Rosenberger *et al.* (1999) found that during 3 years operation under zero wastage conditions that there was no apparent decrease in the volatile solids content. During trials at a range of SRTs Smith *et al.* (2002) found that the MLVSS:MLSS ratio in a submerged MBR treating municipal wastewater displayed a small increase from 0.84 to 0.89 when operated at 4 and 20 day SRT respectively.

6.2.2 CST

The CST is used as an indication of sludge dewaterability. Results at 6 $g.L^{-1}$ show both higher absolute and more variable values as shown in Figures 6.2 and 6.3.

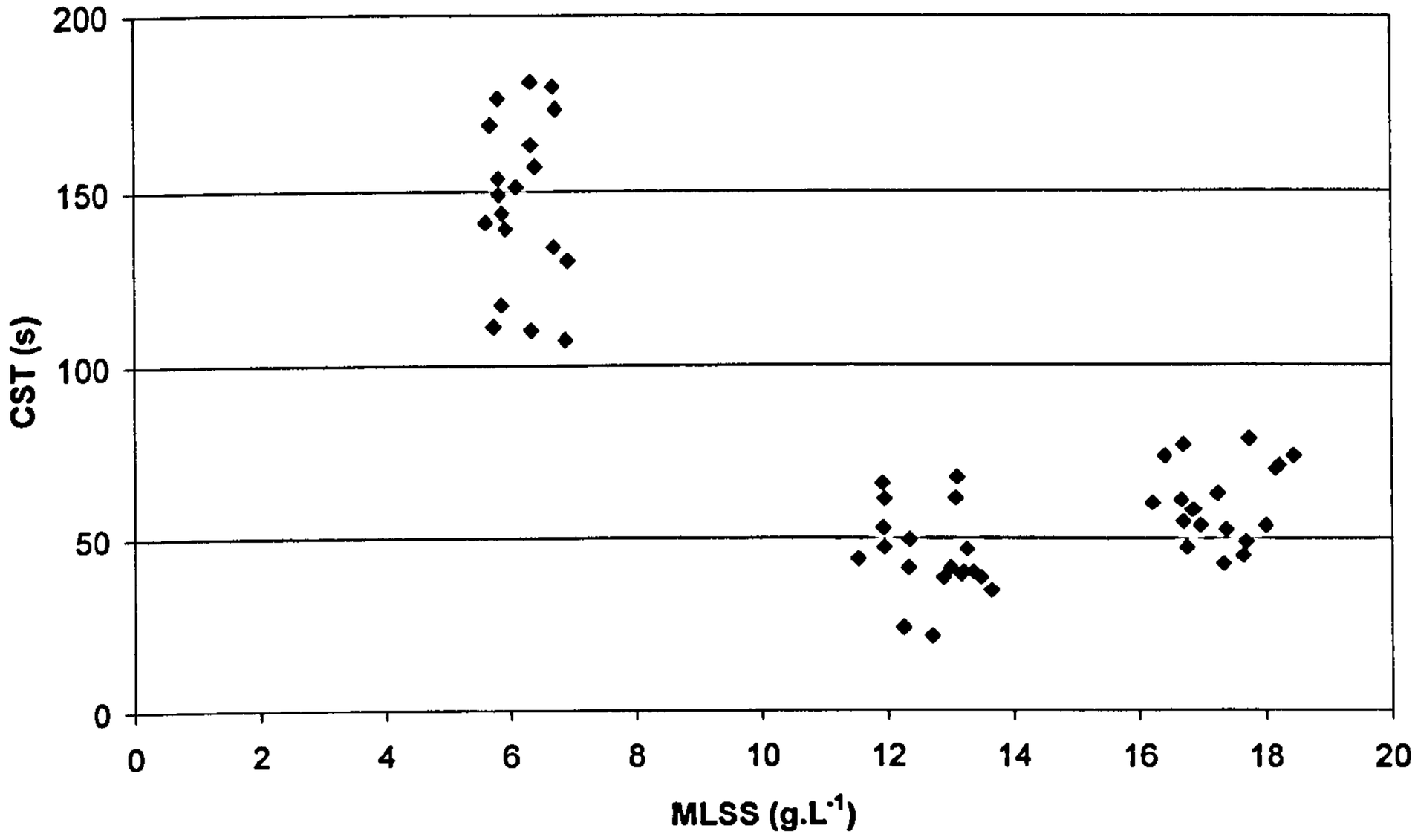

Figure 6.2 CST values at a range of biomass MLSS concentrations MBR system

In contrast to other studies (Houghton *et al.* 2002) an exponential relationship between MLSS concentration and CST was not evident. Bouhabila *et al.* (1998) found dewaterability to increase with increasing sludge age. When normalised for MLSS concentration difference between the two higher biomass concentrations and 6 $g.L^{-1}$ becomes even more evident as seen in Figure 6.3 below.

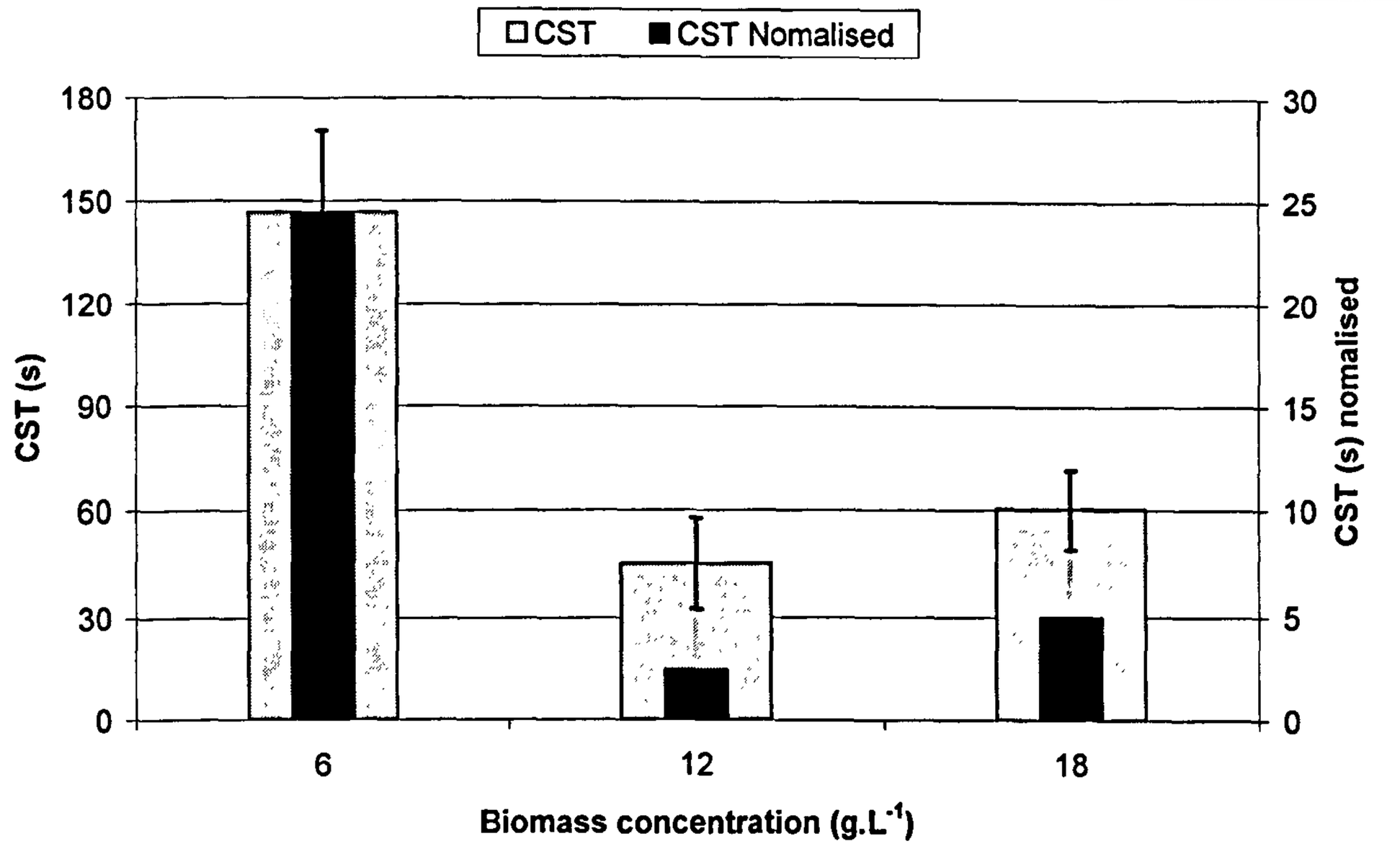

Figure 6.3 CST values at a range of biomass MLSS concentrations MBR system (mean and standard deviation)

6.2.3 Particle size

Results from particle size analysis of the MBR biomass is shown in Figures 6.4 and 6.5. Median particle size (d_{50}) values were 87.1, 103.8 and 77.9 μm for trials at 6, 12 and 18 $g.L^{-1}$ respectively. Data shows no clear trend between biomass MLSS concentration and the mass median particle size (Figure 6.4 and 6.5).

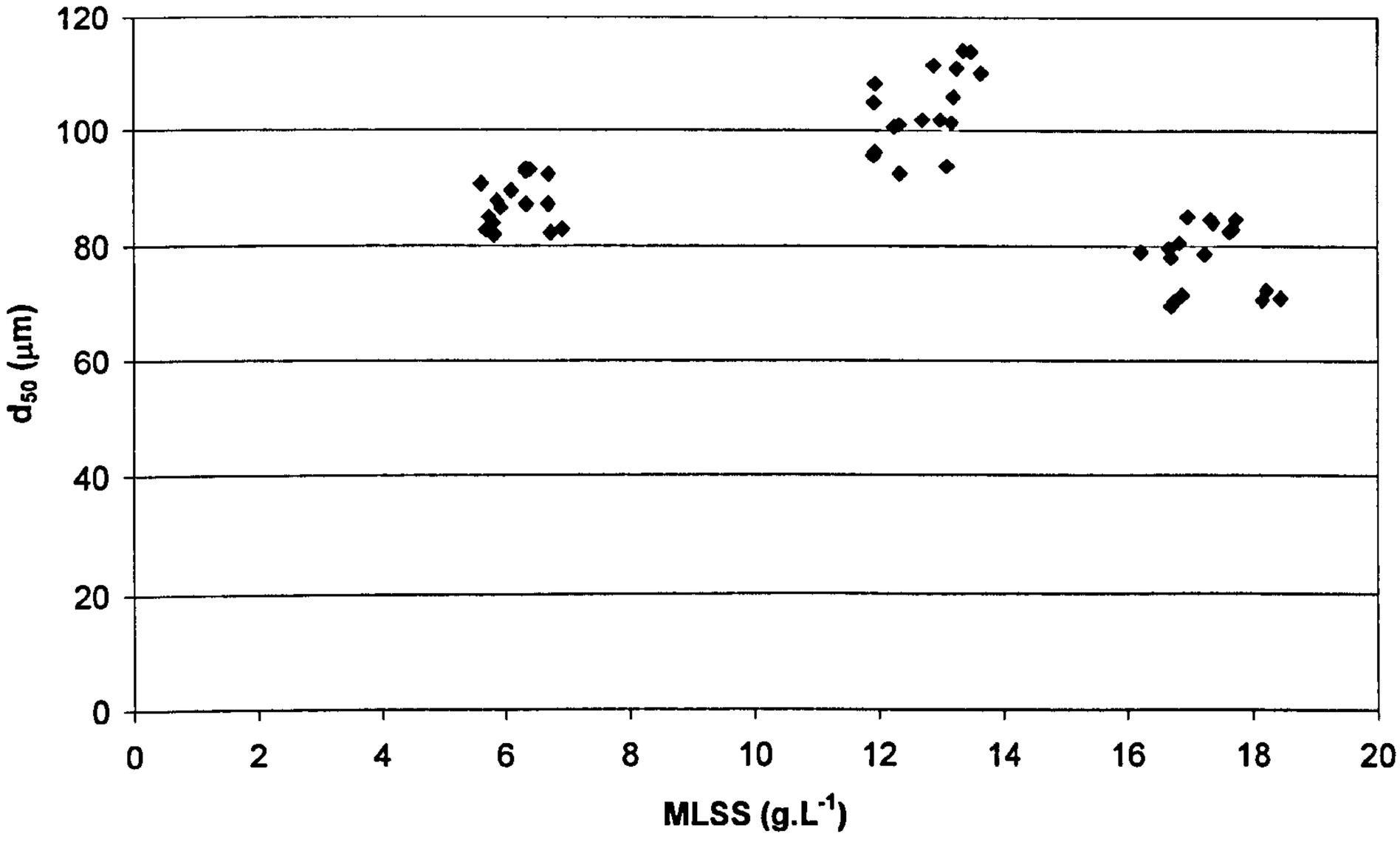

Figure 6.4 Median particle size values at a range of biomass MLSS concentrations MBR system

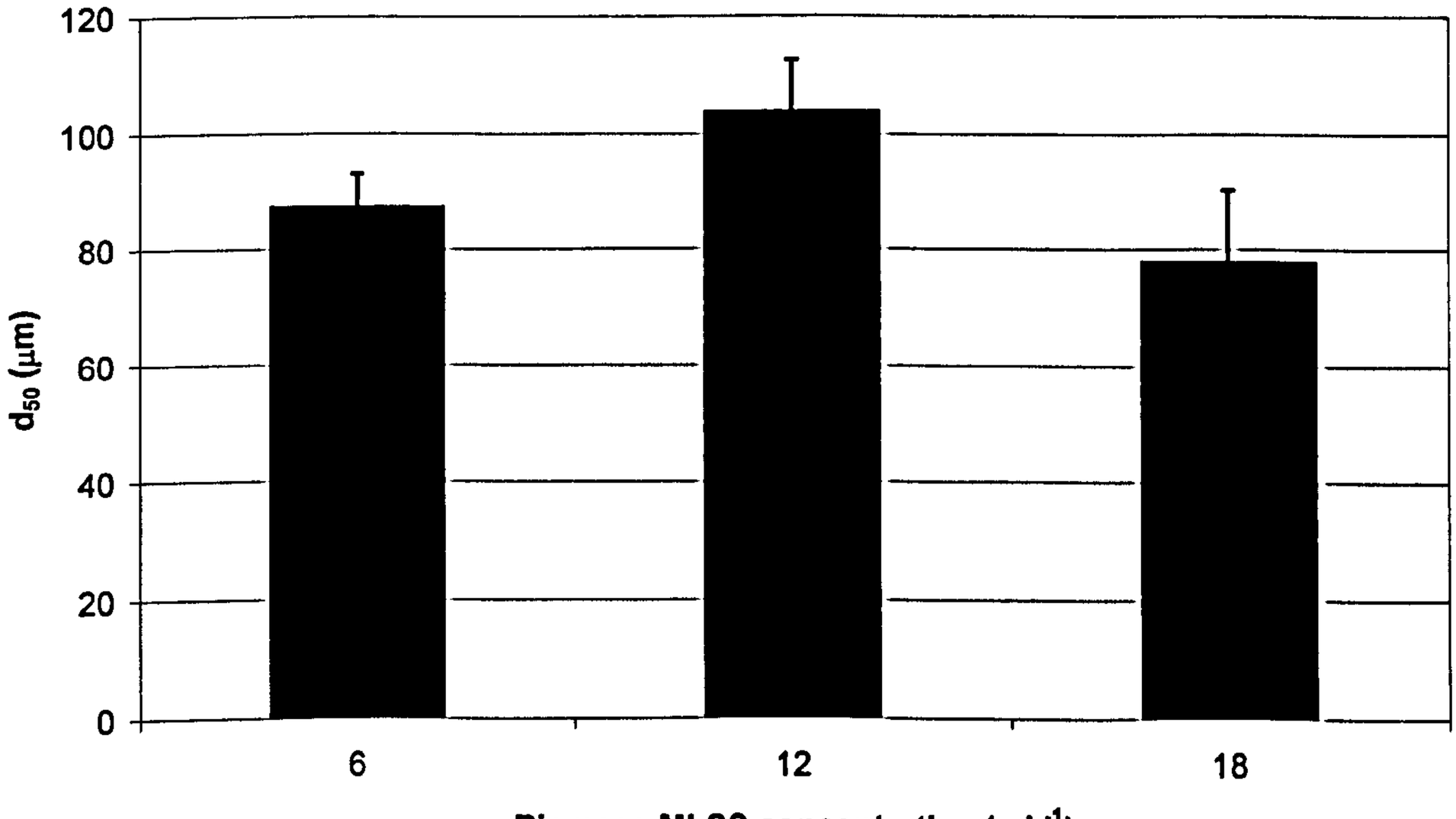

Figure 6.5 Median particle size values at a range of biomass MLSS concentrations MBR system (mean and standard deviation)

6.2.4 EPS and SMP

EPS and SMP are widely considered to be major fouling components of the biomass are known to provide a substantial barrier to filtration, generating up to a 6 - 7 times increase in internal fouling (Laspidou and Rittman, 2002), and up to 90% of the resistance of the cake layer (Chang *et al.* 2002).

Fouling is usually attributed to organic accumulation on or in the membrane in the form of extracellular polymeric substances (EPS) or soluble microbial products (SMP). The former refers to a complex mixture of polysaccharides, proteins, lipids and nuclei acids which form a highly hydrated gel matrix. Whereas, soluble microbial products (SMP) are defined as soluble cellular components that are released during cell lysis and then diffuse through the cell membrane, are lost during synthesis or are extracted for some purpose. According to the unified theory for EPS, SMP, and biomass proposed by Laspidou and Rittman (2002), SMP represent the same fraction as soluble EPS.

Table 6.3 Summary of SMP and EPS content of biomass

Determinant	***Concentration [SD]***		
	6g.L^{-1}	***12g.L^{-1}***	***18g.L^{-1}***
Soluble microbial products (SMP_c) Carbohydrate (mg.L^{-1})	11.35 [7.4]	17.26 [4.9]	22.7 [7.2]
Soluble microbial products (SMP_p) – Protein (mg.L^{-1})	18.7 [9.6]	34.52 [8.2]	48.5 [13.7]
Extracellular polymeric substances (EPS_c) – Carbohydrate (mg.g^{-1})	13.6 [2.7]	10.5 [3.8]	9.3 [5.1]
Extracellular polymeric substances (EPS_p) – Protein (mg.g^{-1})	20.3 [5.8]	31.1 [8.64]	37.3 [12.4]

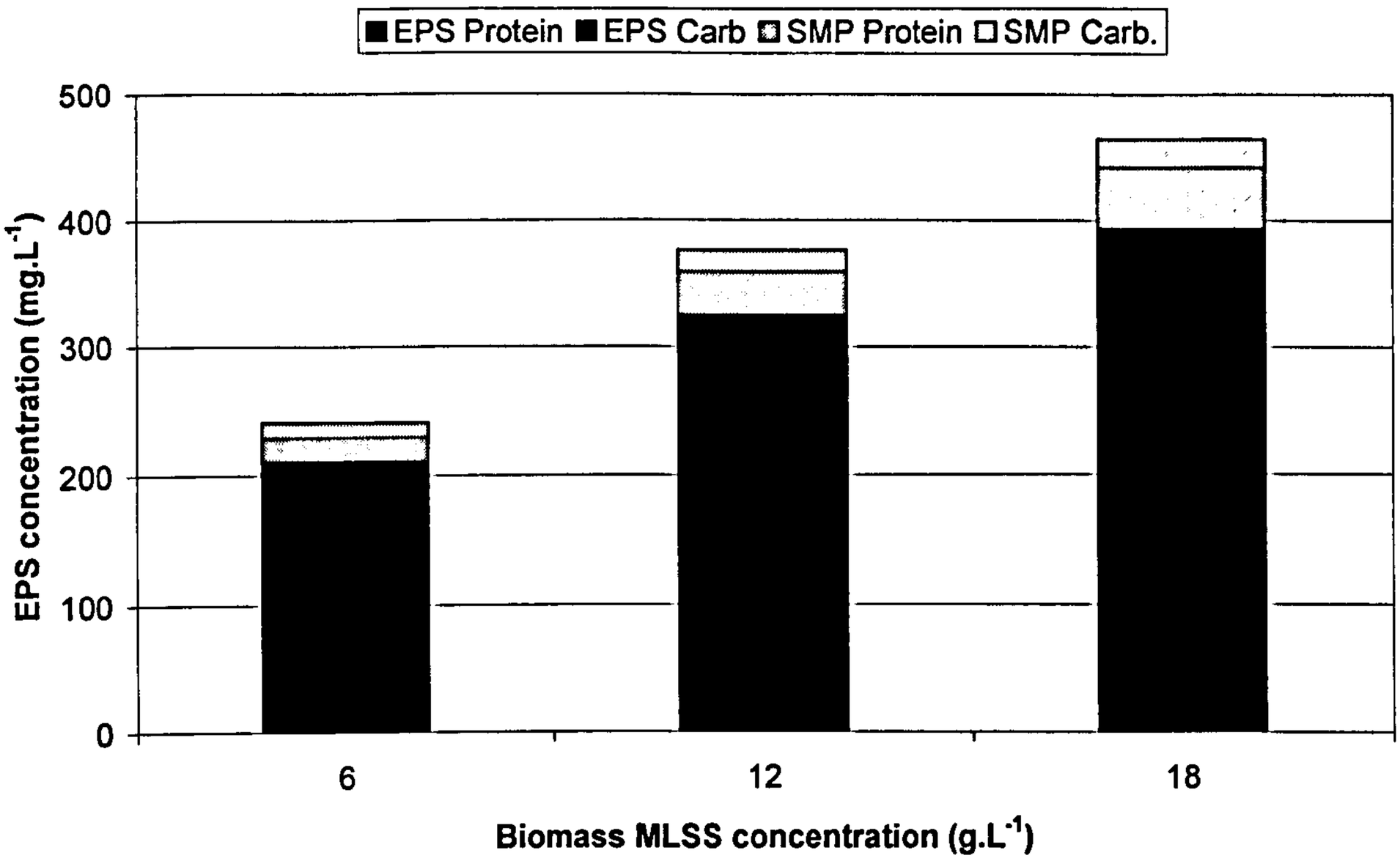

Figure 6.6 EPS and SMP values (expressed as $mg.L^{-1}$) at a range of biomass MLSS concentrations MBR system

Because EPS determination is carried out by extraction from the sludge phase and is not solution it may be expressed as mg per g of MLSS. The results are shown in Figure 6.7.

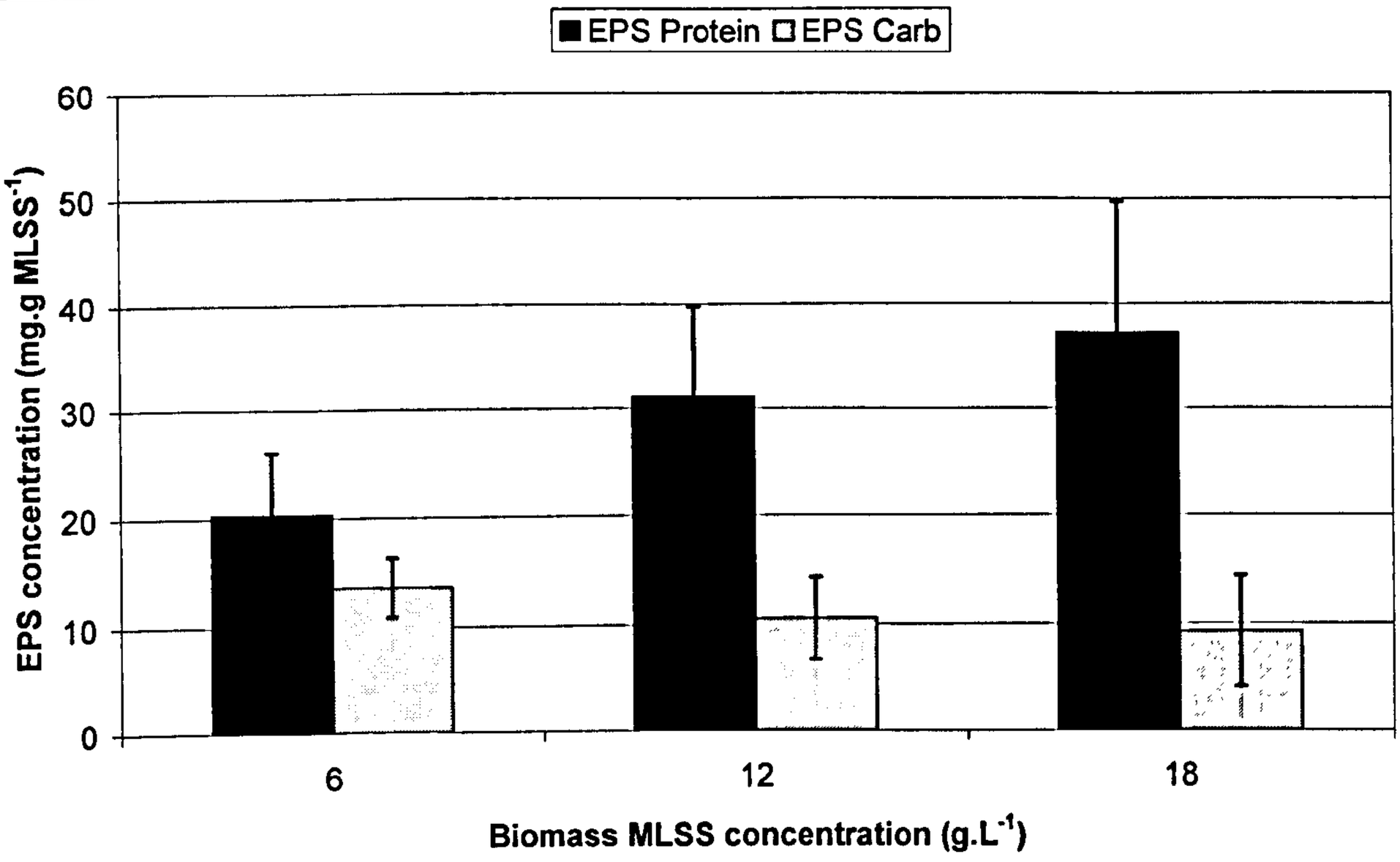

Figure 6.7 EPS values (expressed as mg.g $MLSS^{-1}$) at a range of biomass MLSS concentrations MBR system (mean and standard deviation)

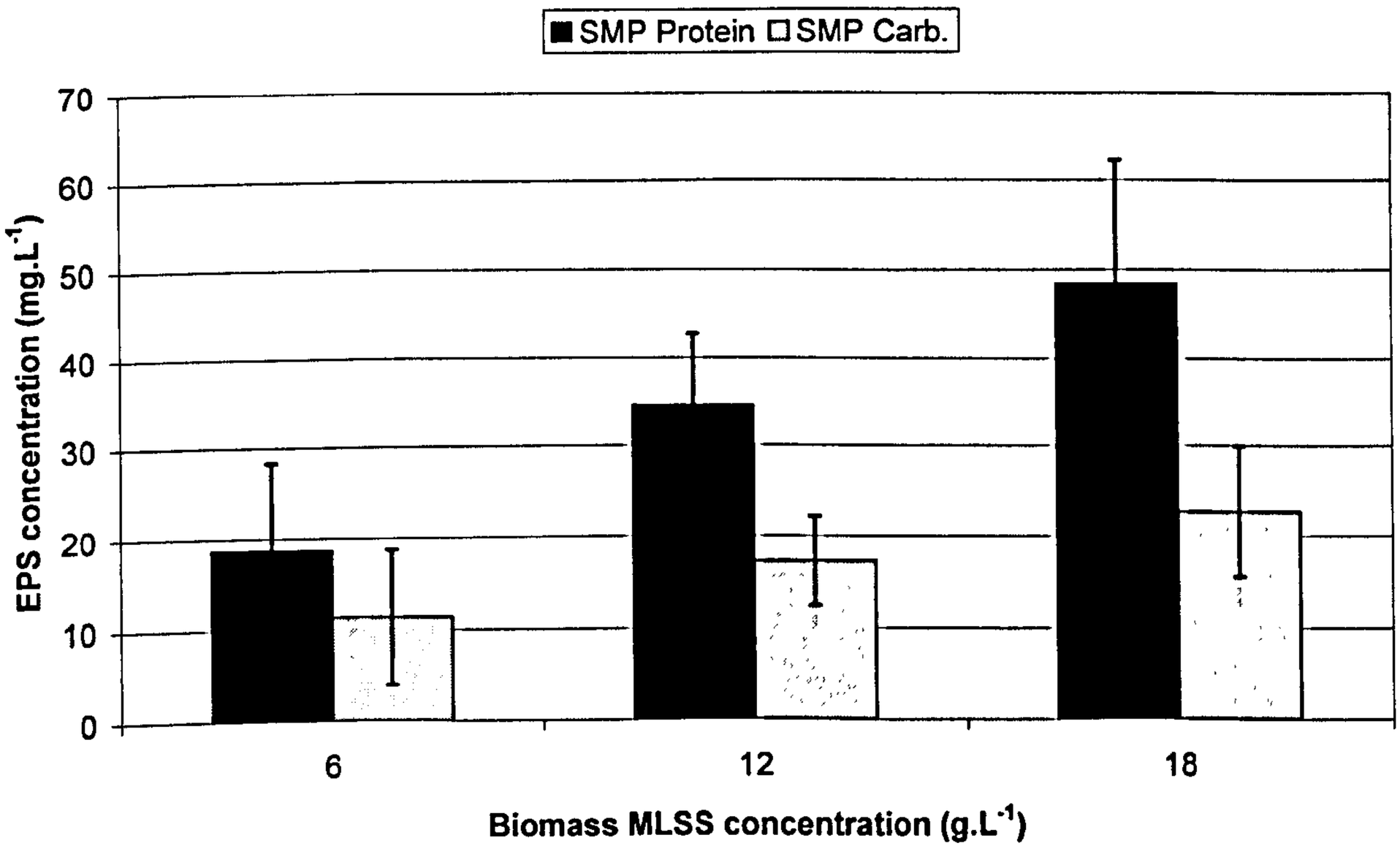

Figure 6.8 SMP values at a range of biomass MLSS concentrations MBR system

At increased biomass MLSS concentration (and so longer sludge age) the sum of SMP and EPS expressed as $mg.L^{-1}$ increased (Figure 6.6). Furthermore both carbohydrate and protein fractions of both SMP and EPS were higher at higher biomass MLSS concentrations (Table 6.3 and Figure 6.8).

The protein content of SMP and EPS was the dominant fraction with higher absolute and normalised values apparent across all biomass concentrations compared to carbohydrate concentrations.

At increasing biomass MLSS concentrations the normalised protein EPS concentration increased at increasing MLSS concentrations from 20.3 to 31.1 and 37.3 $mg.g\ MLSS^{-1}$ at target biomass MLSS concentrations of 6, 12 and 18 $g.L^{-1}$ respectively. Lee *et al.* (2003) reported a similar trend with increasing protein fraction of EPS at longer sludge ages from 20 to 60 days SRT.

Conversely the normalised carbohydrate EPS concentration decreased with increasing MLSS and SRT from 13.6 to 10.5 and 9.3 $mg.g\ MLSS^{-1}$ at target biomass MLSS concentrations of 6, 12 and 18 $g.L^{-1}$ respectively, also agreeing with Lee *et al.* (2003) observation that the carbohydrate concentration decreased.

6.3 Oxygen uptake rates

Respirometric tests to find the oxygen uptake rate can be used as a measure of the biological activity of microorganisms. Both the oxygen uptake rate (OUR) and the specific oxygen uptake rate (SOUR) are shown below for each of the systems in Table 6.4 and 6.5

Table 6.4 Oxygen uptake rates Porous Pot system [standard deviation]

SRT (days)	MLVSS ($g.L^{-1}$)	OUR ($mg\ O_2.L.h^{-1}$)	SOUR ($mg\ O_2.g\ MLVSS.h^{-1}$)
10	2.6 [0.4]	14 [1.5]	4.7
30	4.6 [0.6]	19.8 [1.9]	4
60	5 [0.7]	23.65 [1.8]	3.9

Table 6.5 Oxygen uptake rates MBR system [standard deviation]

SRT (days)	MLVSS ($g.L^{-1}$)	OUR ($mg\ O_2.L.h^{-1}$)	SOUR ($mg\ O_2.g\ MLVSS.h^{-1}$)
10	5.4 [0.7]	30.2 [2.5]	5.6
21	11.4 [1.5]	52.7 [5.7]	4.6
31	15.9 [1.2]	71.6 [6.2]	4.5

In both systems the SOUR reduces slightly at longer sludge ages indicating slightly lower biological activity at longer sludge ages, from 4.7 to 3.9 mg O_2.g MLVSS.h^{-1} in the porous pot system and from 5.6 to 4.5 mg O_2.g MLVSS.h^{-1} in the MBR.

Han *et al.* (2005) studied the effect of sludge activity and sludge age in a submerged MBR treating a synthetic municipal wastewater. The authors noted little change in SOUR with sludge ages between 30 and 70 days with reported values of 3.41, 3.45, 3.5 mg O_2.g MLSS.h^{-1} at SRT of 30, 50 and 70 days respectively. It was only at a prolonged SRT of 100 days the SOUR decreased to 2.7 mgO_2.g MLSS.h^{-1}.

6.4 Microbial abundance and diversity

The microbial abundance and diversity of the system was compared to those of another pilot scale MBR being operated initially fed with municipal wastewater and changed to landfill leachate. Landfill leachate is an industrial feedwater characterised by high COD and ammonia concentrations. Unlike the present study the leachate fed bioreactor was operated with real wastewater rather than synthetic analogue and is subject to changes in feedwater properties. The comparison between the microbial abundance and diversity of the two bioreactors is made in the following sections. Analysis of the produced water fed MBR was made during steady state operation at biomass MLSS concentration of 12 $g.L^{-1}$ and continued as the SRT was increased to attain target MLSS concentration of 18 $g.L^{-1}$.

6.4.1 Bacterial abundance within municipal-leachate and produced water fed MBRs

Throughout the period of analysis, bacterial abundance (represented by total cell counts) remained relatively stable within the produced water fed MBR with a marginal increase observed from day 91. This small increase coincides with an increase in the sludge retention time from approximately 21 days (days 0 to 84) to around 31 days (days 91 to 154) (Figure 6.9).

The municipal-leachate fed bioreactor showed much greater variation (Figure 6.9). The switch in feedwater sources occurred between days 56 and 60 resulting in a decrease in bacterial abundance reaching a minimum value 20 days after change in feedwater.

Following the introduction of leachate bacterial abundance had not returned to level found previously until a further 100 days.

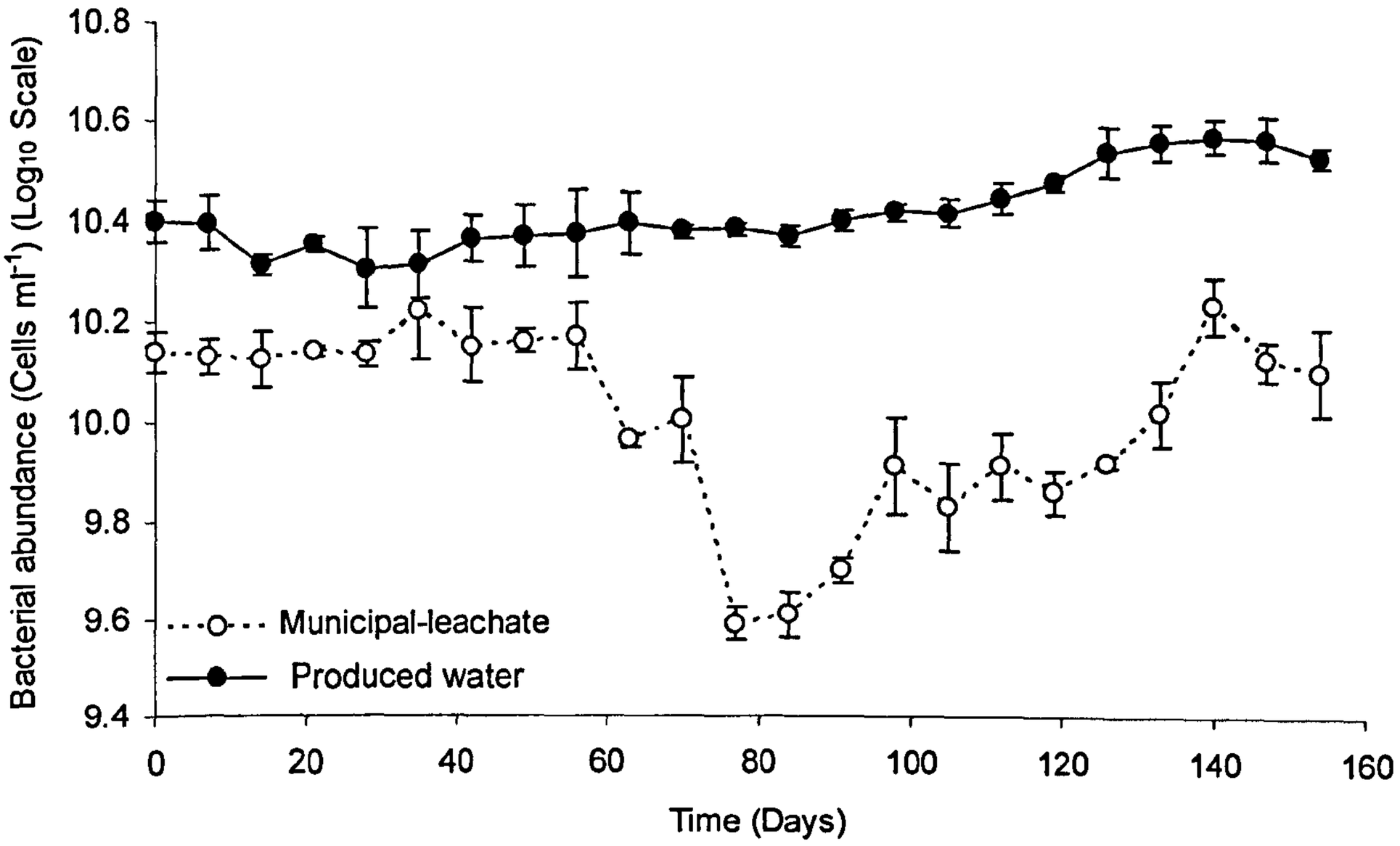

Figure 6.9 Bacterial abundance of produced water and municipal-leachate fed bioreactors.

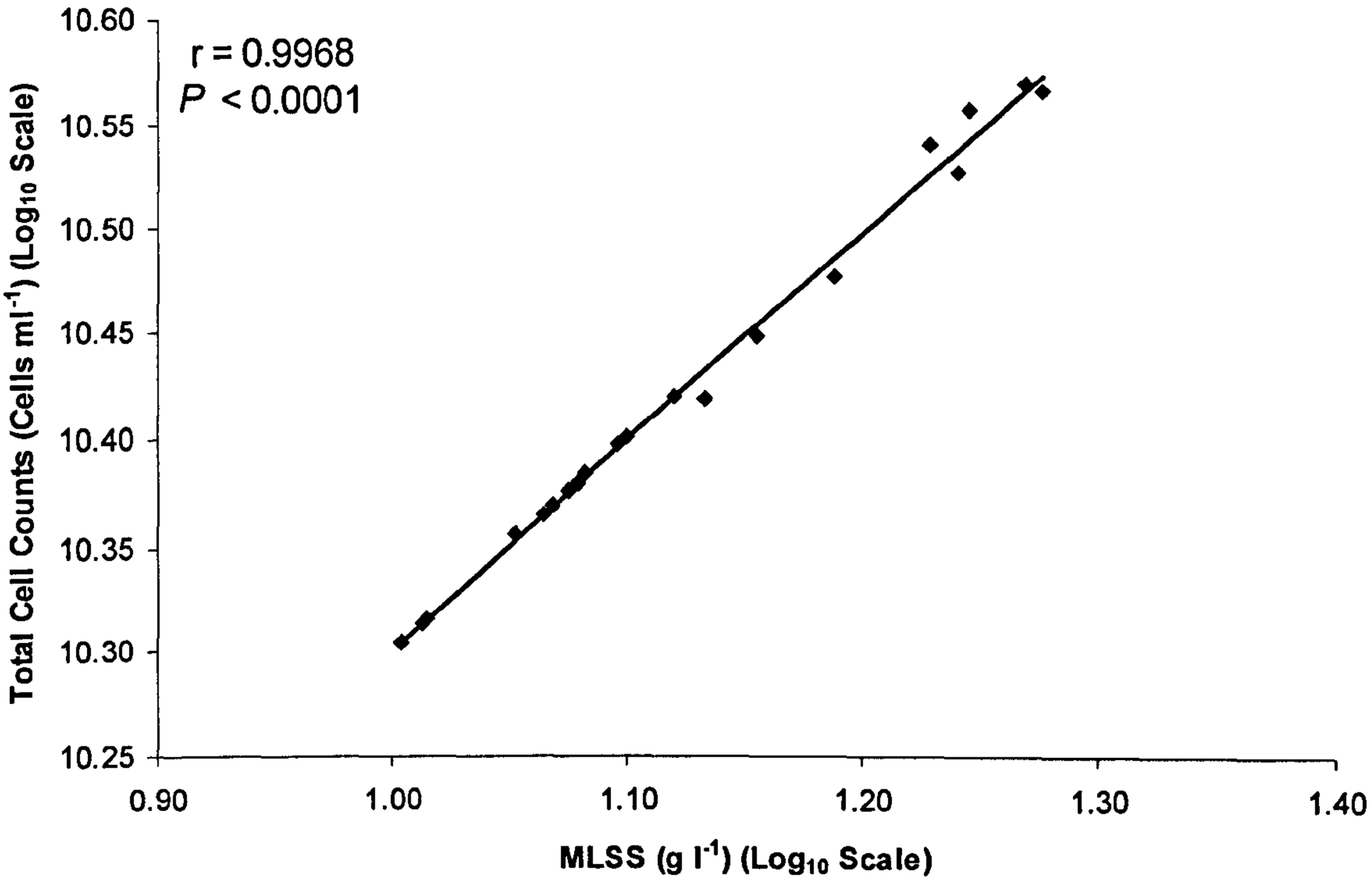

Figure 6.10 Trend between bacterial abundance and mixed liquor suspended solids produced water fed bioreactor

Bacterial abundance showed good correlation with MLSS concentration indicating higher cell counts at higher biomass MLSS concentration.

6.4.2 Bacterial community dynamics

Denaturing gradient gel electrophoresis (DGGE) provides an indication of community complexity though the production of individual bands of DNA producing a molecular "finger print", with each band corresponding to a specific bacterial species. DGGE separates DNA samples based on differences in nucleic acid sequence rather than size and is determined by the individual mobility of denatured DNA across the gel. The number of unique bands produced as a result of varying degrees of denaturisation is representative of the individual species of bacteria present in the community. This

fingerprint allows variations in community structures at different times within a reactor to be observed, giving a detailed picture of species dynamics.

Genotypic profiling by DGGE profiling and subsequent cluster analysis was employed to monitor bacterial community dynamics within both the municipal-leachate and the produced water fed MBR. Dendrograms were constructed using unweighted pair group mathematical averages clustering and showing the relationship between profiles by pair wise comparison of band presence and position (Figure 6.11)

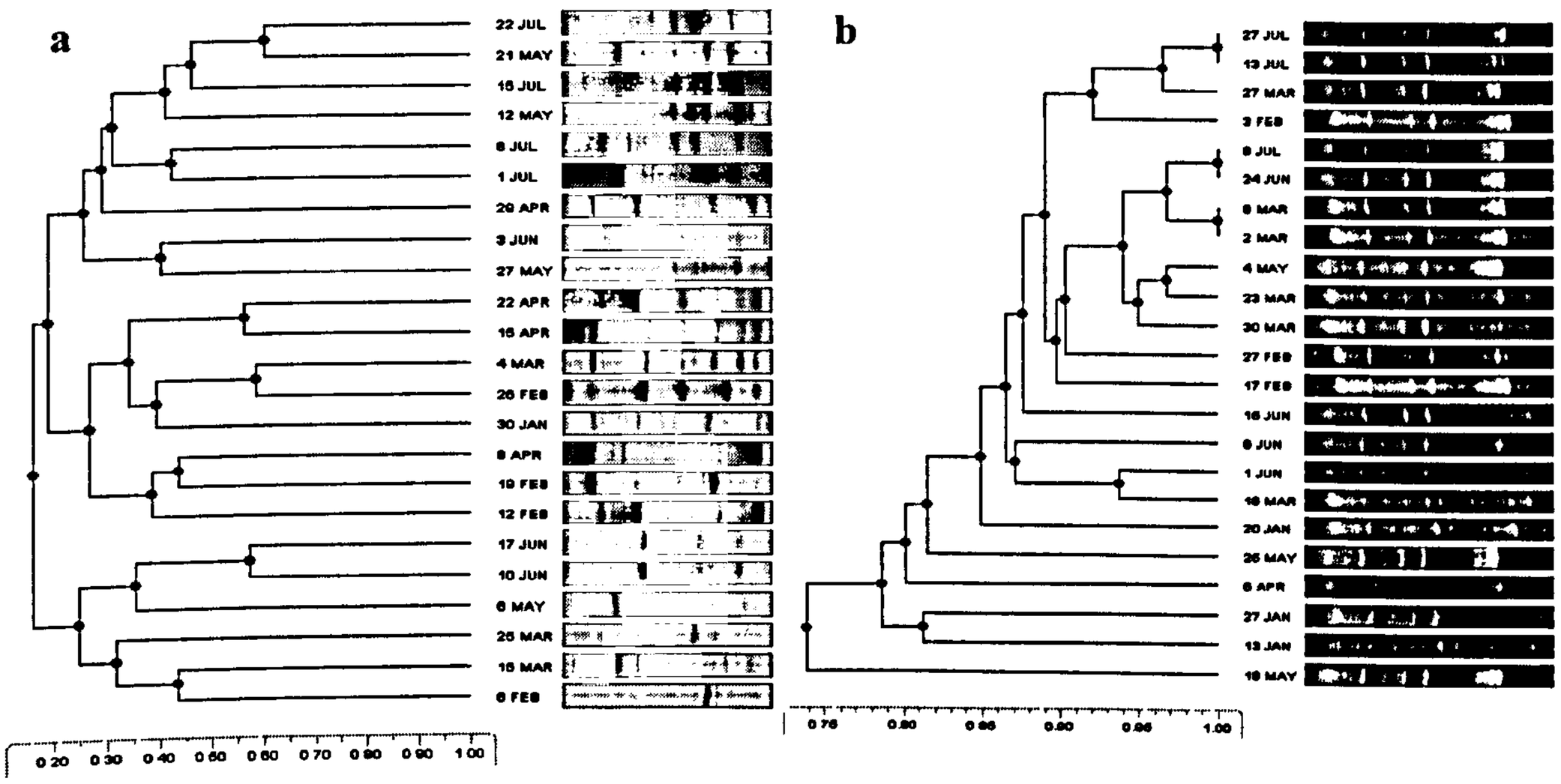

Figure 6.11 Dendrogram representing temporal changes in DGGE bacterial community profiles in a) municipal-leachate and b) produced water membrane bioreactors

Community profiles within the produced water fed MBR were high conserved over time where in contrast the municipal-leachate fed MBR showed more divergent community dynamics characterised by deeply forked branches in the dendrogram. Introduction of the leachate feedwater was made on day 56, but no difference is discernible between the two feedwaters indicating neither wastewater applied an influence on the community profile.

6.4.3 Changes in species richness over time

The number of bands on DGGE profiles was used to infer species richness (S) within the two MBR (Jackson *et al.* 2001). Species richness within the produced water fed MBR was consistent and the cumulative species curve was relatively flat, indicating the establishment of a stable community within the system (Figure 6.12 b).

Within the municipal-leachate MBR, species richness was highly variable, suggesting divergent community dynamics over time and a high species extinction rate (Fig. 6.12 a). In addition, the cumulative species curve was comparatively steep suggesting high influx (immigration) rates of new species and therefore a rapid turnover of bacterial species within that system.

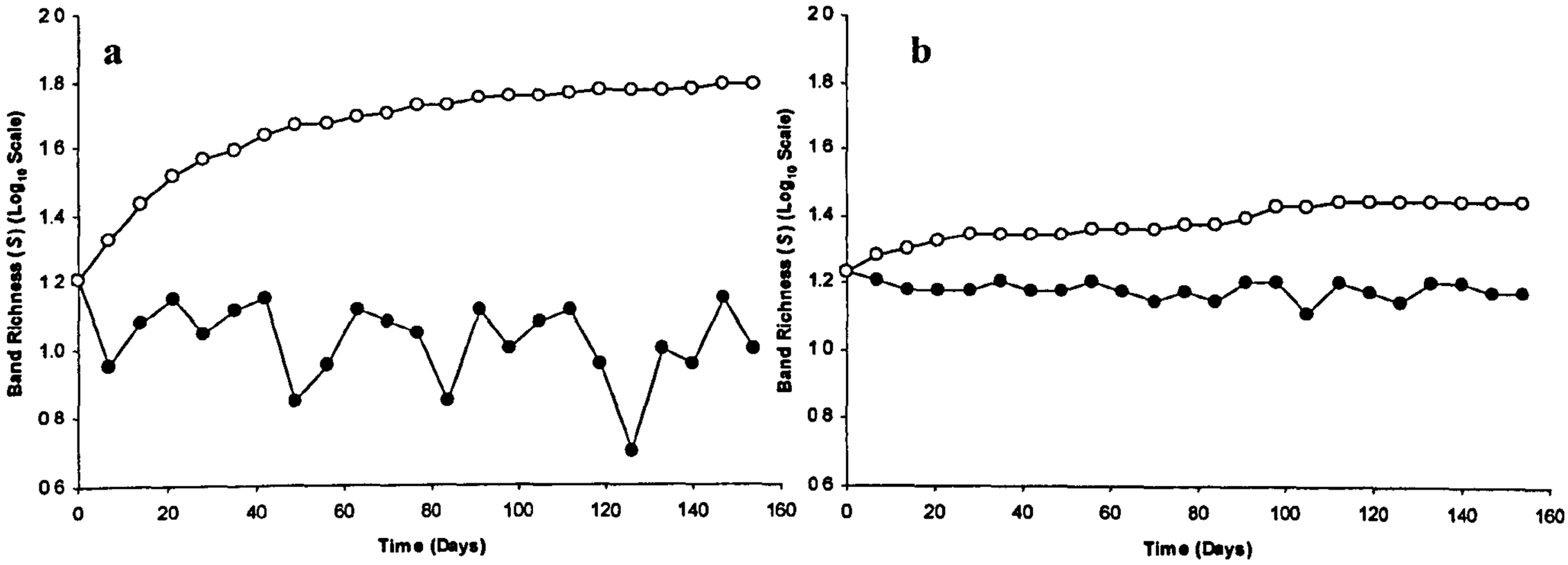

Figure 6.12 Changes in the band ('species') richness (S) of bacterial communities in a) municipal-leachate and b) produced water MBR. Solid circles indicate richness and open circles denote cumulative richness on the temporal scale.

6.4.4 Comparison of meta community compositions

Intensities of DGGE bands within genotypic profiles were used to infer relative species abundances and from this it was possible to plot the rank/abundance curves for the communities contained within both membrane bioreactors (Jackson, et al. 2001; van der Gast, et al. 2005). Relative abundance was inferred from intensity of DGGE bands (y-axis) and species ordered by rank abundance (most abundant first) (x-axis) (Figure 6.13)

The produced water fed bioreactor displayed a steeper rank/abundance curve than the municipal-leachate fed which was characterised by high evenness (flatter slope). Therefore the produced water fed bioreactor displayed a specialised community dominated by fewer species.

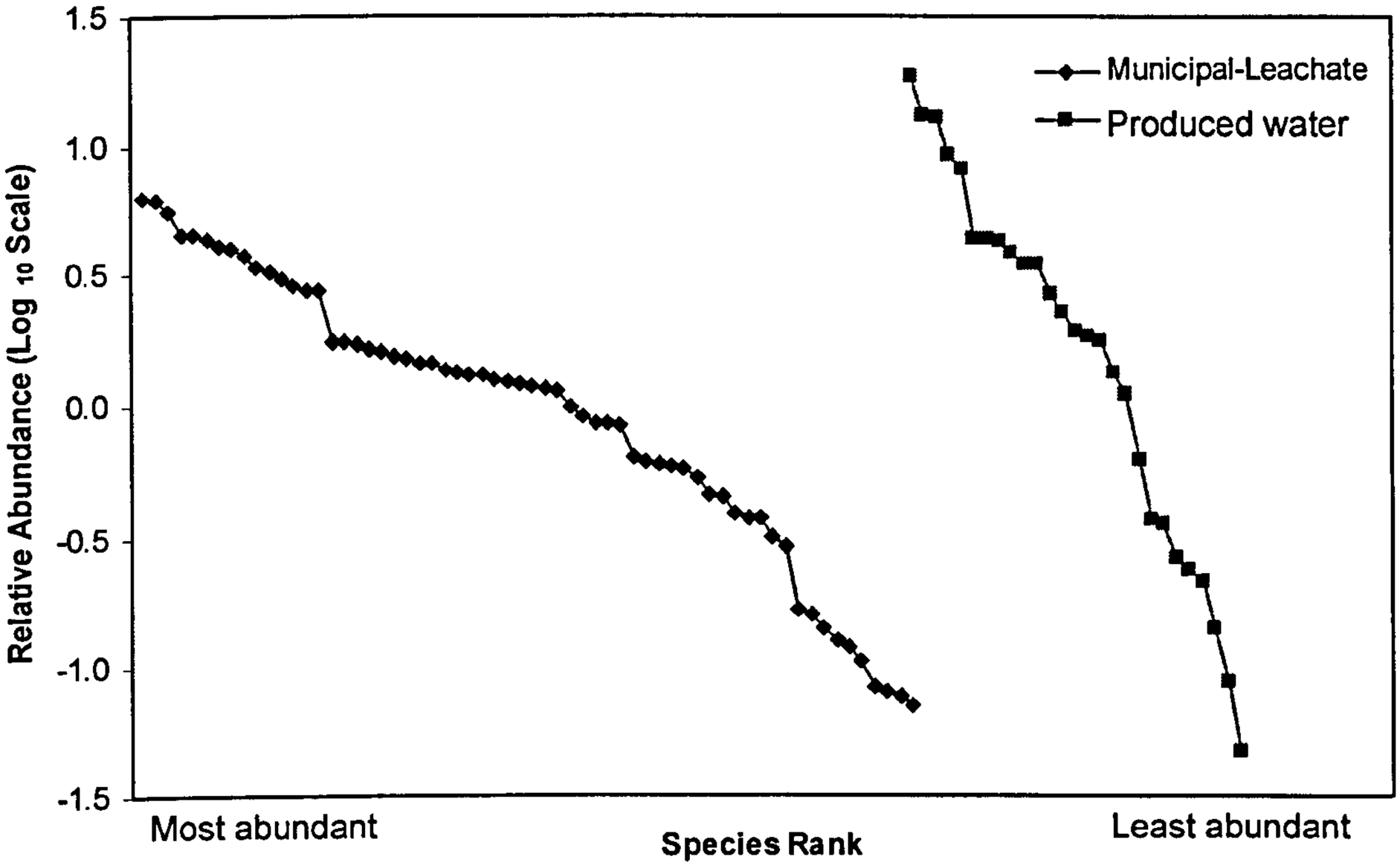

Figure 6.13 Rank/abundance plots of bacterial species from a) municipal-leachate and produced water fed membrane bioreactors

6.5 Summary of biomass characteristics

The results of the biomass characterisation carried out in order may be summarised as follows with key biomass characteristics shown in Table 6.6 below.

- An increase in non-volatile solids was not apparent at longer sludge ages and higher biomass MLSS concentrations.
- In contrast to other studies an exponential relationship between MLSS concentration and CST was not evident.

- SMP and EPS concentrations expressed as $mg.L^{-1}$ increased with increasing biomass (MLSS) concentration. Normalised EPS carbohydrate concentration ($mg.g\ MLSS^{-1}$) decreased with increasing biomass MLSS concentration whilst normalised protein levels increased.
- Results from microbial abundance and diversity analysis show profiles within the produced water MBR were highly conserved over time displaying a specialised and stable community

Table 6.6 Summary of biomass characteristics

Determinant	***Concentration [SD]***		
	6g.L^{-1}	***12g.L^{-1}***	***18g.L^{-1}***
Suspended Solids ($mg.L^{-1}$)	6.2 [0.8]	12.55 [1.8]	17.4 [1.3]
Volatile Suspended Solids($mg.L^{-1}$)	5.4 [0.7]	11.36 [1.5]	15.9 [1.2]
Capillary suction time (s)	146.7 [23.8]	45.1 [12.7]	60.2 [11.3]
Particle size d_{50} (µm)	87.1 [2.8]	103.8 [5.8]	77.9 [8.2]
Soluble microbial products (SMP_c) Carbohydrate ($mg.L^{-1}$)	11.35 [7.4]	17.26 [4.9]	22.7 [7.2]
Soluble microbial products (SMP_p) – Protein ($mg.L^{-1}$)	18.7 [9.6]	34.52 [8.2]	48.5 [13.7]
Extracellular polymeric substances (EPS_c) – Carbohydrate ($mg.g^{-1}$)	13.6 [2.7]	10.5 [3.8]	9.3 [5.1]
Extracellular polymeric substances (EPS_p) – Protein ($mg.g^{-1}$)	20.3 [5.8]	31.1 [8.64]	37.3 [12.4]

7 Membrane Fouling

7.1 Introduction

Membrane fouling during operation of MBRs is one of the most significant barriers to their widespread use; controlling or minimising the effects of fouling therefore represents an important issue to successful operation. The most widely used test for measuring fouling propensity involves incrementally increasing flux over time for a fixed duration at each flux and recording the corresponding transmembrane pressure (TMP) at each flux step. This would be expected to yield a stable TMP at low fluxes which then increases through the duration of the experiment to a maximum value at the highest flux applied. However no single standard protocol of this method exists, such that comparison of values reported in the literature is difficult.

Results from short term fouling trials carried out at a range of MLSS concentrations from 6 to 18 $g.L^{-1}$ are reported in Section 7.2. The extent to which such short term tests characterise long term operation, and so the real sustainability of the process, is not well understood. Long term fouling trials have been completed where the membrane is operated at constant flux over several days (Section 7.3) and the results compared to those from short term tests (Section 7.4). A recently proposed model to describe fouling during long term operation has been examined and used to compare predicted and actual data from the trial (Section 7.5). Section 7.6 details a comparison of fouling experiments carried out in the present work compared to those found in a previous study using an MBR with Millenniumpore membrane to treat sewage and synthetic sewage fed biomass (Le-Clech *et al.* 2003a), thereby gaining an insight to the relative fouling propensity of these feedwater matrices. The ability to operate at higher shear induced

by increasing membrane airflow rate or cross flow velocity by liquid pumping may limit membrane fouling. An initial analysis of the comparable fluxes achieved in such a system and results of fouling trials are presented in Section 7.7. Although produced water is not characterised by having high concentrations of free oil in the wastewater the possibility of free oil entering the system exists from poor removal during upstream processing. A single test was carried out to determine the effect of oil shocking on MBR operation and fouling propensity by dosing free oil directly into the bioreactor in incremental steps over several days directly into the bioreactor, the results are summarised in Section 7.8.

7.2 Short term flux step fouling trials

Methods for flux step fouling trials were carried out as proposed by Le-Clech *et al.* (2003a) to allow comparison with existing data (Section 7.4). Flux was increased in 2 $L.m^{-2}.h^{-1}$ steps with for a duration of 15 minute per step to a maximum flux before stepping back down to the initial flux. The test was repeated five times at each biomass concentration.

Biomass concentrations were increased stepwise by altering the sludge wastage and experiments made at steady state (defined as twice the sludge age once new conditions were attained). For the purposes of comparison of treatment performance the hydraulic retention time was not altered. No membrane relaxation or backwashing was applied between flux steps. Membranes were chemically cleaned with *Ultrasil 75* before each fouling test.

7.2.1 Identification of transitional flux

It has become evident through a number of studies that even at very low fluxes some fouling occurs (Defrance and Jaffrin, 1999; Ognier *et al.* 2004; Cho and Fane, 2002; Le-Clech *et al.* 2003a), such that the original definition of critical flux where there is a flux below which fouling (or permeability decline) does not occur (Field *et al.* 1995) does not apply to MBRs. A more suitable indicator and definition would be 'transitional flux', this representing the change from relatively low and stable fouling to higher fouling rate at the onset of significant fouling. This value is often used as a guide to establish an operating flux for a given system. There is a certain degree of interpretation of values which represent 'low' and 'high' fouling.

An example of the trend from short term fouling test for each biomass concentration tested of 6, 12 and 18 $g.L^{-1}$ is shown in Figures 7.1 to 7.3 respectively.

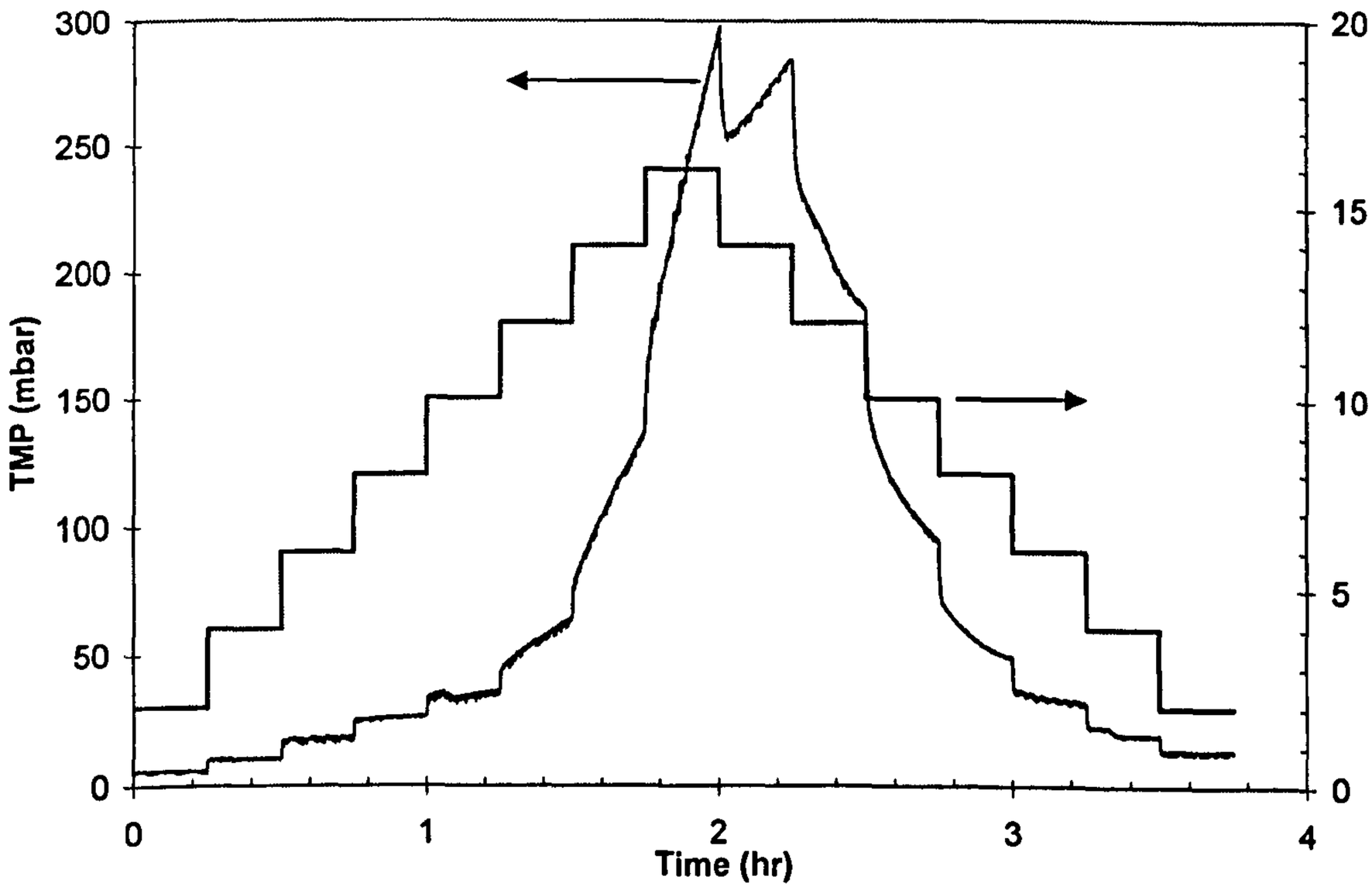

Figure 7.1 Flux step test (Biomass concentration 6 $g.L^{-1}$)

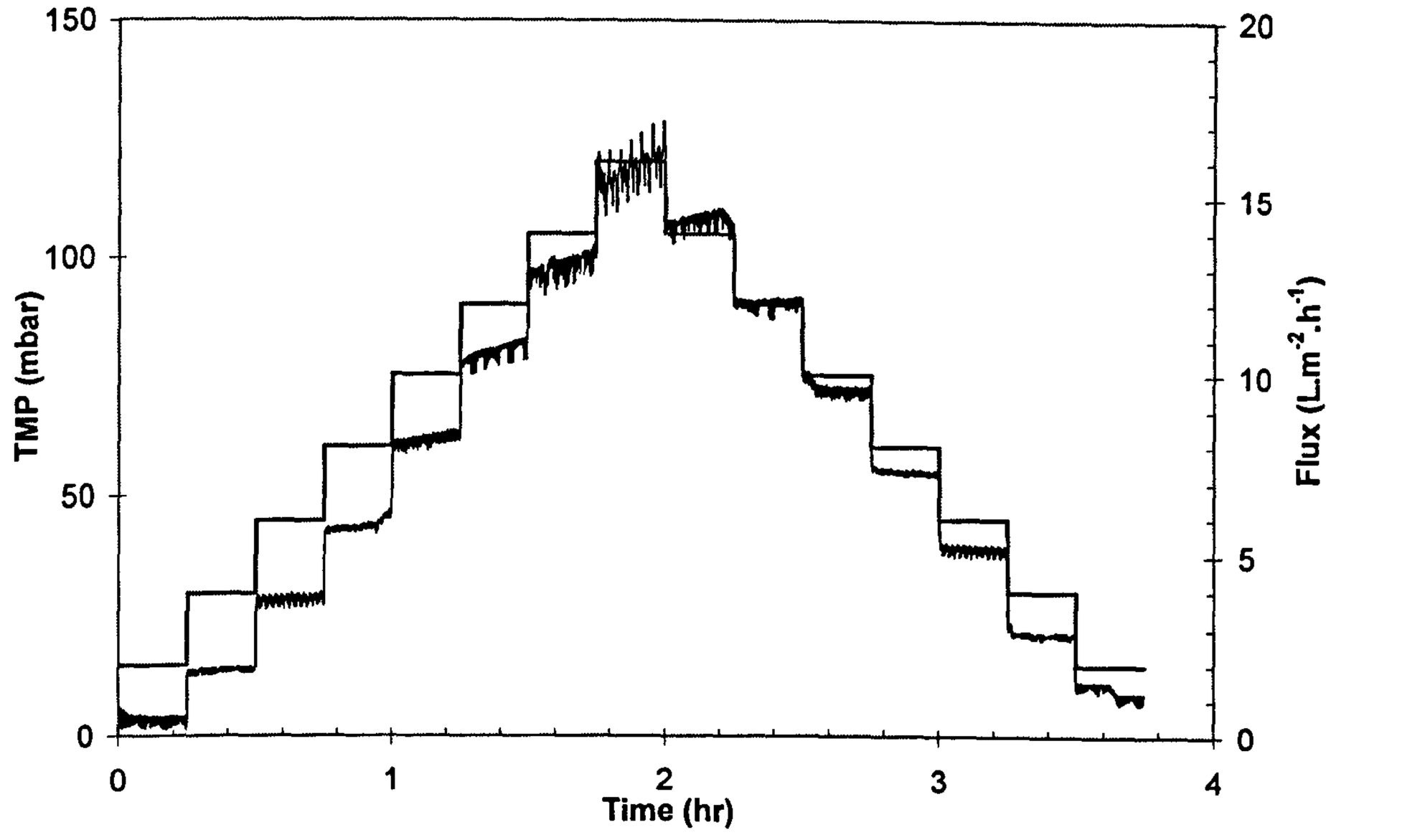

Figure 7.2 Flux step test (Biomass concentration 12 $g.L^{-1}$)

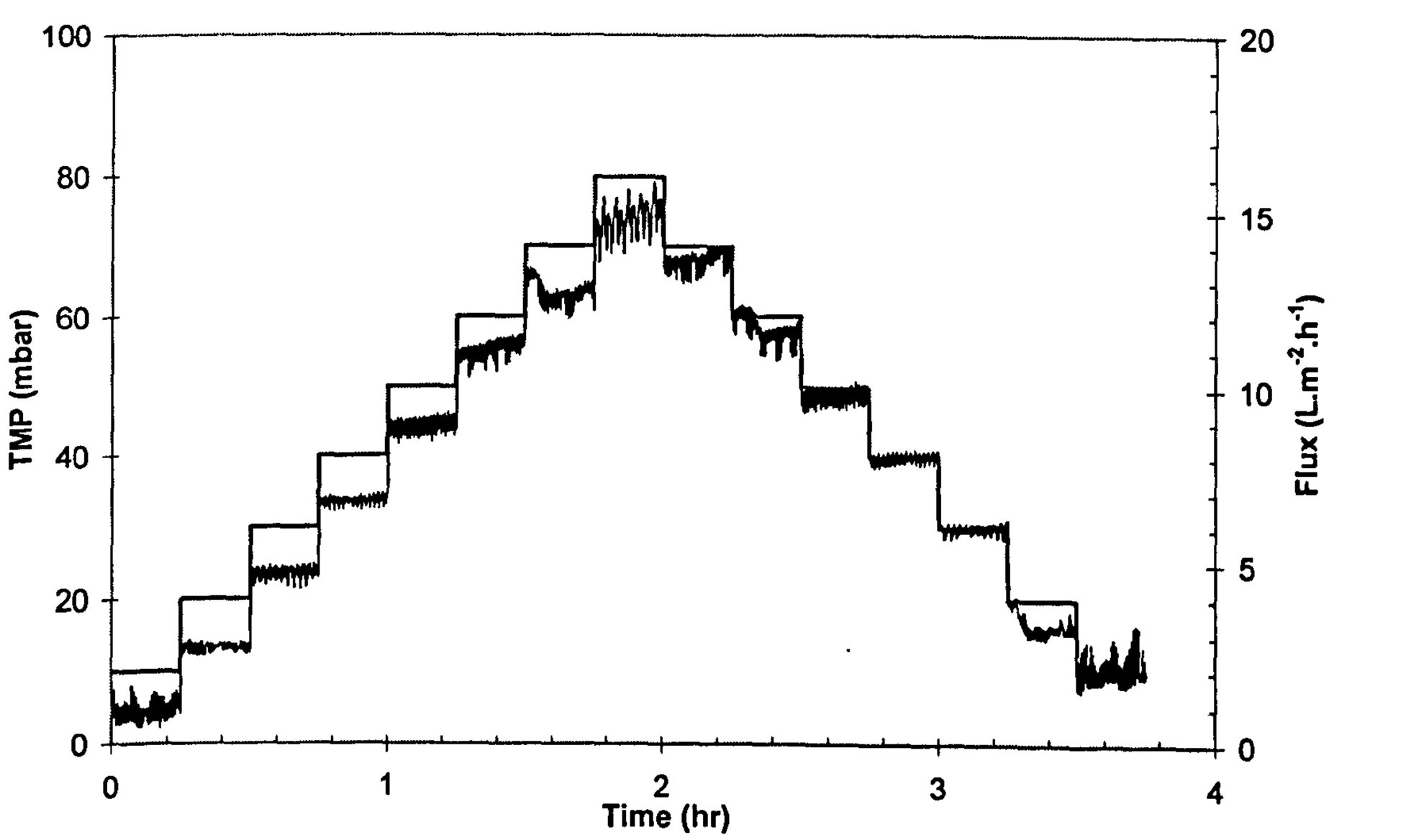

Figure 7.3 Flux step test (Biomass concentration 18 $g.L^{-1}$)

If a threshold fouling rate value of 0.2 mbar.min^{-1} is set, below which fouling may be described as 'low' rate and above is considered 'high', then from Figure 7.4 the value of the transitional flux can be defined as 8 L.m^{-2}.h^{-1} for 6 g.L^{-1}. Above this flux value the fouling rate increases dramatically from 0.09 to 0.389 mbar.min^{-1}. Figure 7.5 shows fouling rates for other biomass concentrations examined. The step change in fouling rate is not so marked at the higher biomass concentrations. However, using the threshold fouling rate value of 0.2 mbar.min^{-1}, the transitional flux for systems at 12 and 18 g.L-1 may be identified as 12 and 14 L.m^{-2}.h^{-1} respectively. Transitional fluxes and fouling rates above and below the transitional flux are displayed in Table 7.1.

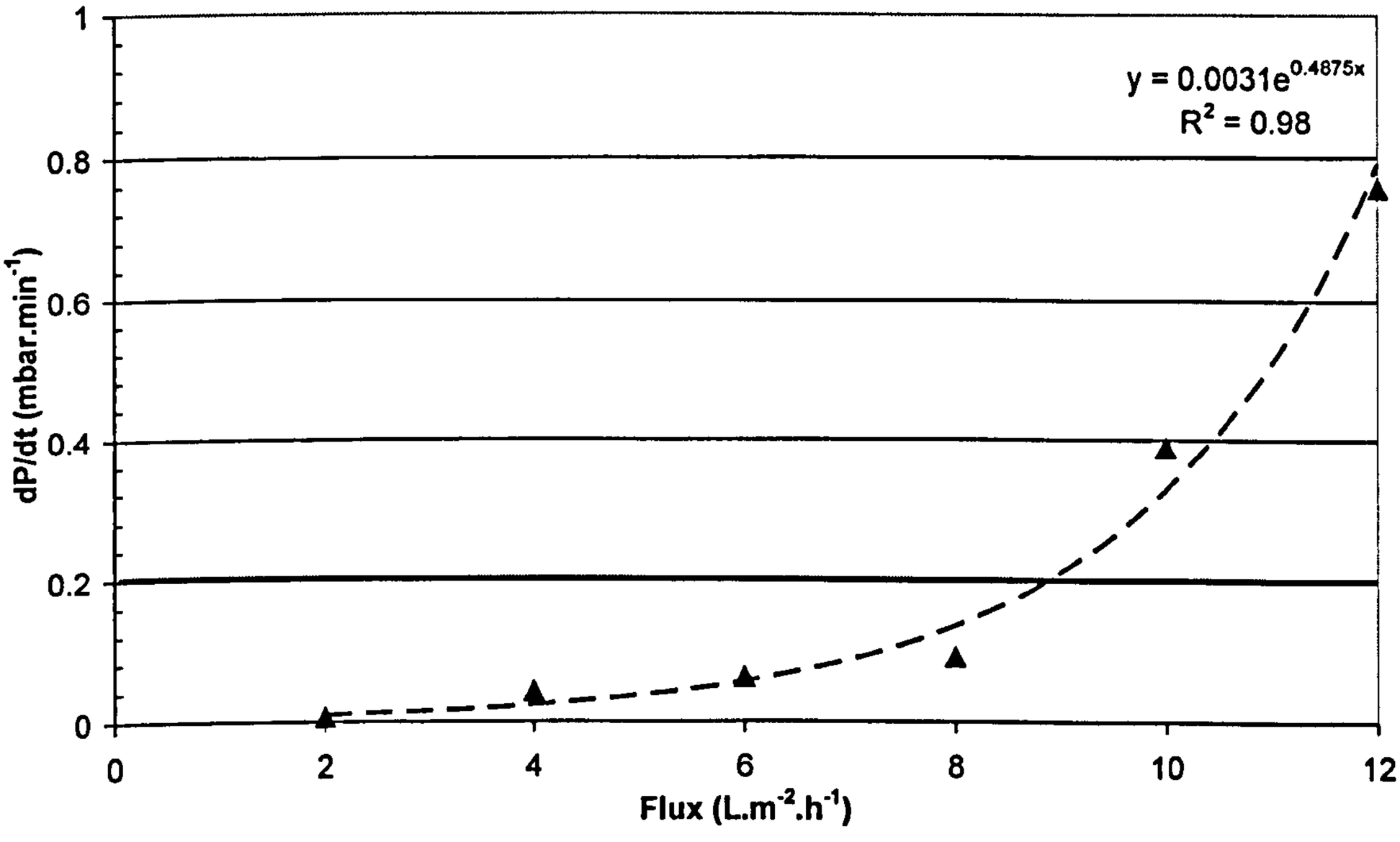

Figure 7.4 Example membrane fouling rates during flux step test (Biomass concentration 6 g.L^{-1}).

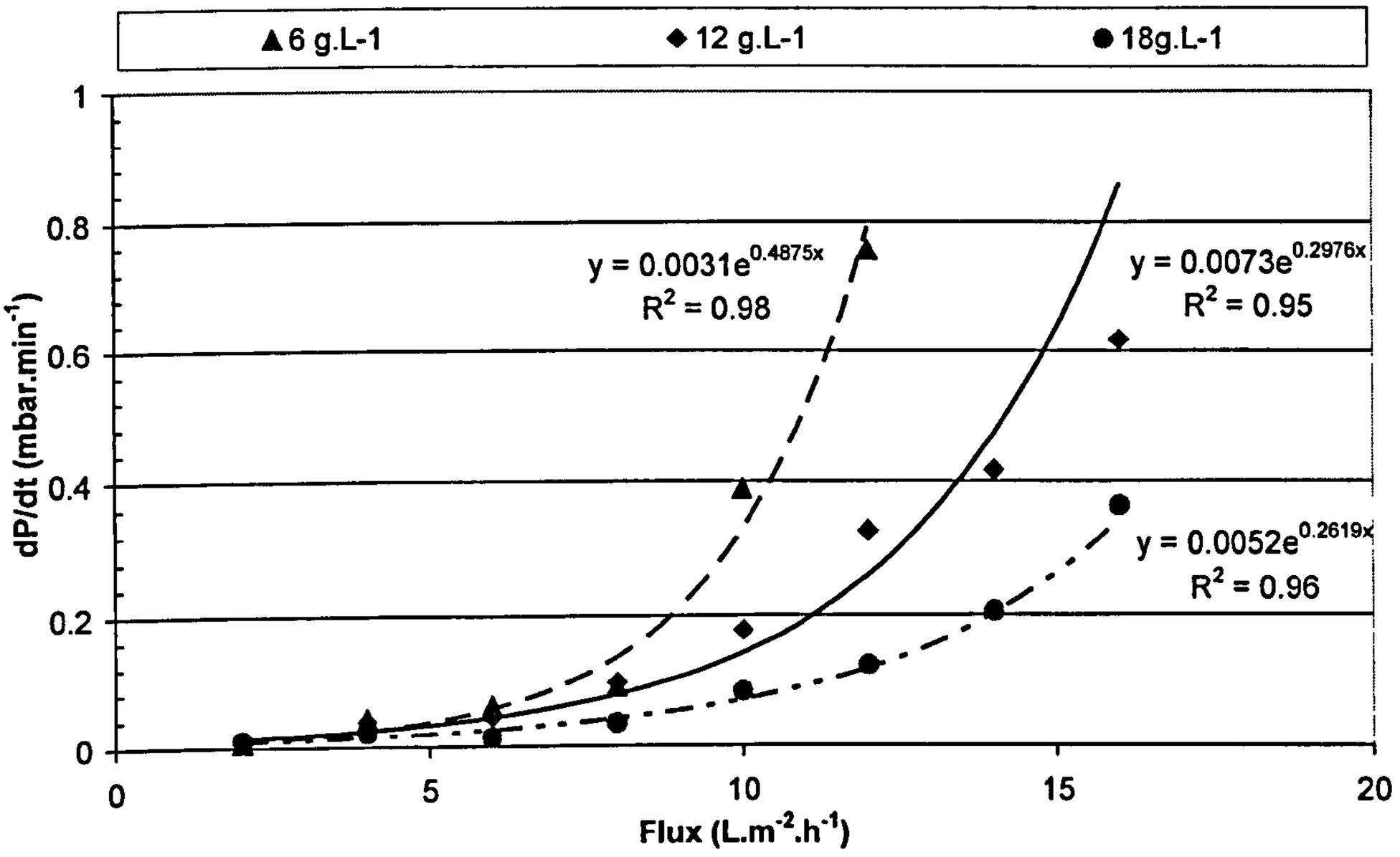

Figure 7.5 Membrane fouling rates for identifying transitional flux during flux step test

Table 7.1 Transitional fluxes and membrane fouling rates

Biomass Conc. ($g.L^{-1}$)	J_{trans} ($L.m^{-2}.h^{-1}$)	dP/dt $J<J_{trans}$ ($mbar.min^{-1}$)	dP/dt $J>J_{trans}$ ($mbar.min^{-1}$)
6	8	<0.092	>0.389
12	12	<0.179	>0.327
18	14	<0.125	>0.206

The effect of differences in MLSS concentration on transitional flux is not straightforward due to the complexity and variability of biomass components (Le-Clech *et al.* 2003b). The mixed liquor represents a mixture of a dominant foulant, biomass solids, and minor or trace foulant, dissolved and colloidal EPS (Cho and Fane, 2002). As such the biomass concentration alone is not the only indicator but may represent a

change in a number of biomass parameters (Chapter 6) including EPS and SMP concentration, CST, viscosity and particle size.

The general trend from the literature is an increasing transitional flux value at low biomass concentrations (Cho and Fane, 2002; Ognier *et al.* 2004; Hwang *et al.* 2003). At lower concentrations the principal foulant, namely the biomass MLSS concentration, is obviously lower. However other studies have found fouling to be unaffected by biomass concentration whereas other studies have conversely shown increased critical hydraulic performance at higher biomass concentration. Le-Clech *et al.* (2003b) reported that a shift in MLSS concentration from 4 to 12 $g.L^{-1}$ resulted in an increase in critical flux of between 60 and 107% depending on membrane tested. In the current study the shift is 50% increase in the transitional flux for increase from 6 to 12 $g.L^{-1}$ and 75% for increase from 6 to 12 $g.L^{-1}$.

7.2.2 Comparison of membrane operation at range of biomass concentrations

Fouling rates increase exponentially with increasing fluxes (Figure 7.6) from minimum dP/dt of 0.0067 $mbar.min^{-1}$ with maximum dP/dt reaching 8.8 $mbar.min^{-1}$ for the final flux step (16 $L.m^{-2}.h^{-1}$) during the 6 $g.L^{-1}$ trial. The corresponding average TMP (P_{ave}) during this step was 230.9 mbar (Table 7.2a). At fluxes below 8 $L.m^{-2}.h^{-1}$ (sub-transitional flux in all cases) the fouling rates are similar. At these low fouling rates of around 0.01$mbar.min^{-1}$ the resolution of the pressure transducer (0.1 mbar) and data logging system is the determining factor. A 0.1 mbar over a 15 minute cycle equates to rate of 0.0067 $mbar.min^{-1}$, the lowest rate recorded (Tables 7.2a-c).

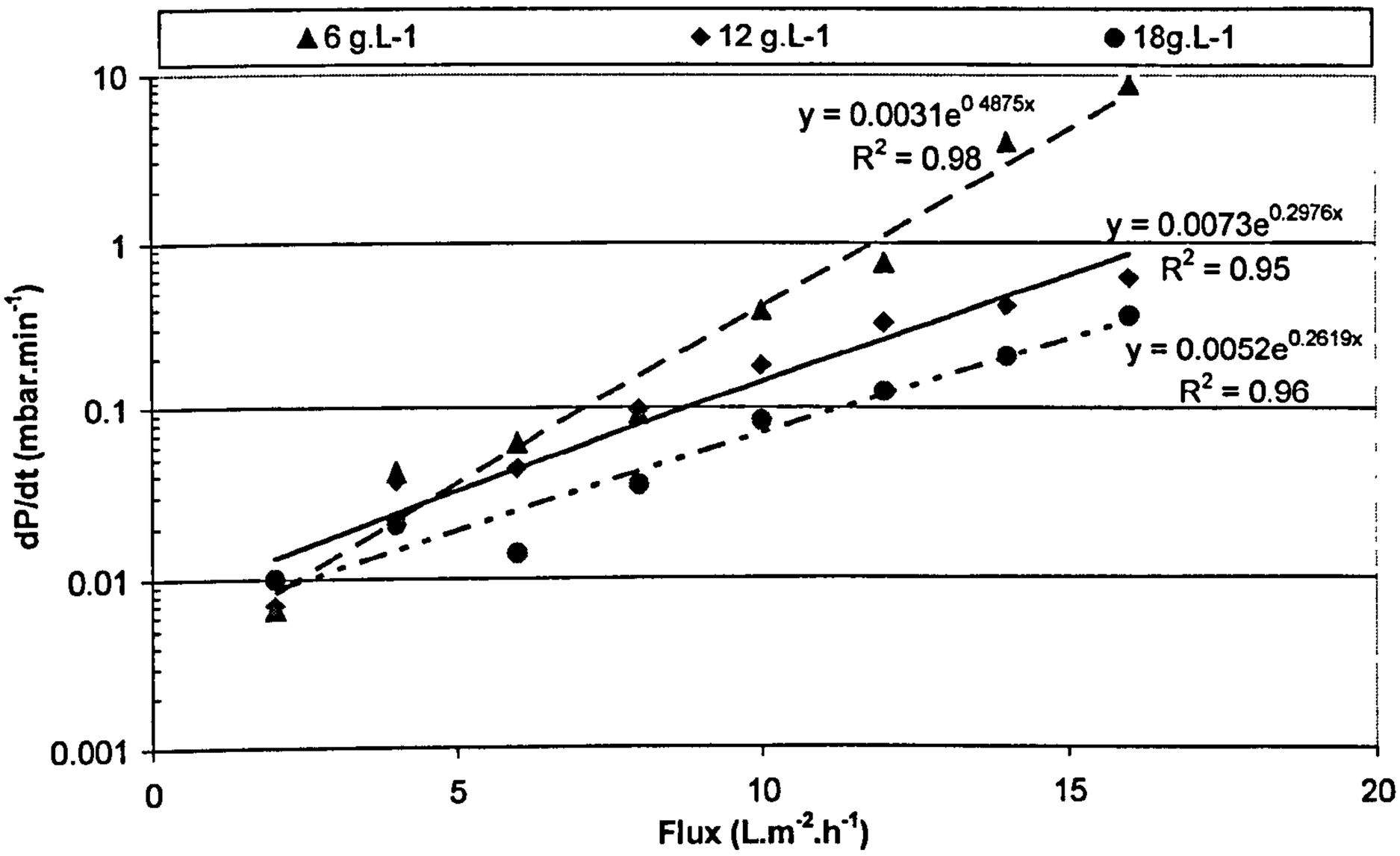

Figure 7.6 Flux step fouling rates at a range of biomass concentrations

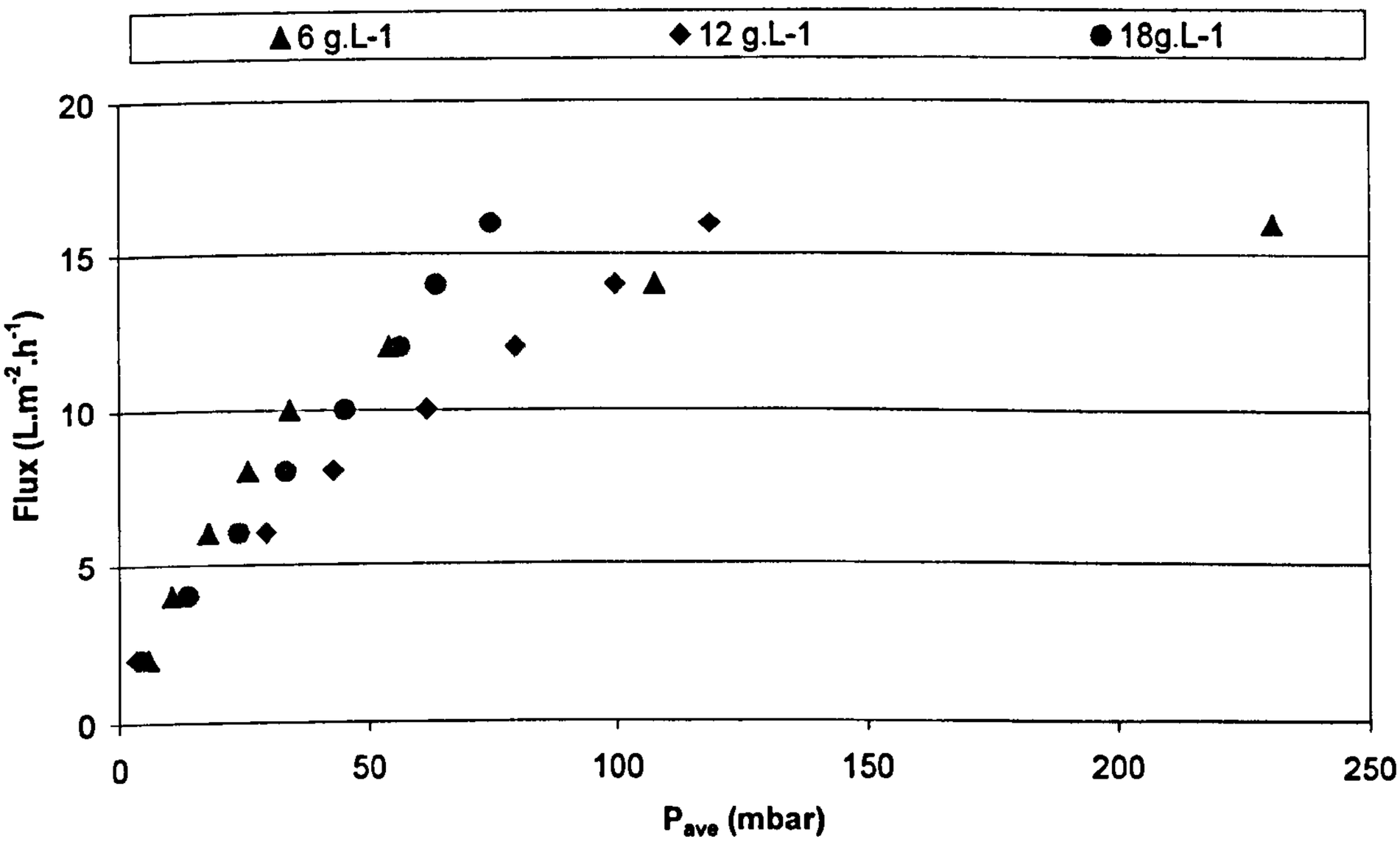

Figure 7.7 Permeability at a range of biomass concentrations

Table 7.2a Summary of TMP based parameters during flux step tests (6g.L^{-1})

J $L.m^{-2}.h^{-1}$	ΔP_0 mbar	dP/dt $mbar.min^{-1}$	P_{ave} Mbar
0	-	-	0
2	5.4 [0.5]	0.0067 [0]	5.7 [1.8]
4	3.5 [0.4]	0.0421 [0.018]	10.5 [3.2]
6	5 [0.5]	0.0625 [0.027]	17.7 [6.1]
8	6.8 [1.2]	0.092 [0.041]	25.7 [8.6]
10	6.9 [1]	0.389 [0.17]	34.1 [14.3]
12	8.2 [1.6]	0.758 [0.33]	54.1 [21.7]
14	11.1 [3.8]	3.97 [1.76]	107.6 [31.5]
16	32.9 [15.5]	8.78 [1.3]	230.9 [67.7]

Table 7.2b Summary of TMP based parameters during flux step tests (12g.L^{-1})

J $L.m^{-2}.h^{-1}$	ΔP_0 mbar	dP/dt $mbar.min^{-1}$	P_{ave} Mbar
0			0
2	3.3 [0.8]	0.00706 [0.001]	3.4 [2]
4	9.5 [1.3]	0.0373 [0.012]	13.8 [4.4]
6	14 [3.8]	0.0442 [0.025]	29.2 [7.8]
8	13.7 [3.5]	0.0973 [0.039]	42.9 [17.3]
10	13.3 [4.1]	0.179 [0.11]	61.8 [16.5]
12	15.3 [3.9]	0.327 [0.18]	79.8 [17.2]
14	11.6 [3.7]	0.417 [0.34]	99.9 [20.5]
16	13.6 [4.2]	0.618 [0.27]	118.5 [31.1]

Table 7.2c Summary of TMP based parameters during flux step tests (18g.L^{-1})

J $L.m^{-2}.h^{-1}$	ΔP_0 mbar	dP/dt $Mbar.min^{-1}$	P_{ave} Mbar
0			0
2	4.1 [1.6]	0.01 [0.002]	4.4 [1.9]
4	7.5 [2.1]	0.021 [0.013]	13.6 [4.7]
6	10.5 [3.2]	0.014 [0.013]	23.8 [6.5]
8	10.1 [3.8]	0.035 [0.016]	33.3 [8.6]
10	10.4 [4.1]	0.084 [0.039]	45.2 [15.1]
12	10.6 [3.6]	0.125 [0.08]	56.3 [16.9]
14	9.3 [3.3]	0.206 [0.074]	63.7 [15.3]
16	6.8 [3.2]	0.363 [0.31]	74.7 [17.5]

The most marked decrease in permeability at fluxes above the transitional flux occurred at a biomass concentration of 6 g.L^{-1}. At fluxes of 2 and 4 L.m^{-2}.h^{-1} the permeability

decline was similar across all systems. At fluxes up to 10 $L.m^{-2}.h^{-1}$ the highest permeability was recorded for at an MLSS level of 6 $g.L^{-1}$ (Figure 7.7). However at the two highest fluxes examined (14 and 16 $L.m^{-2}.h^{-1}$) permeability sharply declined affirming the higher fouling propensity compared to the other higher biomass concentrations.

Table 7.3 summarises biomass characteristics at all concentrations employed (from Chapter 6.2). Contrary to expectations, the most highly fouling biomass at 6 $g.L^{-1}$ had the lowest SMP concentrations and the lowest protein fraction of the EPS with only the carbohydrate fraction of the EPS being higher than those determined at other biomass concentrations. It also, however, had longer CST values - over double those recorded at other biomass concentrations. If the CST value is normalised the mean values show even greater difference – 24, 3.83 and 3.39 s per gram of MLSS for biomass MLSS concentrations of 6, 12 and 18 $g.L^{-1}$ respectively.

Table 7.3 Summary of biomass characteristics

Determinant	***Concentration [SD]***		
	6g.L^{-1}	***2g.L^{-1}***	***18g.L^{-1}***
Suspended solids ($mg.L^{-1}$)	6.2 [0.8]	12.55 [1.8]	17.4 [1.3]
Volatile suspended solids($mg.L^{-1}$)	5.4 [0.7]	11.36 [1.5]	15.9 [1.2]
Capillary suction time (s)	148.8 [82.5]	46.1 [27.3]	61 [21.1]
Particle size d_{50} (µm)	86.7	105.4	75.1
Soluble microbial products (SMP_c) Carbohydrate ($mg.L^{-1}$)	11.35 [7.4]	17.26 [4.9]	22.7 [7.2]
Soluble microbial products (SMP_p) – Protein ($mg.L^{-1}$)	18.7 [9.6]	34.52 [8.2]	48.5 [13.7]
Extracellular polymeric substances (EPS_c) – Carbohydrate ($mg.g^{-1}$)	13.6 [2.7]	10.5 [3.8]	9.3 [5.1]
Extracellular polymeric substances (EPS_p) – Protein ($mg.g^{-1}$)	20.3 [5.8]	31.1 [8.64]	37.3 [12.4]

7.2.3 Fouling reversibility

The flux step test was carried out both in ascending and descending phase. During the descending phase as the flux is reduced, the material causing reversible fouling is largely removed and the average TMP reduces. Figure 7.8 presents hysteresis loops for flux step tests carried out at all biomass concentrations.

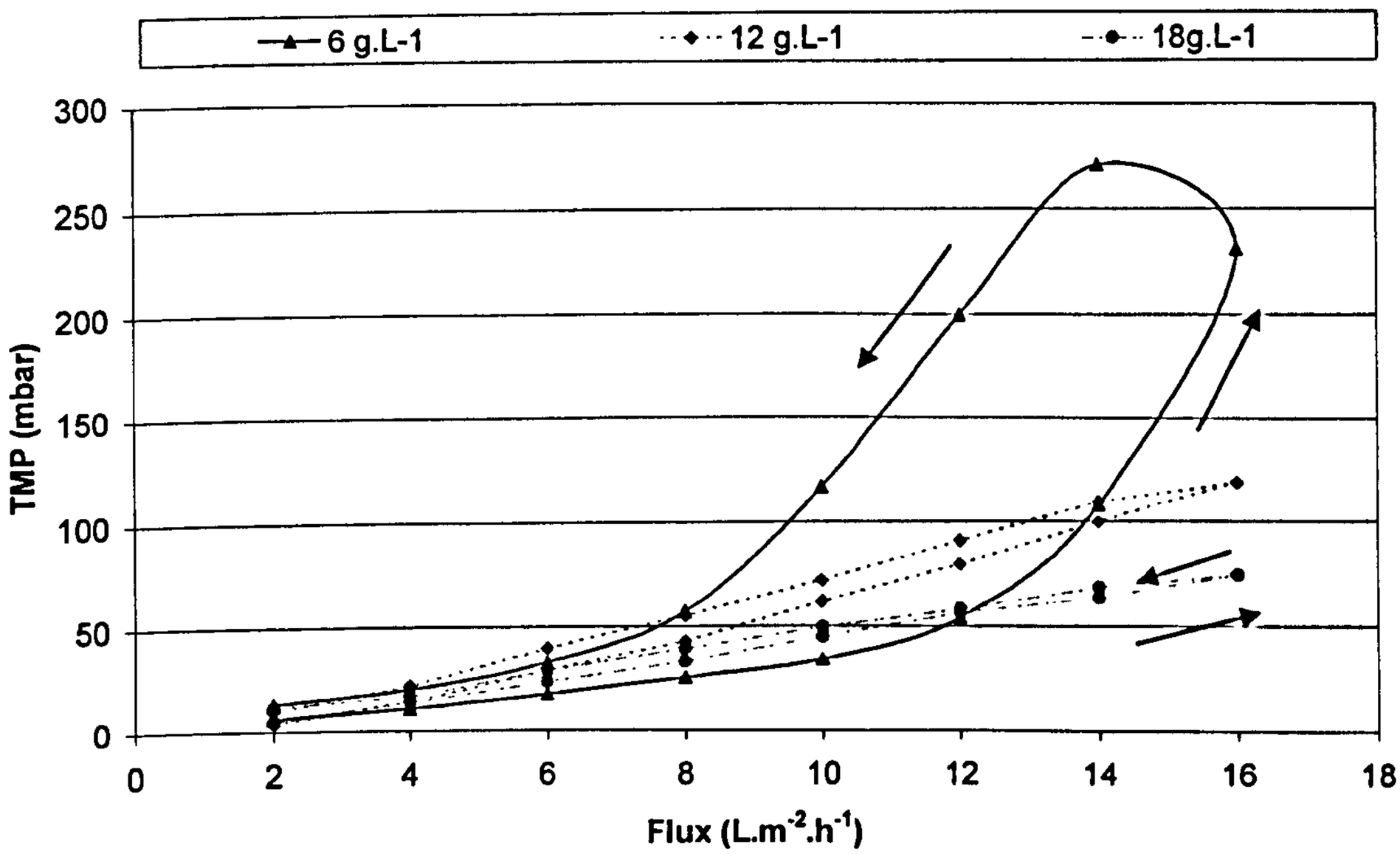

Figure 7.8 Hysteresis curves for tests at all biomass concentrations

The results from all tests display higher TMP on downward phase, with the most marked difference apparent from the trail at the biomass concentration of 6 $g.L^{-1}$. At the lowest flux of 2 $L.m^{-2}.h^{-1}$ the average TMP was 5.7 mbar in the ascending phase and 17.2 mbar in the descending phase. Continued operation at this lowest flux may lead to the TMP decreasing further towards its initial value as the step duration (15 minutes) was relatively short. At 14 $L.m^{-2}.h^{-1}$ the average TMP was 108 mbar in the ascending phase and 268 mbar in the descending phase. At the higher biomass concentrations the

difference between the ascending and descending phases was less than 15% of the TMP during the ascending phase as well as yielding a lower average TMP at each flux step.

7.3 Long term fouling trials

Although the two-stage fouling phenomena discussed earlier has been exhibited in other studies (Le-Clech *et al.* 2003, Cho and Fane, 2002, Ahn *et al.* 1999, Ognier *et al.* 2002, 2004) a lack of comprehensive data has constrained correlation between applied flux and either fouling rate or time of stable operation (t_{filt}). The only other reported study of sub-critical fouling rates and flux has been by Wen *et al.* (2004).

Operation at fluxes between 2 and 10 $L.m^{-2}.h^{-1}$ for a biomass concentration of 6 $g.L^{-1}$ demonstrated fouling dynamic behaviour to depend on flux (Figure 7.8). At a flux of 10 $L.m^{-2}.h^{-1}$ no stable low fouling period was exhibited, but rather a linear fouling from the beginning of experiment (corresponding to $dP/dt = 0.036$ $mbar.min^{-1}$) followed by rapid fouling up to 130 mbar after 2 days of operation. When operated at the lowest flux of 2 $L.m^{-2}.h^{-1}$ the TMP was stable for up to 10 days without the onset of accelerated fouling noted earlier. However, the TMP increased from 2 to 12 mbar within the 10 first days of filtration ($dP/dt = 7.10^{-4}$ $mbar.min^{-1}$) confirming that even at very low fluxes some fouling still takes place.

Fouling rates recorded at other fluxes reveal the same pattern with a period of stable operation (t_{filt}) before a sudden increase in fouling rate. Initial membrane permeability values for all trials were 550-600 $L.m^{-2}.h^{-1}.bar^{-1}$ compared with 70-80 $L.m^{-2}.h^{-1}.bar^{-1}$ when filtration was stopped. Trends shown in Figure 7.8 are based on single runs; results from a duplicated trial at 8 $L.m^{-2}.h^{-1}$ are presented in Figure 7.9.

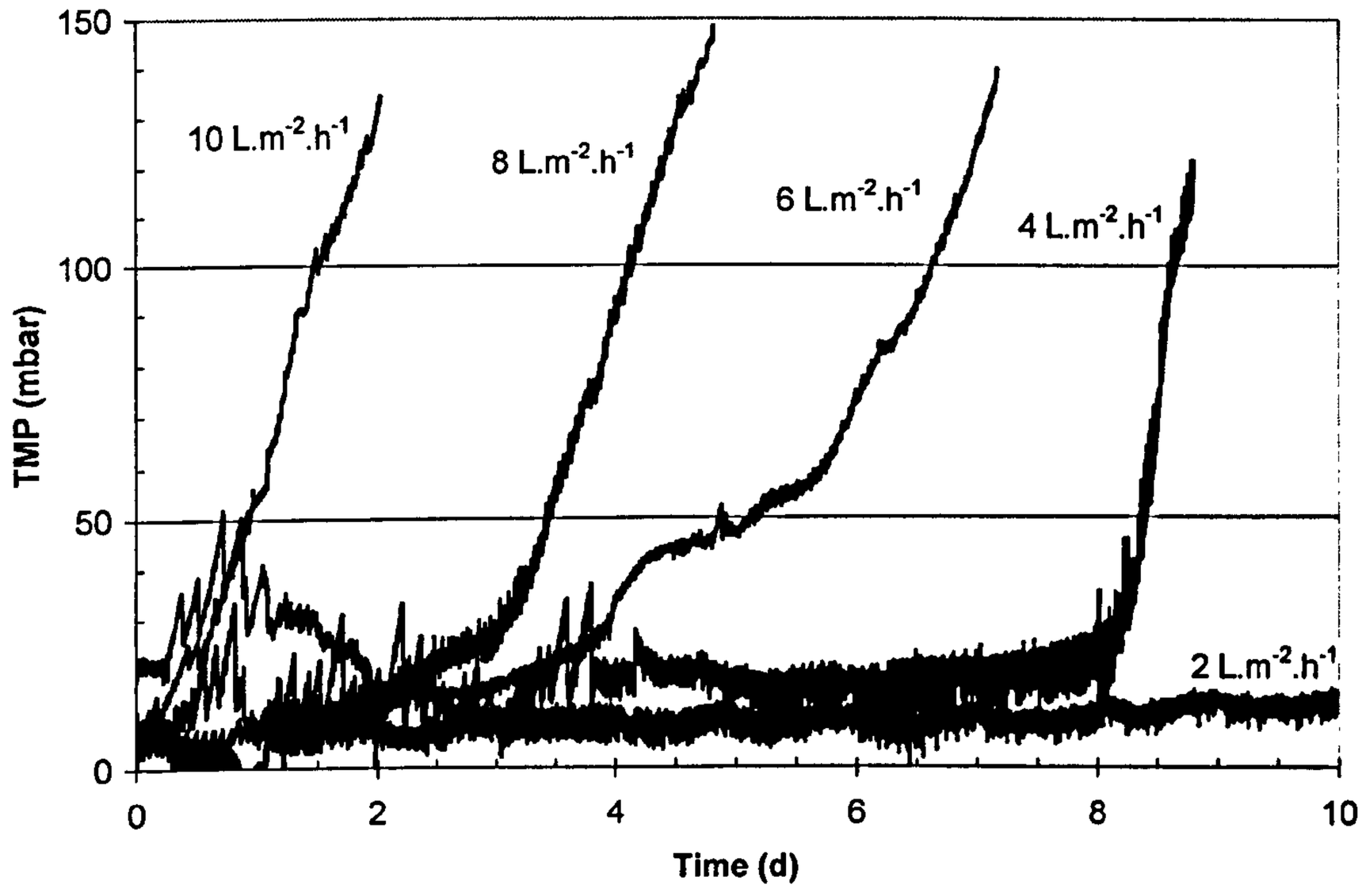

Figure 7.8 TMP transients for long term trials at a range of fluxes, biomass 6 $g.L^{-1}$

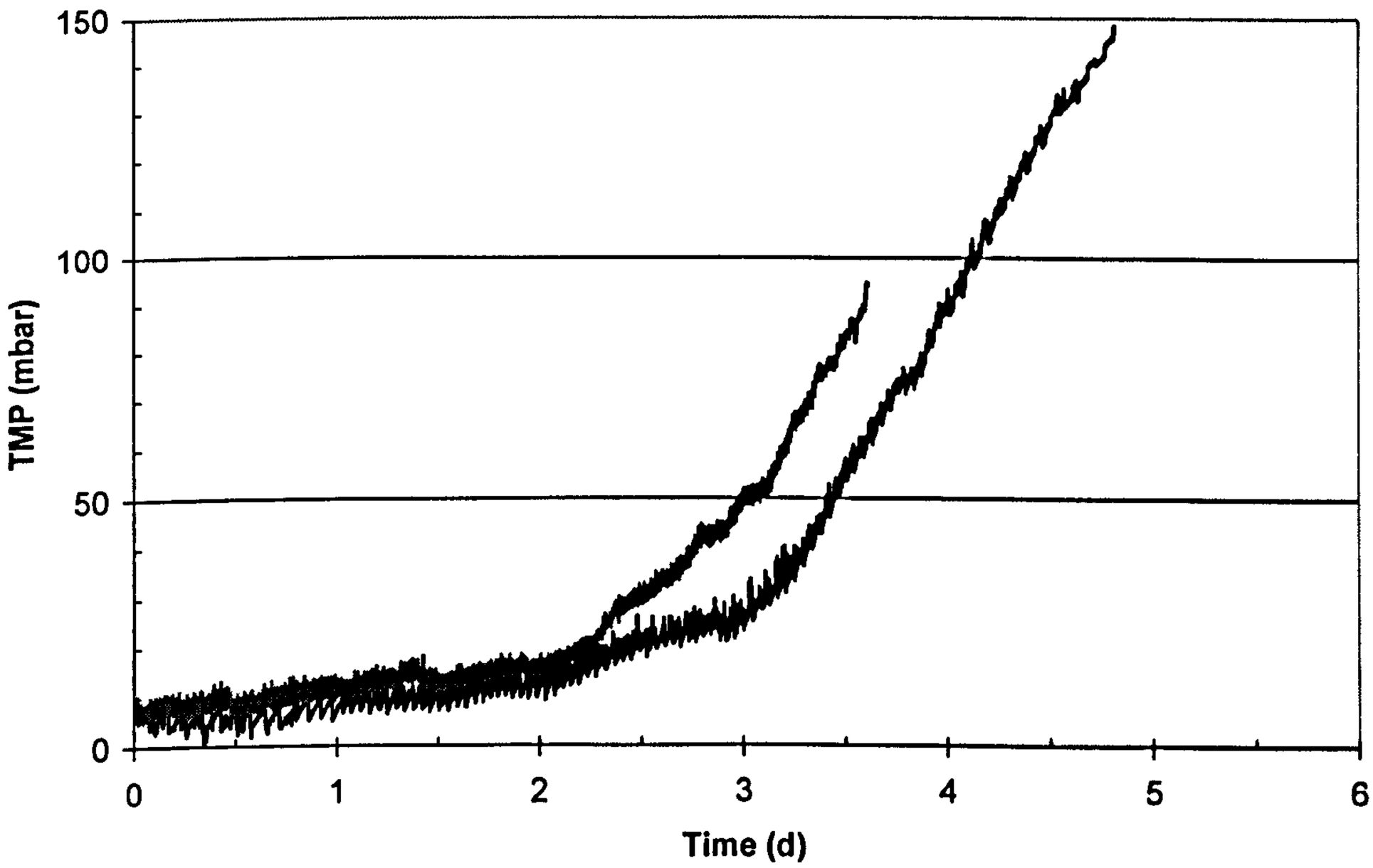

Figure 7.9 Repeat of long term fouling test at 8 $L.m^{-2}.h^{-1}$

In the current study the two-stage fouling phenomenon was only exhibited at the lowest biomass concentration investigated (6 $g.L^{-1}$). Results from operation at 12 $g.L^{-1}$ and 18 $g.L^{-1}$ display no such characteristic discontinuity, suggesting that the two-stage fouling phenomenon is a feature only of low biomass concentrations and/or short solids retention times – and possibly only specific feedwater matrices (Section 7.6.2).

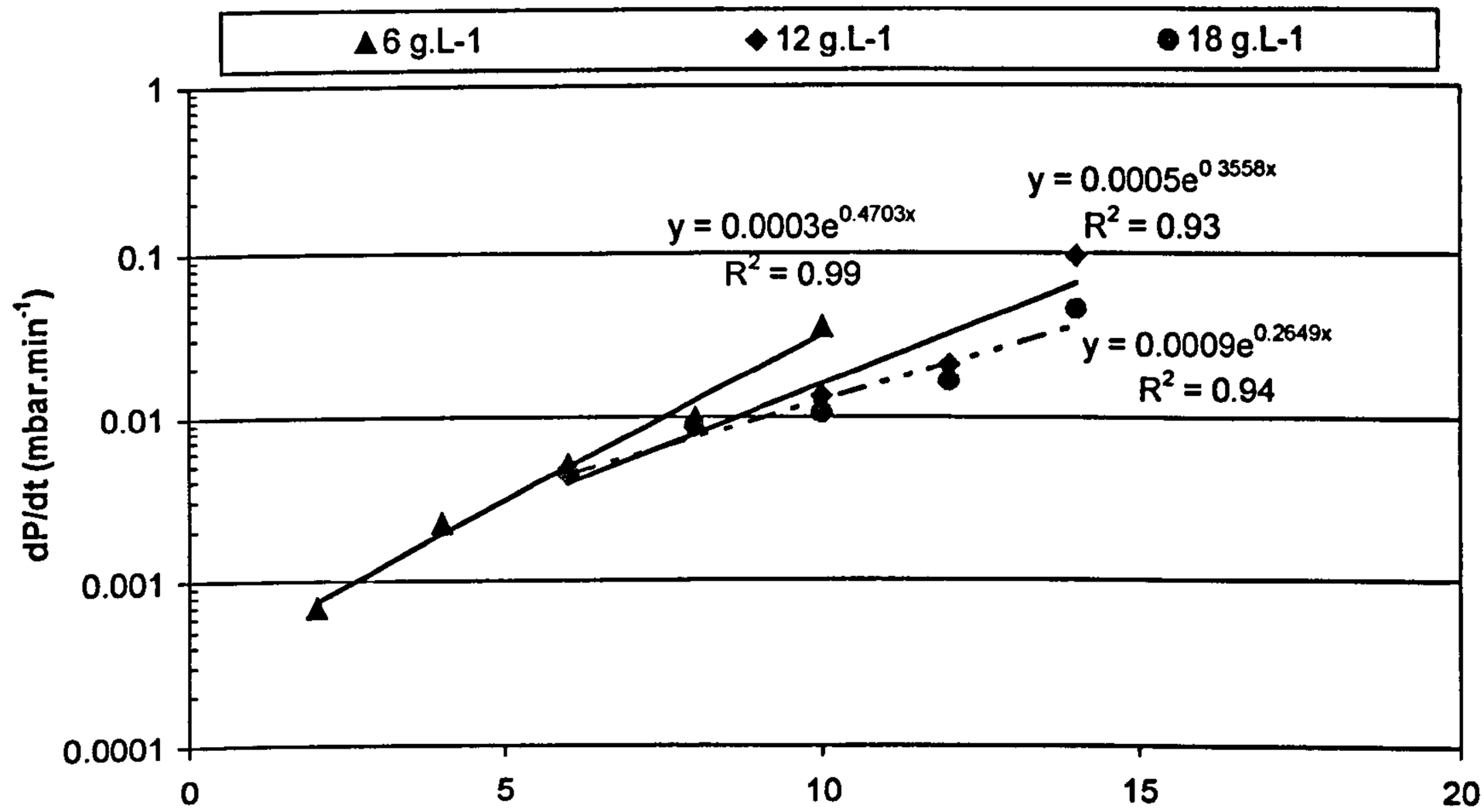

Figure 7.10 Fouling rates from long term experiments

Long term fouling rates at low fluxes, 6 and 8 $L.m^{-2}.h^{-1}$, were similar at all biomass concentrations: 0.0045 – 0.005 $mbar.min^{-1}$ and 0.009 – 0.01 $mbar.min^{-1}$ respectively. It was only at higher flux operation (higher than the transitional flux in all cases) that the differences in fouling behaviour were apparent. At these elevated fluxes a higher fouling rate was apparent at a biomass level of 6 $g.L^{-1}$ compared with that at 12 and 18 $g.L^{-1}$; fouling rates recorded at 10 $L.m^{-2}.h^{-1}$ were 0.036 $mbar.min^{-1}$, 0.014 $mbar.min^{-1}$ and 0.011 $mbar.min^{-1}$ at biomass concentrations of 6, 12 and 18 $g.L^{-1}$ respectively. Trials conducted at 12 and 18 $g.L^{-1}$ MLSS yielded similar rates up to 12 $L.m^{-2}.h^{-1}$, 0.021 $mbar.min^{-1}$ compared with 0.017 $mbar.min^{-1}$. At 14 $L.m^{-2}.h^{-1}$, above the transitional flux

for the system, the fouling rate at 12 $g.L^{-1}$ was double that recorded at 18 $g.L^{-1}$ (0.097 $mbar.min^{-1}$ cf. 0.046 $mbar.min^{-1}$).

Figure 7.11 shows t_{filt} to decrease linearly with increasing fluxes. If the foulant is assumed to be entrained in the flow of liquid through the membrane (i.e. not substantially removed by back diffusion) then it may be postulated that this linear relationship is associated with a critical filtration volume or mass of foulant deposited per unit membrane area, with fouling increasing rapidly once this critical mass has been reached.

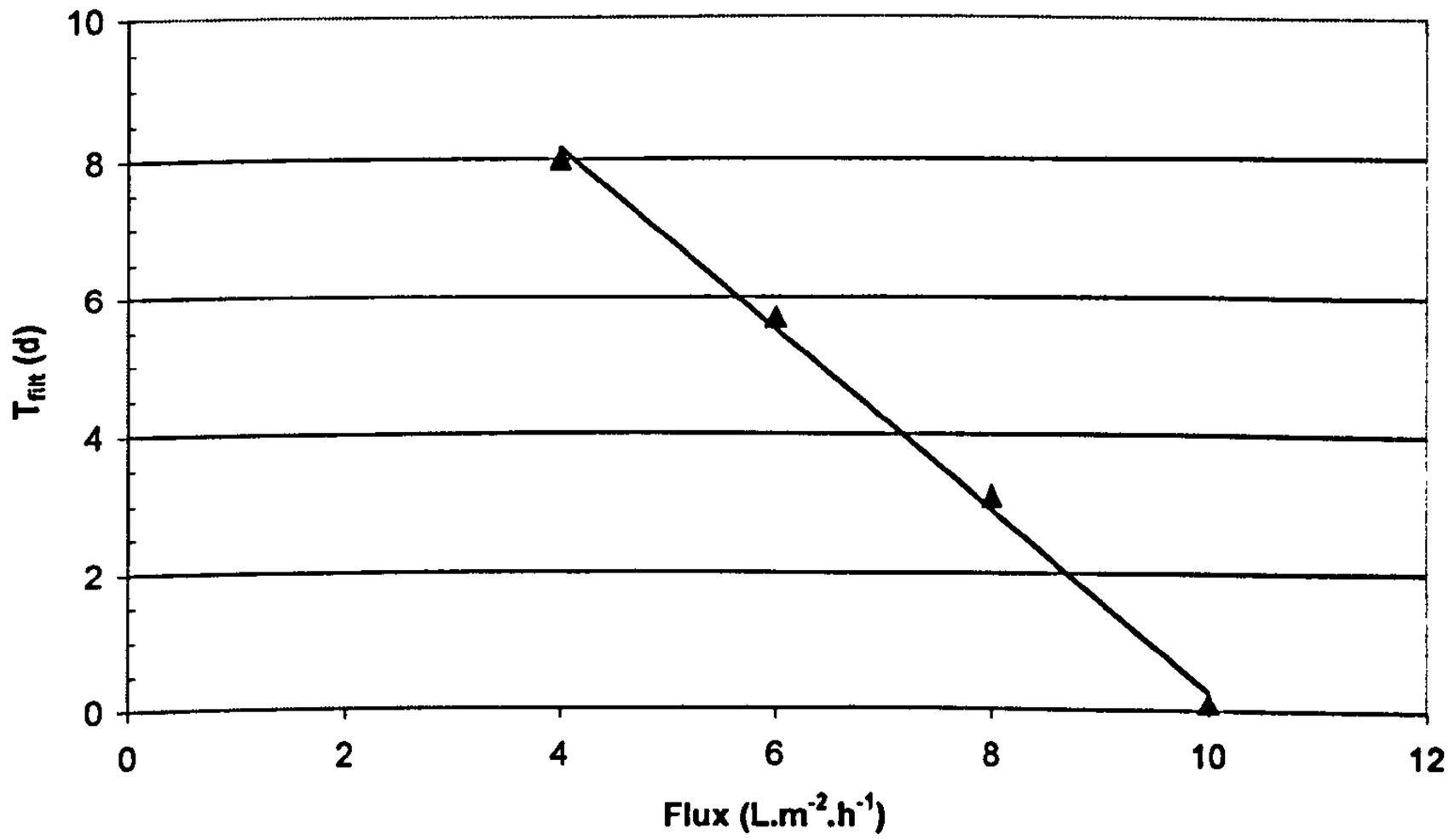

Figure 7.11 T_{filt} for a range of fluxes, 6 $g.L^{-1}$

It has been suggested that the period beyond t_{filt} reflects solids (i.e. sludge) deposition (Cho *et al.* 2002, Ognier *et al.* 2004). This being the case, and based on Darcian flow, an increase in flux would be expected to produce a proportional increase in dP/dt at $t>t_{filt}$. However, recorded data do not reflect this (Figure 7.8 and Table 7.4), with the

post-t_{filt} fouling rate varying little with flux. Non-Darcian flow would be expected to further increase dP/dt with flux due to cake compression, solids migration, etc. In contrast it has been reported by Wen *et al.* (2004) that the post t_{filt} fouling rate can actually decrease with applied flux. It must therefore be concluded that fouling at $t>t_{filt}$ cannot be attributed solely to solids deposition. Differences in the cake structure and porosity will affect the rate of fouling and given the low number of long term tests conducted more work will need to be undertaken to further examine the phenomena.

Table 7.4 TMP behaviour under long term operation

Flux $L.m^{-2}.h^{-1}$	MLSS $g.L^{-1}$	T_{filt} Hr	1st phase $dp.dt^{-1}$ ($t<t_{filt}$) $mbar.min^{-1}$	2nd phase $dp.dt^{-1}$ ($t>t_{filt}$) $mbar.min^{-1}$
2	6	-	2.2×10^{-3}	-
4	6	192	2.2×10^{-3}	0.14
6	6	137	5.1×10^{-3}	0.031
8	6	74	0.01	0.047
10	6	-	0.036	-
6	12	-	4.3×10^{-3}	-
8	12	-	8.8×10^{-3}	-
10	12	-	0.014	-
12	12	-	0.021	-
14	12	-	0.097	-
6	18	-	4.5×10^{-3}	-
8	18	-	8.8×10^{-3}	-
10	18	-	0.011	-
12	18	-	0.017	-
14	18	-	0.046	-

7.4 Comparison of short and long term fouling data

Using the fouling rates identified during flux step tests to set an operational flux for a system would indicate exceptional low fluxes to minimise fouling. How well these values relate to sustainable long term operation is not fully understood since fouling

rates recorded for long term operation have been reported as being between 10 and 100 times lower than those measured for short term trials (Le-Clech *et al.* 2003a).

Fouling rates measured during the flux step experiments (Section 7.2) reveal an exponential relationship between dP/dt and flux, as found by other authors (Le-Clech *et al.* 2003a; Fan *et al.* 2000). The fouling rates from the long-term trials (Section 7.3) at all fluxes studies also exhibit the same exponential relationship, with the value of the exponent being about the same as for that obtained for the flux-step experimental data but with the actual fouling rates being around an order of magnitude lower:

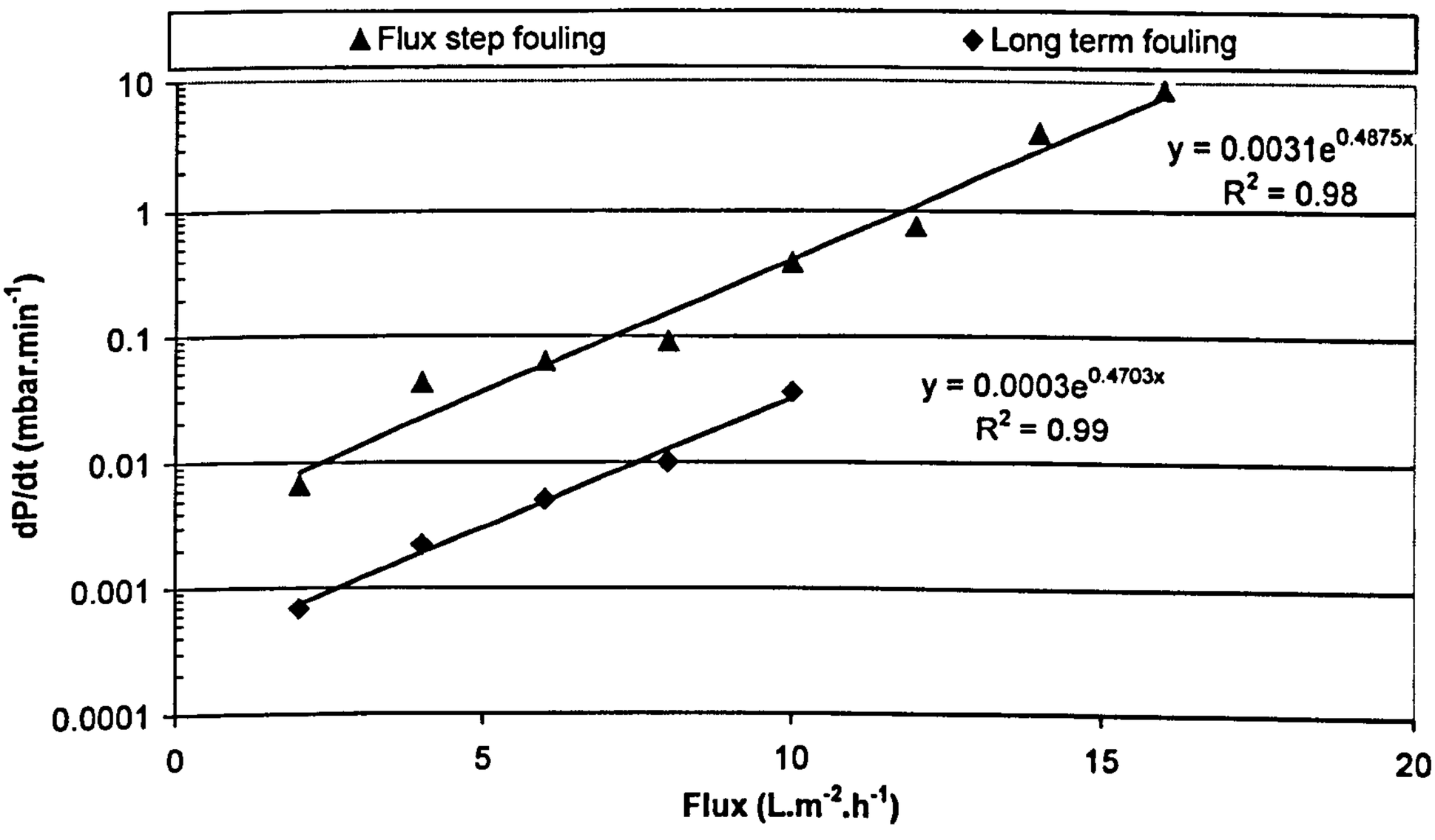

Figure 7.12 Comparison fouling rates short and long term operation (Biomass concentration 6 g.L^{-1})

- dP/dt = $0.0031e^{0.49J}$ for flux-step studies cf. $0.0003e^{0.47J}$ for the long-term trials at 6 g.L^{-1}, Figure 7.12;

- $dP/dt = 0.0073e^{0.30J}$ for the flux-step studies cf. $0.0005e^{0.36J}$ for the long-term trials at 12 $g.L^{-1}$; Figure 7.13;
- $dP/dt = 0.0052e^{0.26J}$ for the flux-step studies cf. $0.0009e^{0.26J}$ for the long-term trials at 18 $g.L^{-1}$. Figure 7.14.

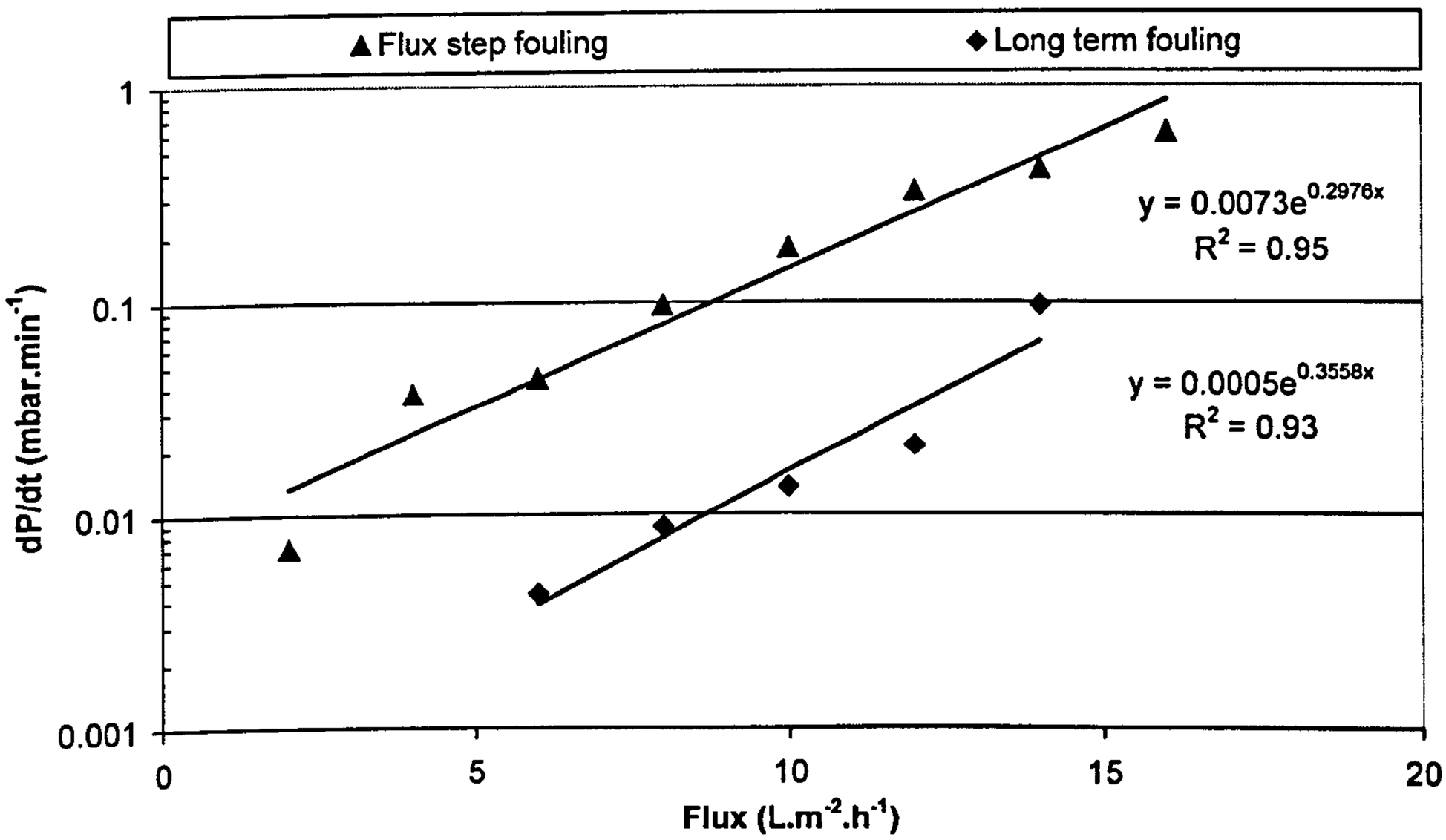

Figure 7.13 Comparison fouling rates short and long term operation (Biomass concentration 12 $g.L^{-1}$)

The benefit of operating at the higher MLSS concentrations only becomes apparent at higher fluxes, since very similar fouling rates are observed during both long term trials and short term flux step tests at fluxes below 8 $L.m^{-2}.h^{-1}$ and 6 $L.m^{-2}.h^{-1}$ for trials at 12 $g.L^{-1}$ and 18 $g.L^{-1}$ respectively (Figure 7.6 and 7.9). Differences in fouling rate observed between short term and long term trials may be influenced by methodology. No relaxation or membrane backwashing was carried out between flux steps such that material at the membrane surface causing increase the reversible fouling during a flux

step may not be removed, instead adding to filtration resistance in the subsequent flux step and so greater fouling rates being observed.

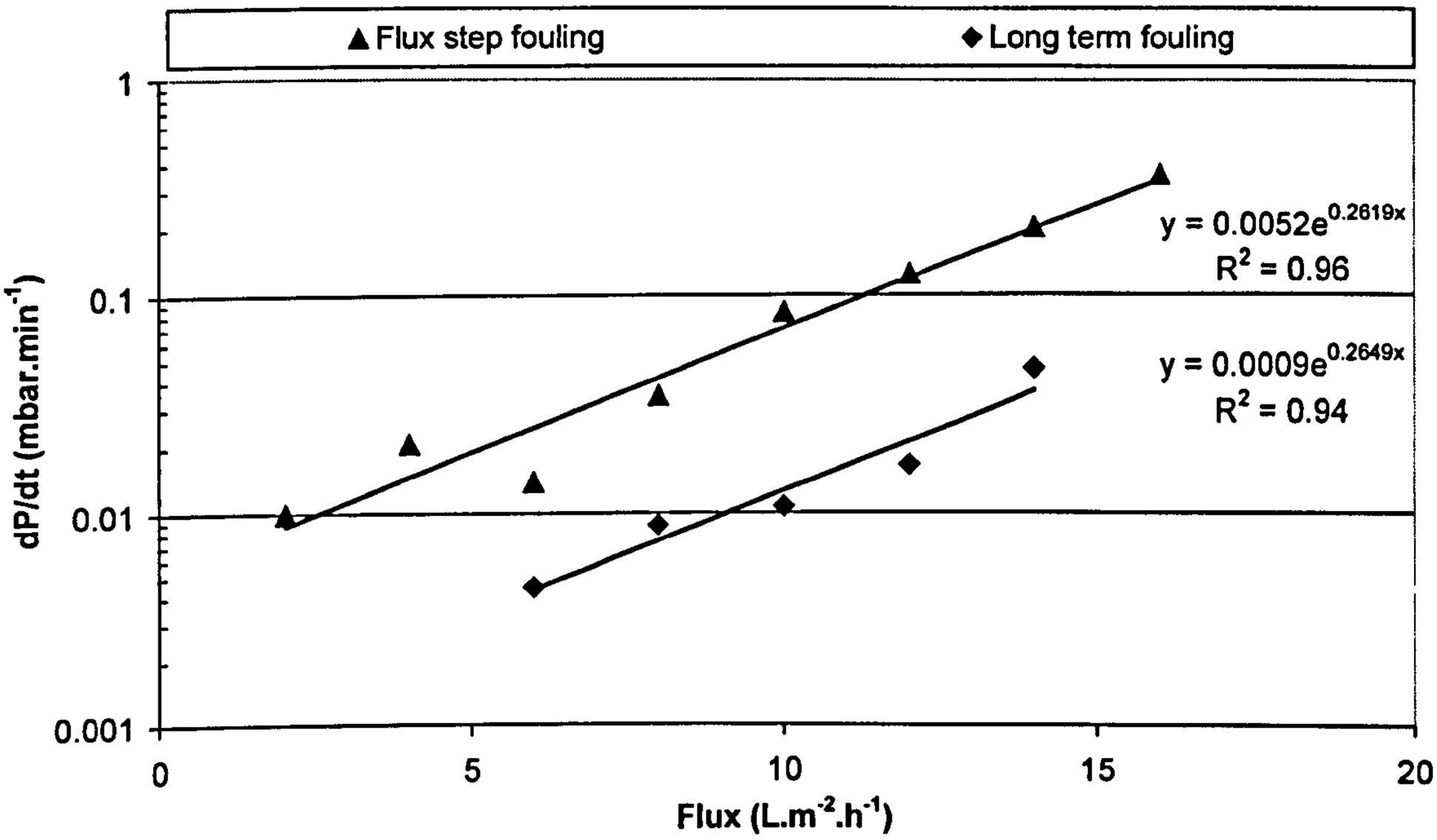

Figure 7.14 Comparison fouling rates short and long term operation (Biomass concentration 18 g.L^{-1})

7.5 Application of an existing fouling model for sustainable flux operation

Trends from long term membrane fouling trials outlined in Section 7.3 may be used to ascertain the validity and potential use of a model describing sub-critical flux fouling recently proposed by Ognier *et al.* (2004). Fouling behaviour prior to the end of stable operation (t_{filt}) is considered. Data obtained during fouling trials carried out at biomass concentration of 6 g.L^{-1} are used, since this being the only conditions that the two phase fouling trend was encountered.

The conceptual framework of the model can be briefly summarised as follows: when the membrane operates at values lower than the critical flux, the soluble particles interact with the membrane surface, thus reducing the number of open pores available for filtration (n_p). To continue operating at the same overall flux, local fluxes at other areas on the membrane surface must increase. When the local flux in available pores becomes equal to or exceed the critical flux (previously determined by short term flux-step tests) a sudden increase in TMP takes place due to solids accumulation and cake formation on the membrane surface. A diagrammatic representation is shown in Figure 7.15 below.

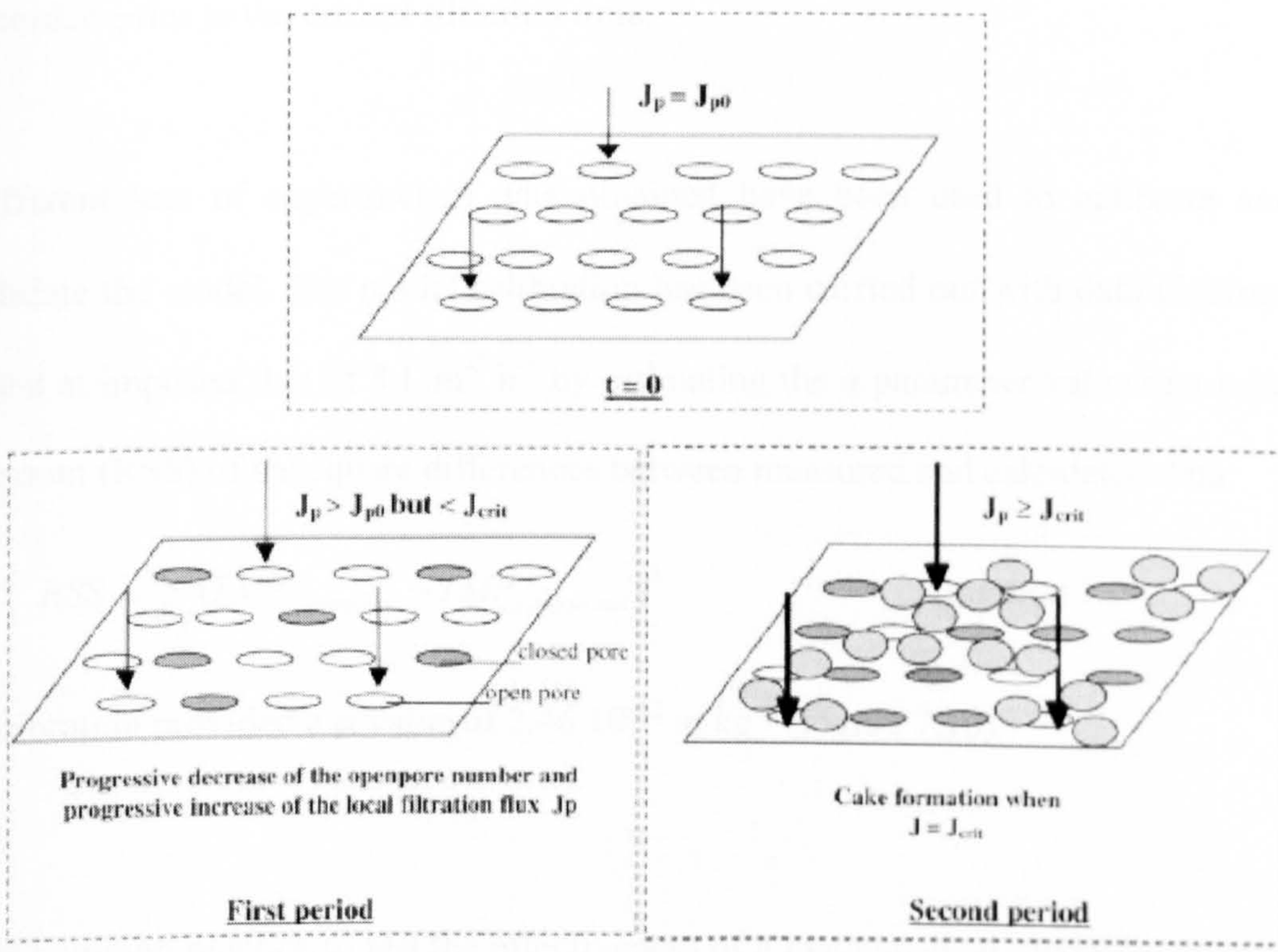

Figure 7.15 Diagrammatic representation of two stage fouling (Ognier *et al.* 2004)

The model is expressed as:

$$TMP(t) = \frac{TMP_0}{1 - \frac{\alpha \cdot TMP_0 \cdot t^2}{2}} \qquad \textit{Equation 7.1}$$

where TMP_0 is the transmembrane pressure at the start of the filtration and α is an adjustable parameter incorporating both membrane and suspension characteristics.

The term α includes two proportionality constants referring to the mass transport of foulants towards the membrane surface and the gradual decrease in open pore area; α takes into account geometric and physical membrane properties (pore section S_p and hydraulic resistance R_p). The value of α can be determined from experimental data recorded prior to the critical filtration time.

Different sets of experimental data obtained have been used to calibrate and then validate the model. The model calibration has been carried out with data obtained from a test at imposed flux of 8 $L.m^{-2}.h^{-1}$ by estimating the α parameter value that minimizes the sum (RSS) of the square differences between measured and calculated data:

$$RSS = \sum_{j=1}^{N} \left(TMP_{j,measured} - TMP_{j,calculated} \right)^2 \qquad \textit{Equation 7.2}$$

Calibration provided a α value of 2.46 10^{-12} m kg^{-1} (Figure 7.16).

It is common practice to test the effectiveness of a mathematical model by conducting a validation phase to evaluate the behaviour of the model when the mathematically determined value of a given parameter (α in this case) is used to predict another series of data. Therefore the α value obtained at 8 $L.m^{-2}.h^{-1}$ was used to verify the capability of the model to predict long term fouling profiles at other fluxes examined (2 $L.m^{-2}.h^{-1}$, 4 $L.m^{-2}.h^{-1}$, 6 $L.m^{-2}.h^{-1}$). The error associated with the models prediction according to Equation 7.3, ranged between 23.3 % and 84.5 %, thus showing a poor fit with the

experimental data collected at different fluxes but under otherwise identical conditions of calibration in terms of MLSS, SRT and membrane conditions.

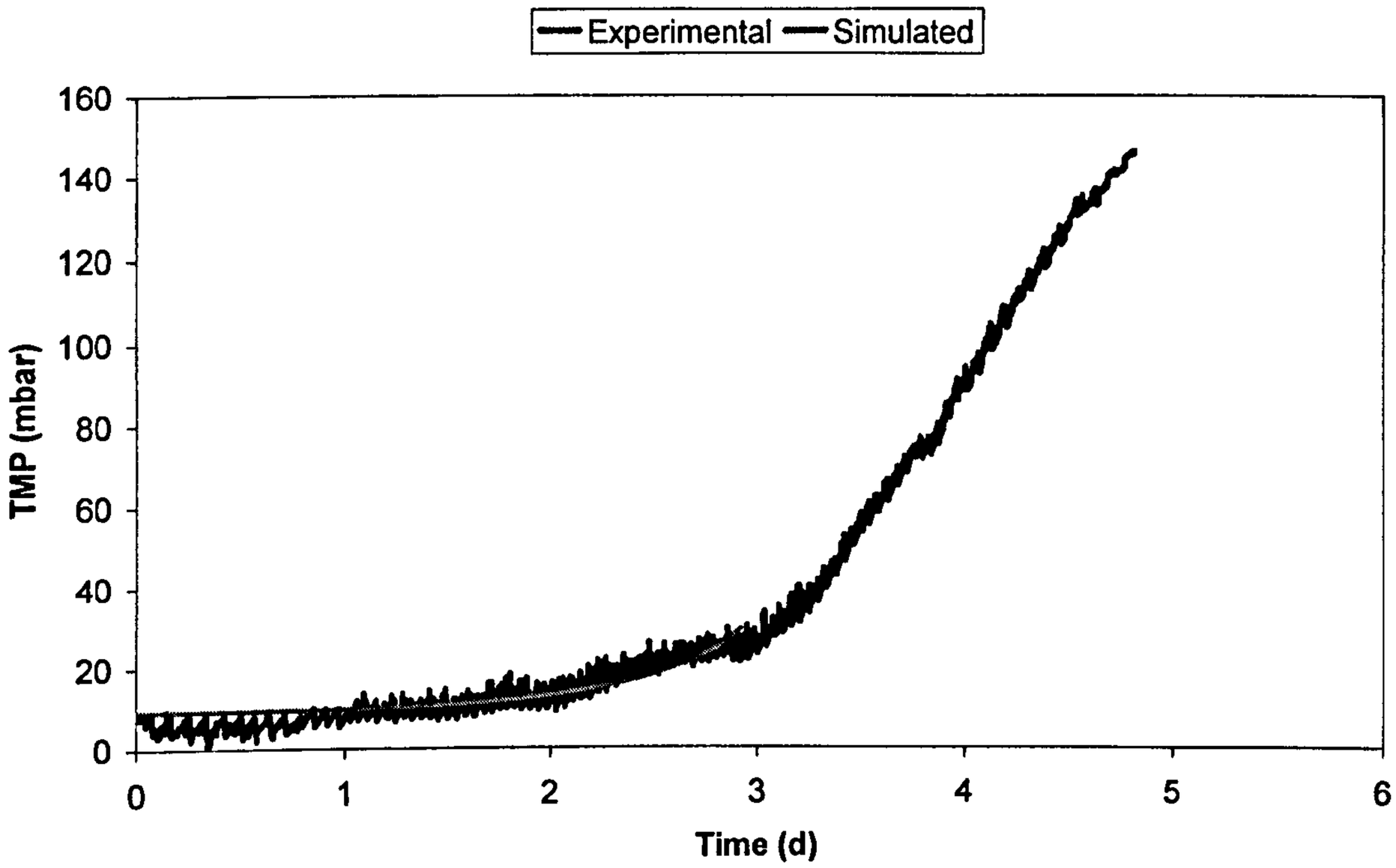

Figure 7.16 Mathematical calibration of the α value at 8 L m^{-2} h^{-1}

$$\%Error = \frac{\sum_{j=1}^{N} \left| TMP_{measured} - TMP_{simulated} \right|}{\sum_{j=1}^{N} TMP_{measured}} \qquad \textit{Equation 7.3}$$

The trend of predicted and experimental data at an imposed flux of 4 L.m^{-2}.h^{-1} is displayed in Figure 7.17 and demonstrates the underestimation of the model with respect to the actual TMP profile. Table 7.5 shows the values of α with the best fit for the series of data under consideration.

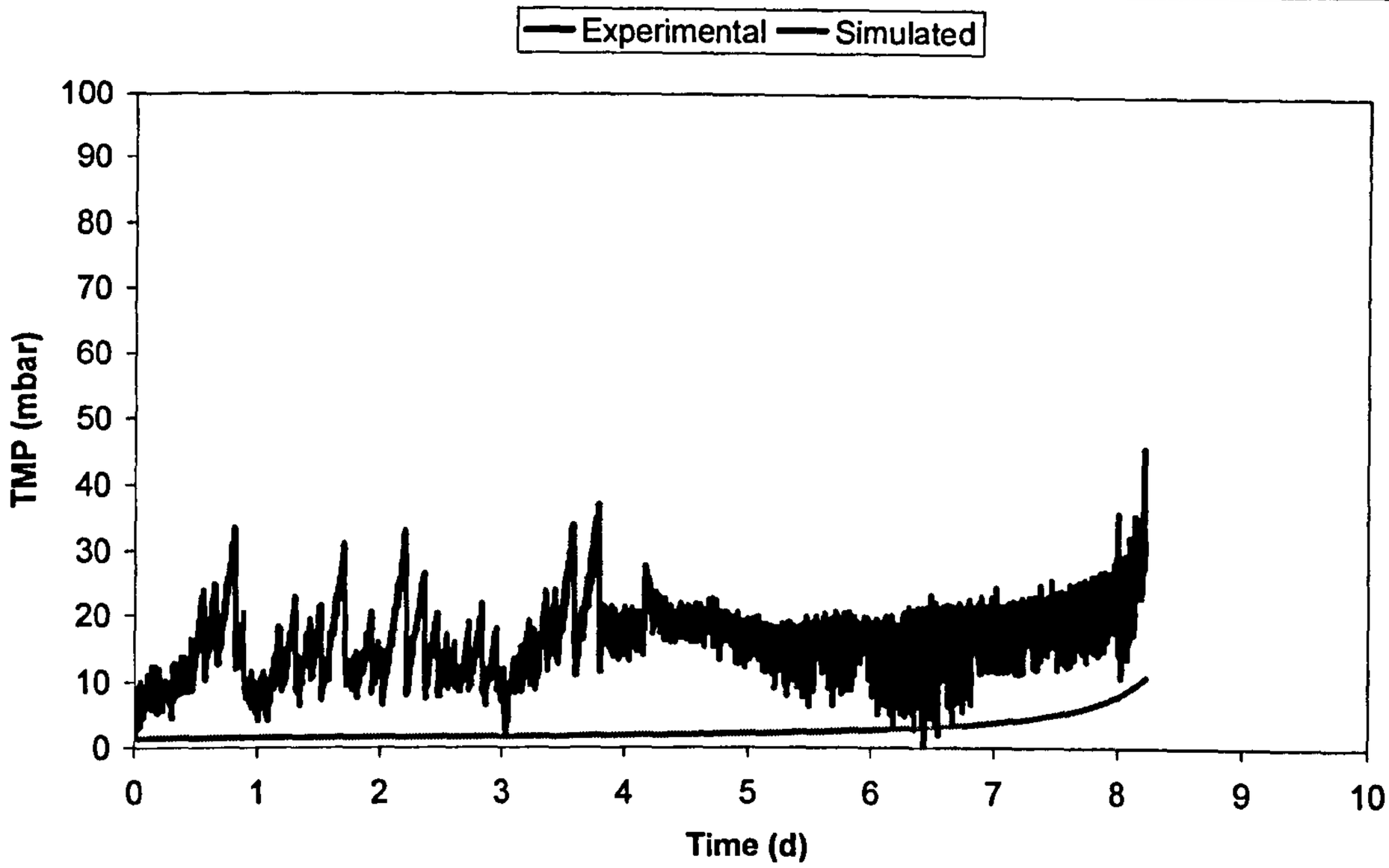

Figure 7.17 Model validation at 4 L m^{-2} h^{-1}

Table 7.5 Optimal values of the α parameter for different fluxes under long term operation

J L.m^{-2}.h^{-1}	α value (Best fit) m.kg^{-1}
2	3.70 10^{-13}
4	5.36 10^{-12}
6	2.51 10^{-13}
8	2.46 10^{-12}

Recorded experimental TMP data is "noisy" due to the sensitivity of the pressure logging software and the bioreactor level operating on a high and low level for feed cycles, partly accounting for the poor fit. Another possible contributing factor may lie with the conceptual approach of the model. Many components are incorporated into the

α parameter, which is assumed to be constant with time. Given that operation is over a prolonged period (up to 10 days for the test at 2 $L.m^{-2}.h^{-1}$) and fouling constituents are likely to change because of the heterogeneity of the feed suspension this assumption may not be valid, such that α should more correctly be expressed as a function of time.

7.6 Comparison of feed-water sources

Feed waters from different sources and of different strength (BOD, COD, DOC, N etc) will lead to the development of biomass of differing nature and with, ultimately, different fouling propensities. For the purposes of this study methods outlined by Le-Clech *et al.* (2003a) will be followed as to allow comparison of data.

7.6.1 Short-term fouling experiments

Flux step experiments were carried out and compared with those found for municipal wastewater and synthetic municipal sources from a previous study using the same pilot scale rig (Le-Clech *et al.* 2003) to determine the relative fouling propensity of this type of high strength industrial wastewater in comparison to sewage-fed bioreactors. A step height of 2 $L.m^{-2}.h^{-1}$ for produced water and synthetic municipal wastewater and 3 $L.m^{-2}.h^{-1}$ for municipal wastewater were employed, each with step durations of 15 minutes. The systems were kept at steady state with an MLSS concentration of 6 $g.L^{-1}$ for produced water bioreactor and 3 $g.L^{-1}$ for real and synthetic municipal wastewater fed bioreactors.

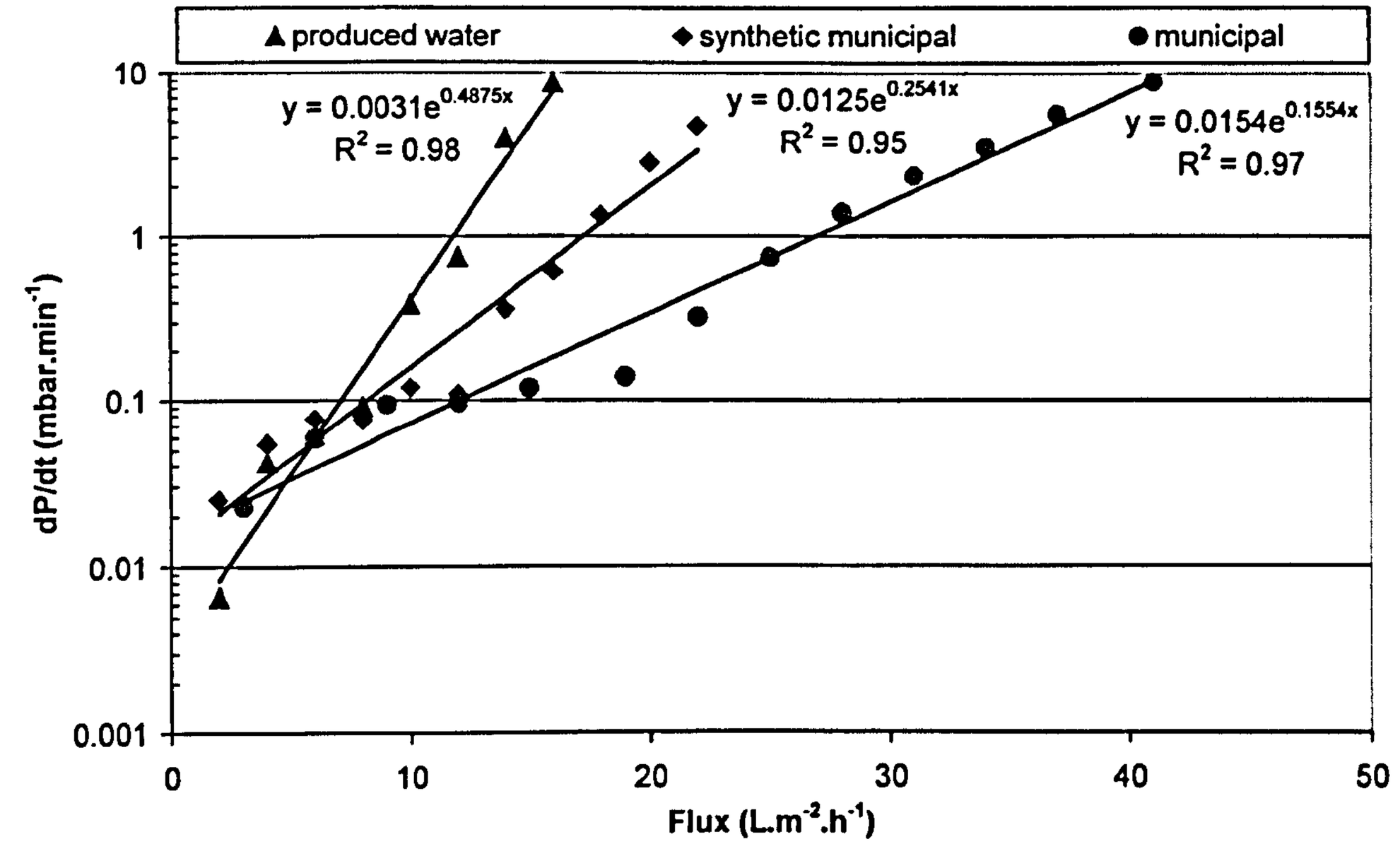

Figure 7.18 Comparison flux step fouling rates for range of feedwater matrices (data from current study together with synthetic municipal and municipal data from Le-Clech *et al.* 2003a)

The comparable fouling rate values determined at the same flux for real and synthetic sewage fed bioreactors were substantially lower than those measured for the produced water analogue at fluxes above 8 $L.m^{-2}.h^{-1}$ (Figure 7.18).

7.6.2 Long-term fouling trials

Data from long-term experiments conducted for the produced water-fed MBR operating at a flux of 8 $L.m^{-2}.h^{-1}$ are compared with those from both synthetic and real sewage matrices at fluxes of 7 $L.m^{-2}.h^{-1}$ and 9 $L.m^{-2}.h^{-1}$ respectively (Figure 7.19).

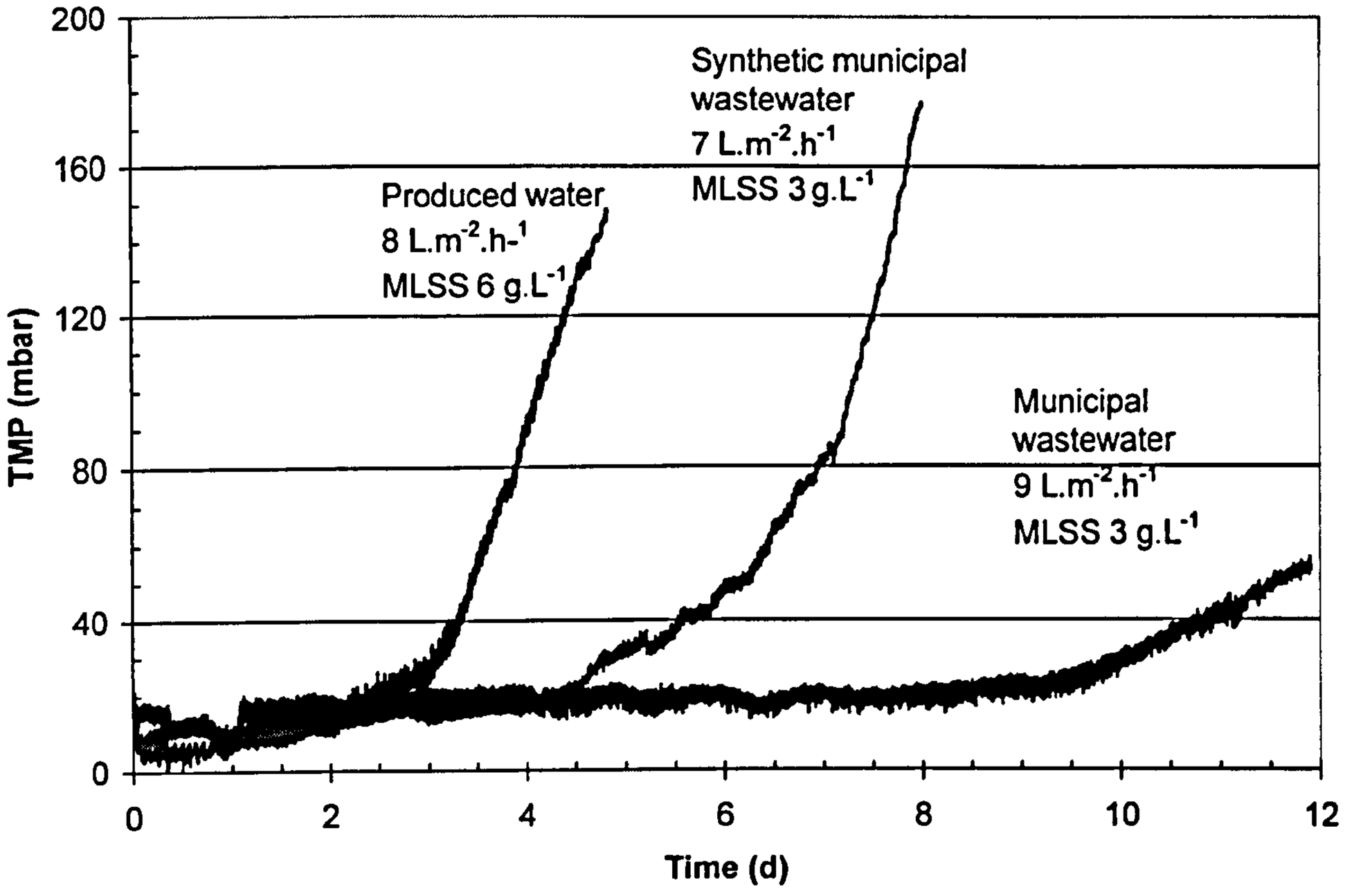

Figure 7.19 Comparison long term pressure transients for range of feedwater matrices (data from current study together with synthetic municipal and municipal data from Le-Clech *et al.* 2003a)

Trends from produced water show TMP to increase fairly slowly for the first three days (from 4 to 25.2 mbar, corresponding to dP/dt = 0.005 mbar.min^{-1}) and then rapidly up to 147 mbar at Day 4. In the case of the analogue sewage TMP increased only very slowly for the first four days (from 11 to 17 mbar, corresponding to dP/dt = 0.001 mbar.min^{-1}) and then exponentially up to 176 mbar by Day 8. For the real sewage operating at the lower flux of 9 L.m^{-2}.h^{-1}, the TMP seemed stable for up to 10 days. However, the TMP increased from 14 to 22 mbar within the first 9 days of filtration (dP/dt = 7.10^{-4} mbar.min^{-1}). From Day 10, the fouling rate accelerated to a TMP of 54 mbar on Day 12. Clearly, produced water has a significant fouling propensity even at lower, supposedly

sub-critical, flux values, and certainly greater than that of both synthetic and real municipal wastewater, from both long-term and flux step test data.

Results from similar studies cited in the literature arise from experiments carried out at a relatively low MLSS concentration of 6g.L^{-1} or below (Table 7.6). Figure 7.20 compares fouling rates found in the present trial to those in the literature (Table 7.6). Results arising from the present study at low fluxes indicate the purported higher fouling propensity of this feedwater.

It is evident that during both short and long term test the bioreactor fed with produced water produces a biomass of significantly greater fouling at lower applied flux than classical sewage biomass. The transitional flux was significantly lower than that reported for either of the two sewage fed reactors, and the period of stable operation (t_{filt}) was lower for constant low-flux, long-term operation.

Table 7.6 Sub-critical long-term data calculated from results of different investigations

System type and volume (membrane)	Feed	Flux $L.m^{-2}.h^{-1}$	MLSS $g.L^{-1}$	t_{filt} Hr	1st phase $dp.dt^{-1}$ ($t<t_{filt}$) $mbar.min^{-1}$	2nd phase $dp.dt^{-1}$ ($t>t_{filt}$) $mbar.min^{-1}$	Ref
SS MBR 20L Tub. (0.05 µm)	Syn. Mun.	10	1.8	550	$<8.3 \times 10^{-3}$	0.45	Ognier *et al.* (2004)
SS UASB Bench FP (0.22 µm)	Syn. Mun.	30	0.3-0.55	360	$< 6 \times 10^{-3}$	0.046	Cho and Fane (2002)
Subm. 40L Tub. (0.1 µm)	Mun.	9	3	240	7×10^{-4}	0.01	Le-Clech *et al.* (2003)
Subm. 40L Tub. (0.1 µm)	Syn. Mun.	7	3	100	0.001	0.028	Le-Clech *et al.* (2003)
SS MBR 50L HF. (0.22 µm)	Syn. Mun.	22	5 - 6	1220	1.8×10^{-3}	0.71	Wen *et al.* (2004)
SS MBR 50L HF. (0.22 µm)	Syn. Mun.	25	5 - 6		4×10^{-3}	0.045	Wen *et al.* (2004)
SS MBR 50L HF. (0.22 µm)	Syn. Mun.	30	5 - 6		0.012	0.03	Wen *et al.* (2004)
Subm. 40L Tub. (0.03 µm)	Syn. Ind.	4	6	192	2.2×10^{-3}	0.14	Current study
Subm. 40L Tub. (0.03 µm)	Syn. Ind.	6	6	137	5.1×10^{-3}	0.031	Current study
Subm. 40L Tub. (0.03 µm)	Syn. Ind.	8	6	74	0.1	0.047	Current study

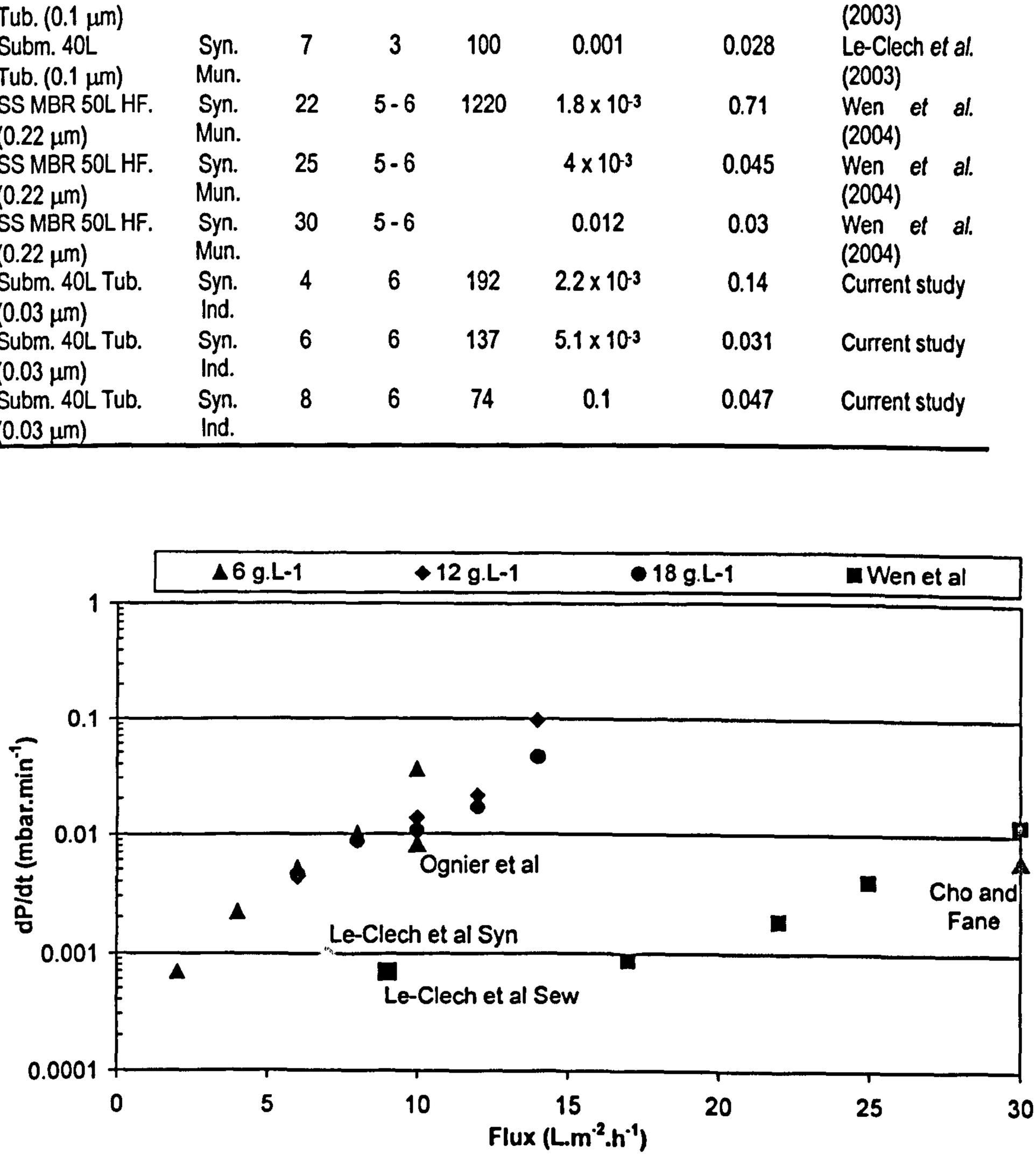

Figure 7.20 Fouling rates during long term operation

During the reported trial (Le-Clech *et al.* 2003a) EPS protein and carbohydrate were measured at 73 and 30 mg per g of MLSS for an MBR fed with synthetic municipal wastewater, and slightly lower (60 and 17 mg per g of MLSS for protein and carbohydrate respectively) for real sewage. The significantly lower proteinaceous EPS level measured for sewage may account for the lower fouling rate recorded for this matrix. However EPS values found for produced water-fed bioreactor are significantly lower (20.3 and 13.6 mg per g of MLSS for protein and carbohydrate respectively), suggesting that other biomass quality determinants besides the measured EPS level impact upon fouling. A key difference between the three different feedwaters compared (Sewage, synthetic sewage and produced water) is the feedwater strength. The COD of the system in the current study was significantly greater than either the synthetic municipal or municipal fed bioreactors (1575 $mg.L^{-1}$, 460 $mg.L^{-1}$, 150-250 $mg.L^{-1}$).

Differences in membrane material and pore size, biomass characteristics and operation including membrane air flow rates all have an influence on fouling (Section 2.2).

7.7 Effect of shear in side-loop airlift system and pumped air lift trial

A modification was made to the pilot MBR in the final phase of the study described in Section 4.3.3 to examine the flux attainable during operation at higher shear provided by increased airflow and hence cross flow velocities to the membrane.

7.7.1 Air-lift system

Results from flux step tests conducted at three cross flow velocities tested are shown in Figures 7.21 – 7.23.

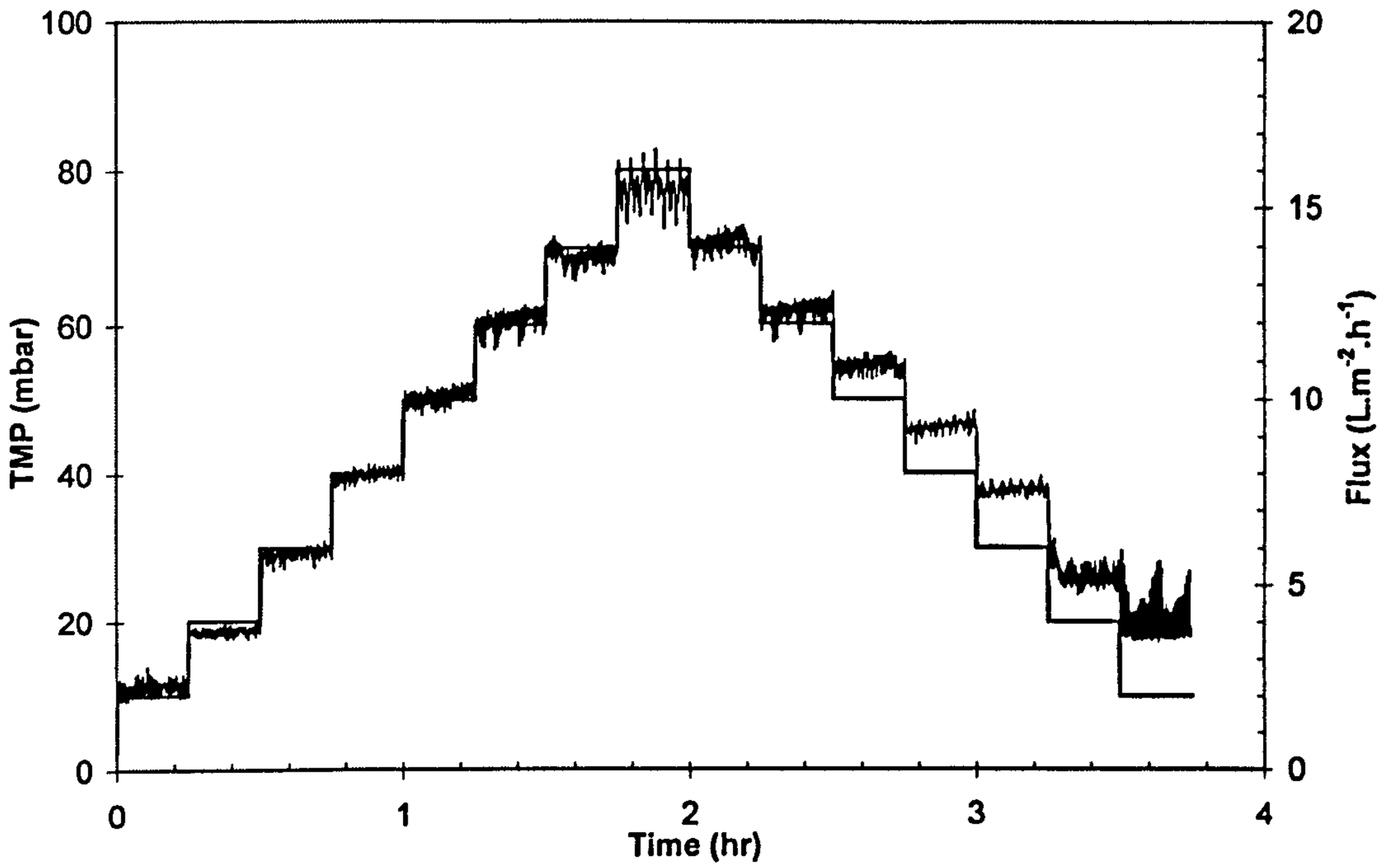

Figure 7.21 Flux step test (CFV = 0.5 $m.s^{-1}$)

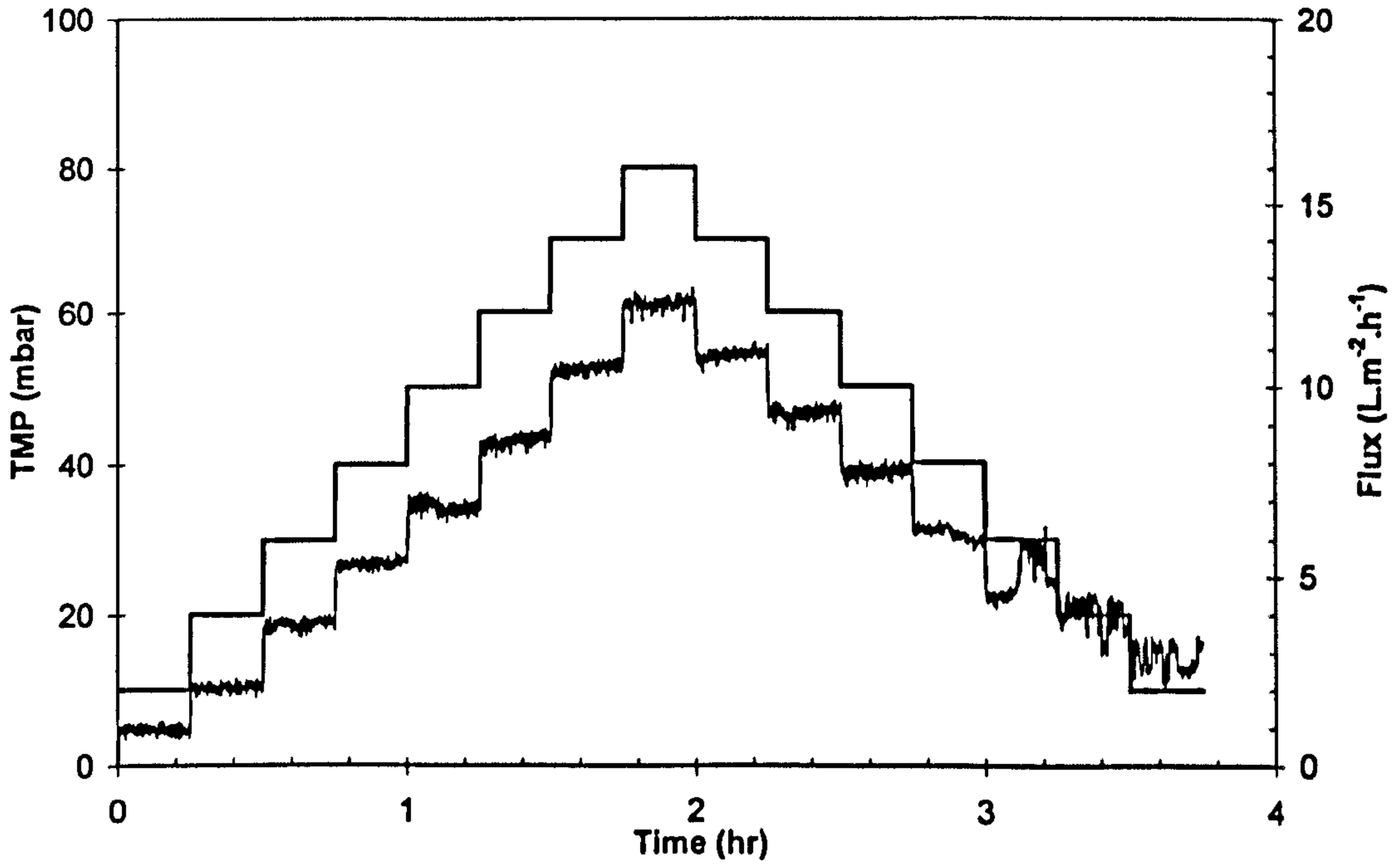

Figure 7.22 Flux step test (CFV = 1 $m.s^{-1}$)

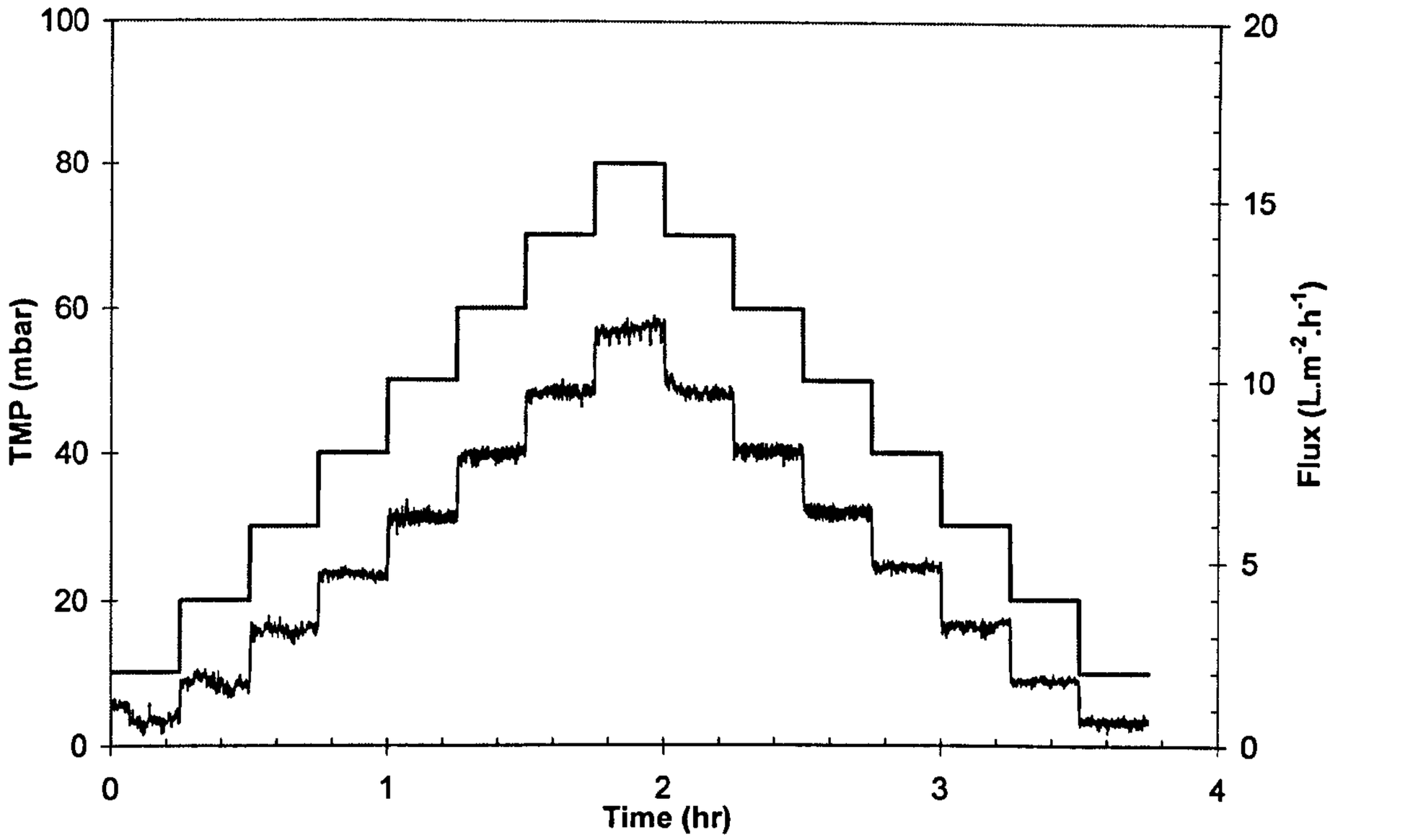

Figure 7.23 Flux step test (CFV = 1.5 $m.s^{-1}$)

Fouling rates were lower during tests at higher cross flow velocities. According to the definition used earlier where transitional flux is defined as an acceptable fouling rate of 0.2 $mbar.min^{-1}$ all fluxes examined were below the transitional flux at all cross flow velocities.

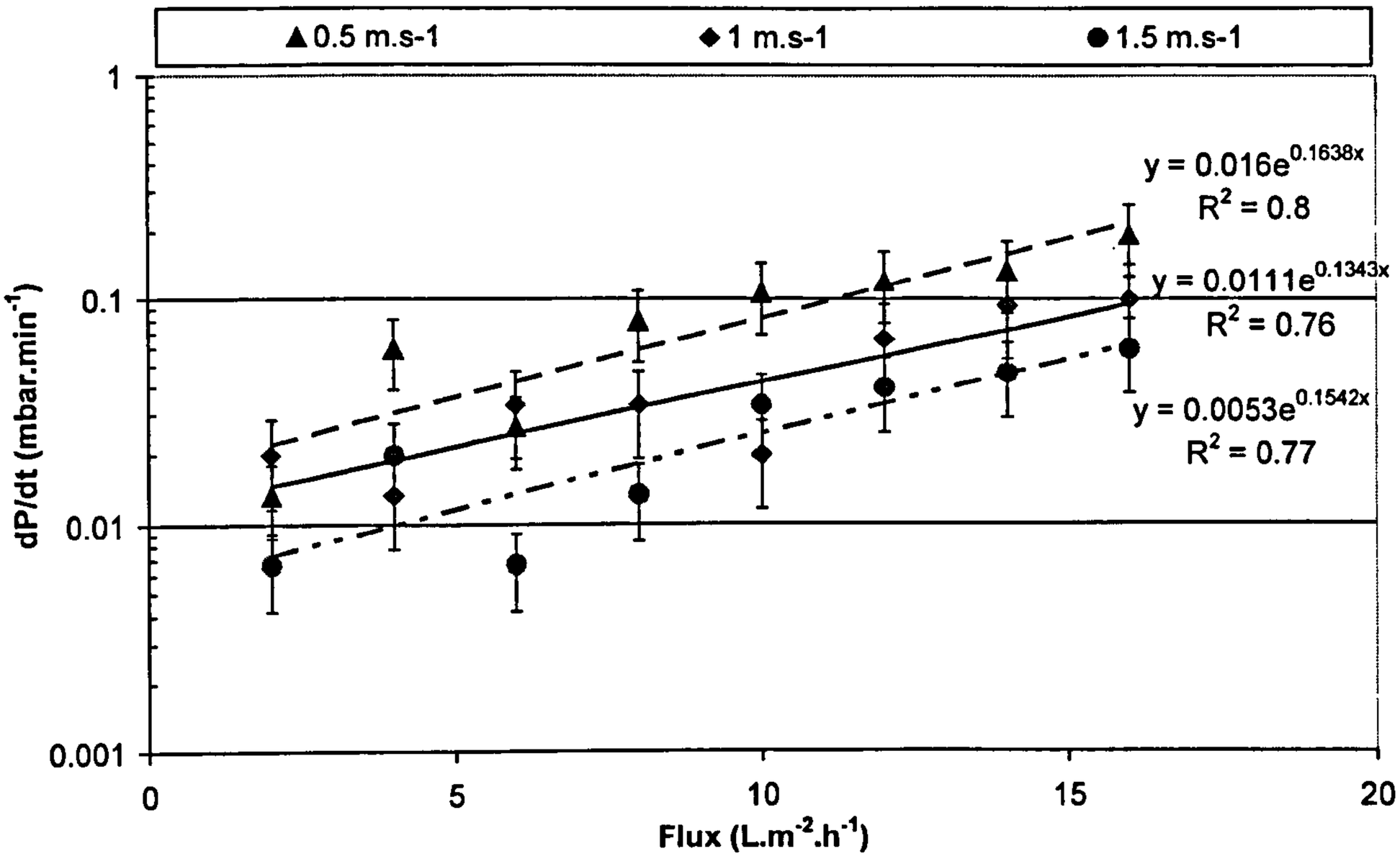

Figure 7.24 Fouling rates at a range of cross flow velocities (Biomass 18 g.L^{-1})

7.7.2 Pumped side-stream system

A second modification was made to the sidestream rig where a pump was installed within the side loop to circulate biomass through the membrane module and return to the reactor. Shear was provided by liquid velocity and also by air through the module. Operating conditions of the system were a TMP of 1.1 bar and cross flow velocity of 3.5 m.s^{-1}, slightly lower than typical operating pressures for crossflow operation (1.5 – 3 bar) and mid- range with respect to crossflow velocities.

During the first day of operation the flux attained was 48 L.m^{-2}.h^{-1} (Fig. 7.25). Over the 7 day duration of the trial flux decreased to a lowest value of 39 L.m^{-2}.h^{-1} but returned to 47 L.m^{-2}.h^{-1} without requiring relaxation backwash and chemical cleaning. In contrast Zaloum *et al.* (1994) reported a flux decline of 48% using tubular sidestream system at

an operating pressure of 2.4 bar and Scholz and Fuchs (2000) experienced 33% flux decline from 90 to 60 $L.m^{-2}.h^{-1}$ at TMP of 1.5 bar and cross flow velocity of 2.2 $m.s^{-1}$.

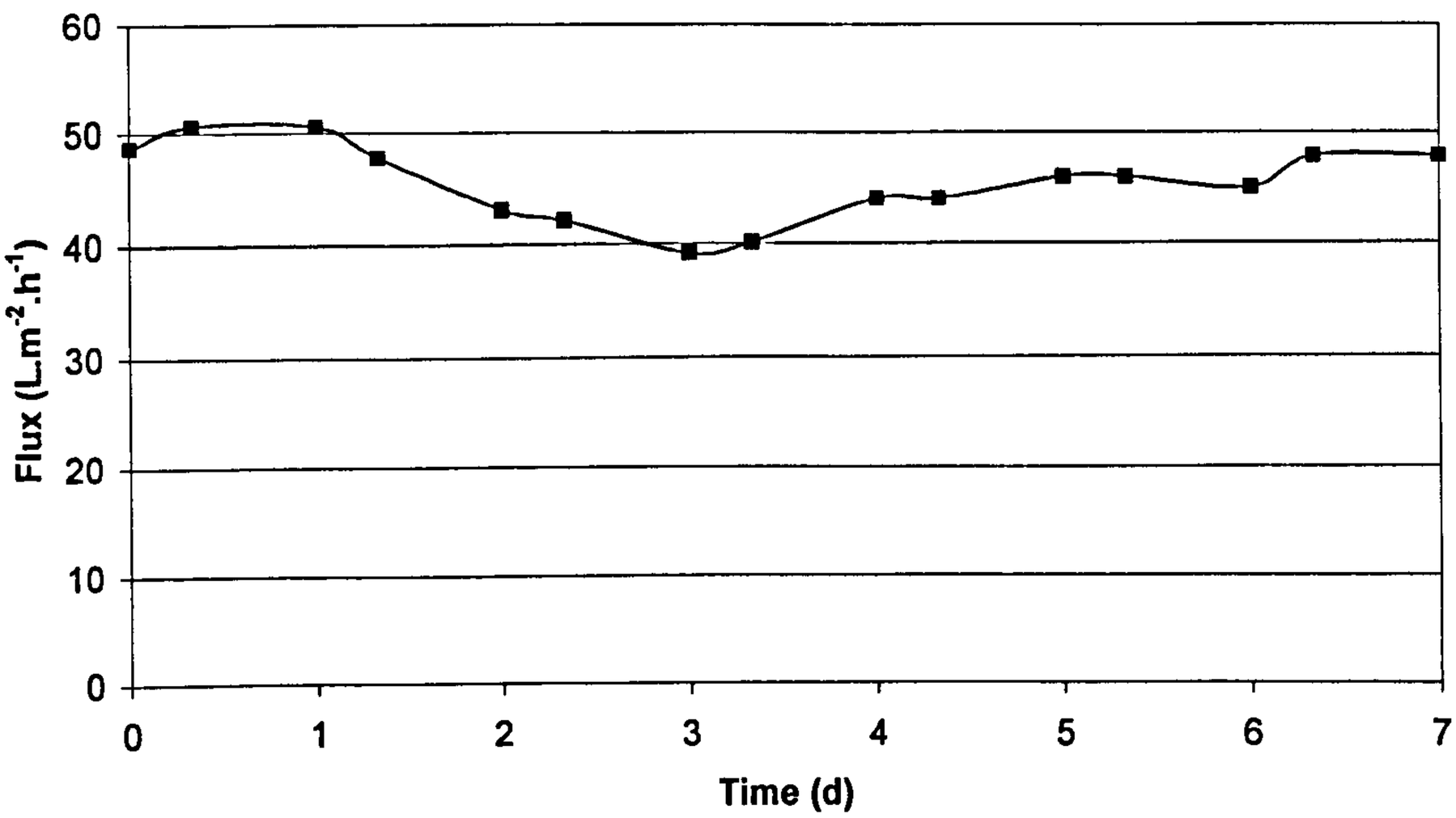

Figure 7.25 Flux behaviour under constant pressure trial

7.8 Oil shocking trials

Brent crude oil was dosed stepwise directly into the bioreactor operating at 18 g L^{-1} MLSS using 5mL of methanol containing mineral oil at concentrations (ppmv of the bioreactor) and timescales indicated in Table 7.7. Oil concentration represents the cumulative concentration. Oil droplet size was not controlled. The applied membrane flux was 4 $L.m^{-2}.L^{-1}$ to minimise the effect of fouling under normal long term operation as identified in Section 7.3. Results are shown in Figure 7.26.

Table 7.7 Dosed oil concentration

Time	Oil concentration (ppmv)
0	0
10	5
24	10
34	25
48	50
58	100
72	200
82	500

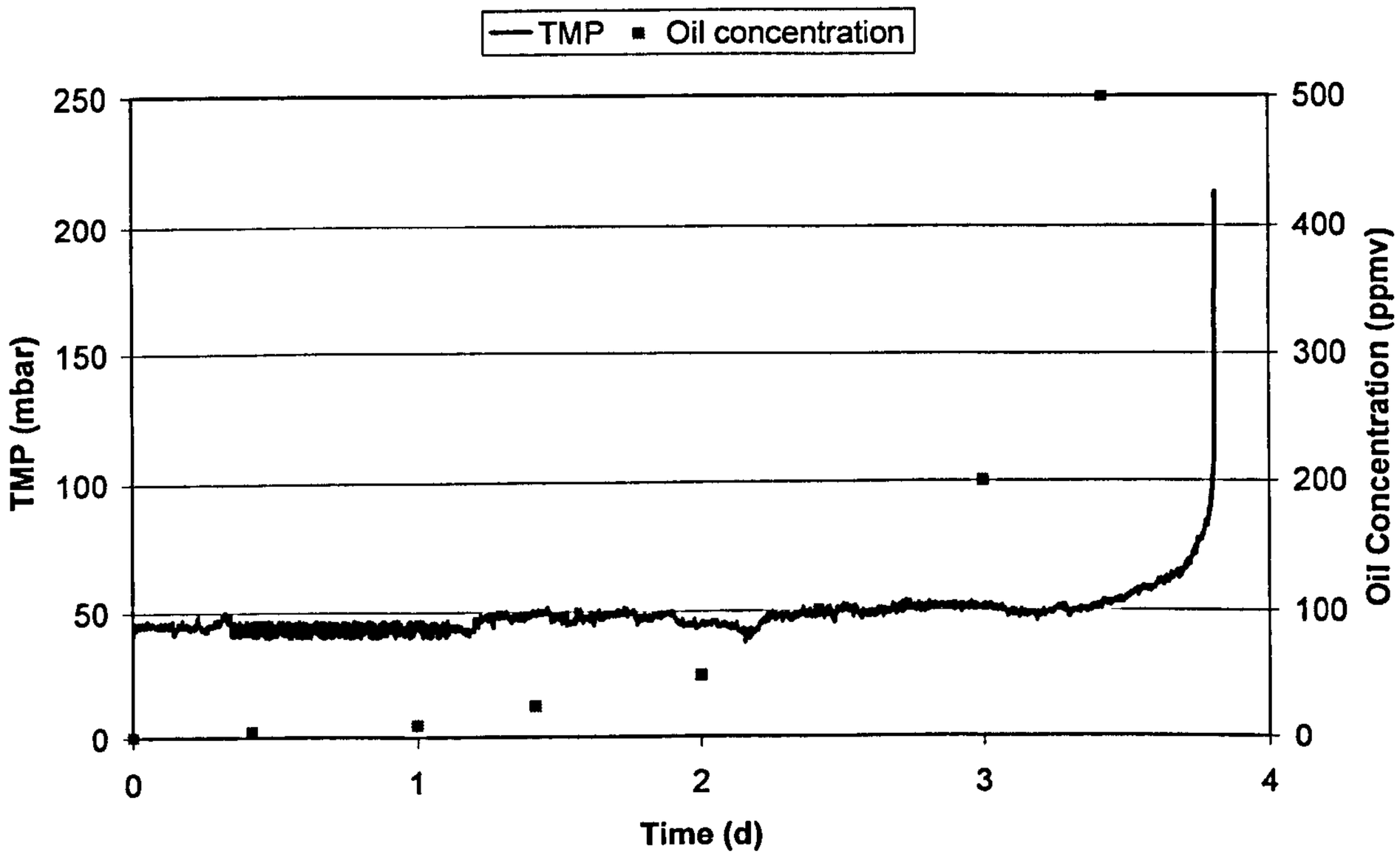

Figure 7.26 Long term pressure transient during oil shocking trial

Membrane fouling up to Day 3, by which point the total concentration of added oil was 200 ppmv, was low at 1.4×10^{-3} mbar.min^{-1}. Long-term membrane fouling at 4 L.m^{-2}.h^{-1} was not studied at biomass MLSS concentration of 18 g.L^{-1}. It is however below the fouling rate recorded at 6 L.m^{-2}.h^{-1} and 18 g.L^{-1} which was 4.5×10^{-3} mbar.min^{-1} and at 4 L.m^{-2}.h^{-1} and 6 g.L^{-1} of 2.2×10^{-3} mbar.min^{-1}.

Immediately after dosing oil to the 500 ppmv the fouling rate started to rise exponentially in a similar manner to the two stage fouling behaviour although the fouling rate during the second stage was higher at 8 mbar.min^{-1} reaching TMP of 213 mbar. Anecdotal evidence of the increasing oil concentration was manifested as visible oil deposits on the sides of the bioreactor and at the surface, attached to the biomass.

7.9 Membrane fouling summary

The results from the fouling trials may be summarised as follows:

1. A transitional flux a marking change from low fouling to high fouling conditions was identified as 8 L.m^{-2}.h^{-1} for 6 g.L^{-1} and 12 L.m^{-2}.h^{-1} for 12 and 18 g.L^{-1} biomass MLSS concentration
2. Higher fouling rates are evident at lower biomass concentration above the transitional flux.
3. Fouling behaviour below the transitional flux is similar for all biomass MLSS concentrations both during long term and short term operation.
4. A two-stage fouling phenomenon under long term operation is exhibited at the lowest biomass concentration studied of 6 g.L^{-1}, but is not evident at higher biomass concentrations.
5. The critical filtration time for low-fouling operation (t_{filt}) decreases with increasing flux.
6. An equation describing dynamic trend in pressure vs. time provided by Ognier *et al.* (2004) does not appear to predict fouling behaviour, as defined by data recorded in the current study.

7. There is no clear relationship between SMP/EPS levels and fouling rate according to data produced from this study, contrary to previously reported trends.

8. It is evident that during both short and long term tests the bioreactor fed with produced water displays significantly greater fouling at lower applied flux.

9. Operation at higher shear by increasing membrane airflow rate in airlift sidestream system led to lower fouling rates than obtained during submerged operation. The membrane airflow under normal submerged conditions could be optimised i.e. increased and could be reasonably expected to yield similar benefits

10. Operation of a pumped sidestream system at a higher operating pressure of 1.1 bar and cross flow velocity of 3.5 $m.s^{-1}$ led to a sustainable flux of 48 $L.m^{-2}.h^{-1}$

11. The effect of free oil shocking on MBR operation and fouling propensity showed no accelerated fouling that could be attributed to the oil concentration over 3 days and up to 200 ppmv oil concentration, but on increasing the oil concentration to 500 ppmv rapid and exponential fouling ensued.

8 Conclusions, recommendations and future work

Experiments conducted on a submerged tubular membrane bioreactor used for the treatment of a BTEX-laden produced water analogue have revealed a number of facets of treatment performance, biomass properties and fouling behaviour, as outlined below.

8.1 Treatment performance

- Excellent COD and TOC removal rates were found, between 90 and 97%, somewhat higher than many removal data found in the literature. This would appear to reinforce the view that MBR technology is a good process option for produced water treatment.
- SRT and biomass MLSS concentration has little effect on COD and TOC removal.
- Benzene, Toulene, Ethylbenzene and Xylene were removed to above 99% in liquid phase with loss to atmosphere between 0.3 and 1%.
- Loss of BTEX to the atmosphere by stripping during aerobic treatment was not significant for either the porous pot or MBR systems despite high air to liquid ratios. Concentrations were 4 orders of magnitude lower than UK OEL values indicating vanishingly small health and safety risk unless compounds are allowed to concentrate, for example in the head space of the reactor

8.2 Biomass characterisation

- An increase in non-volatile solids was not apparent at longer sludge ages and higher biomass MLSS concentrations with the MLVSS:MLSS ratio between 0.87 to 0.93 at the highest MLSS concentration showing potential to operate at long sludge ages and so low sludge wastage conditions

- In contrast to other studies an exponential relationship between MLSS concentration and CST was not evident, indicating that sludge dewaterability would be unaffected by operating at high MLSS concentrations.
- SMP and EPS concentrations expressed as $mg.L^{-1}$ increased with increasing biomass (MLSS) concentration. Normalised EPS carbohydrate concentration ($mg.g\ MLSS^{-1}$) decreased with increasing biomass MLSS concentration whilst normalised protein levels increased.
- Results from microbial abundance and diversity analysis show profiles within the produced water MBR were highly conserved over time. Cell counts remained relatively consistent, species richness was stable and the cumulative species curve was relatively flat, indicating the establishment of a stable community within the system. A rank/abundance plot demonstrated high abundance by a few members of the community. This stability and consistency may be explained by the constant concentration and composition of produced water analogue being fed into the MBR throughout operation, and is unlikely to be reproduced in practice using real wastewater.

8.3 Membrane fouling

- A transitional flux a marking change from low fouling to high fouling conditions was identified as 8 $L.m^{-2}.h^{-1}$ for 6 $g.L^{-1}$ and 12 $L.m^{-2}.h^{-1}$ for 12 and 18 $g.L^{-1}$ biomass MLSS concentration, lower than those evident for municipal and synthetic municipal fed bioreactors. This demonstrates that the produced water fed biomass has a higher fouling propensity than other feedwater sources identified from the literature.
- Fouling rate dP/dt is exponentially related to flux for both short term and long term trials, as found in previous studies

- Fouling behaviour below the transitional flux is similar for all biomass MLSS concentrations both during long term and short term operation. However, higher fouling rates are evident at lower biomass concentration above the transitional flux.
- The flux step data yields the same exponent value for the dP/dt:J correlation as the long term experiments. Short-term fouling experiments may thus be helpful in detecting fouling under sub-critical flux operating conditions and allow comparative studies of different feeds, operating conditions, etc.. True sustainability of low flux operation is only revealed through long-term trials where fouling rates may be an order of magnitude lower than that obtained for short term flux step tests. This may in part be explained by the nature of the flux step tests where fouling from previous steps may be carried over to subsequent flux steps
- A two-stage fouling phenomenon is exhibited at the lowest biomass concentration studied of 6 $g.L^{-1}$, but is not evident at higher biomass concentrations. Similar behaviour has been reported in three other studies. The critical filtration time for low-fouling operation (tfilt) decreases with increasing flux.
- There is no clear relationship between SMP/EPS levels and fouling rate according to data produced from this study.
- An equation describing the dynamic trend in TMP vs. t provided by Ognier et al. (2004) does not appear to predict fouling behaviour, as defined by data recorded in the current study. This may be due to non-steady behaviour impacting on the parameter α.

- For $t > t_{filt}$, recorded pressure trends are inconsistent with solids deposition according to simple Darcian relationships where fouling rate due to solids accumulation should increase with flux.
- Operation at higher shear by increasing membrane airflow rate in airlift sidestream system led to lower fouling rates than obtained during submerged operation. The membrane airflow under normal submerged conditions could be optimised, i.e. increased, and could be reasonably expected to yield similar benefits. Operation of a pumped sidestream system at a higher operating pressure of 1.1 bar and cross flow velocity of 3.5 $m.s^{-1}$ led to a sustainable flux of 48 $L.m^{-2}.h^{-1}$ over a 7 day period of constant operation.
- The system showed resilience to free oil shocking up to an oil concentration of 200ppmv. Following an increase in oil concentration to 500 ppmv rapid and exponential fouling ensued.

8.4 Recommendations and choice of system

The biomass developed at 6 $g.L^{-1}$ displayed comparable organics treatment performance but significantly higher fouling propensity as flux increased. Recorded transitional flux values were 8 $L.m^{-2}.h^{-1}$ for 6 $g.L^{-1}$ and 12 $L.m^{-2}.h^{-1}$ for 12 and 18 $g.L^{-1}$ biomass MLSS concentrations. If the system is to be operated in a sustainable manner the operating flux would have to be maintained below these values. Operation at these relatively low fluxes has important implications in terms of membrane area and hence cost and footprint. Results from initial analysis of increasing shear by higher airflow rates and/or liquid pumping demonstrated decreased fouling rates and extended sustainable operation, albeit at increased energy consumption. However, a higher energy demand is likely to be of less importance than footprint for the duty of offshore produced water treatment, and the same would apply to niche industrial effluent applications

Depending on the type of system full scale MBR operation often includes fouling controlling measures such as membrane relaxation, periodic backwashing or maintenance cleaning. Under these circumstances fouling could be expected to be reduced and more sustainable operation over longer periods established compared with that attained in the current study.

Performance in terms of organics removal and membrane operation was very similar between biomass MLSS concentrations of 12 and 18 $g.L^{-1}$. By operating at high sludge ages less sludge is wasted, such that disposal costs would be reduced. Against this costs associated with aeration have been shown to increase at elevated MLSS concentrations.

Based on the results from the current study a system using submerged membranes at a biomass concentration of 12 or 18 $g.L^{-1}$ at increased shear by increasing membrane airflow rates may offer best compromise between capital cost, footprint, operating cost and robustness.

8.5 Future work

The following work could be pursued in order to further develop understanding of issues surrounding treatment of produced water in MBRs:

1. A synthetic feedwater was chosen for the current study due to difficulty of procuring, storing and ensuring consistency of the feedwater between phases of the investigation. The composition was based on a typical gas field condensate. Trials conducted at pilot scale should be based on a real feedwater to confirm current results.

2. From current work SRT shows little influence on treatment performance. The other main parameter of HRT was only briefly investigated. A more thorough investigation of the effect of running at decreased HRT at a single SRT or biomass MLSS concentration should be made for the sake of completeness.
3. The fate of PAHs and phenol and BTEX compounds would warrant further analysis. A decrease in performance over time and at extended SRTs was not evident in the current study, however accumulation of these components in the biomass is possible. The concentration of these compounds in the permeate was not examined individually therefore examination of their fate during treatment would confirm their biodegradation.
4. An examination of the effects of shear on membrane fouling during short and long term tests would be required to determine optimum operating conditions.
5. Comparison of short term flux step fouling rates with those from long term operation reveal a difference of an order of magnitude, with short term trials overestimating fouling. The influence of the flux-step protocol should be investigated to establish whether membrane relaxation or backwashing between steps would yield fouling behaviour more representative of long term operation.
6. Further analysis of the trend after the period of stable operation during long term operation should be conducted to confirm if the second phase is related to solids deposition or some other factor. The two-stage fouling phenomena was only exhibited at the lowest biomass MLSS concentration of 6 $g.L^{-1}$ in the current study and below or equal to this concentration in the literature. Further work would to examine if the phenomena pertains only to low-MLSS operation would be worthwhile.

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