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Anaerobic Membrane Bioreactors for Municipal Wastewater Treatment

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Anaerobic Membrane Bioreactors for Municipal Wastewater Treatment

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Philosophy

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ABSTRACT

Anaerobic treatment has historically been considered unsuitable for the treatment of domestic wastewaters. The work presented in this thesis focuses on the incorporation of membranes into the anaerobic bioreactor to uncouple solid retention time and hydraulic retention time. This in turn prevents biomass washout and allows sufficient acclimatisation periods for anaerobes. However, the exposure of membranes to anaerobic biomass comes with its own inherent problems namely fouling. Fouling was found to take place in two stages; a rapid phase characterised by solid and bacterial cell deposition and a slow phase characterised by the travel of colloidal matter to the membrane surface. Gas sparging was also found to attenuate fouling to a considerable extent despite the fact that biomass characteristics were critical factors in the fouling of the system. In addition, side stream membranes showed differing characteristics to submerged membranes.

A comparison of anaerobic membrane bioreactors to conventional anaerobic systems and aerobic membrane bioreactors highlighted the advantage of this system over other comparable technologies. The anaerobic membrane bioreactor is less energy intensive than the aerobic membrane bioreactor, fouls differently to this system and achieves much better performance than would be seen if conventional anaerobic systems were used in the treatment of domestic or municipal wastewaters.

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I would also like to thank God who kept me sane, gave me strength to see this through and made it alright in the end. I owe a huge debt to my family (my parents and brothers) who have been the loudest voices cheering me on and have stood by me through thick and thin even when I have not deserved it.

My sincere gratitude to my friends (especially the LLGs, Kemi, Kunle, Konyin, Deola and Sanmi) who were there for me through all the moments of self doubt as well as all the tears and tantrums. I could not ask for better friends.

Finally, I would like to dedicate this thesis to those who said I should not or could not do this. Thank you for making me a tougher and better ‘fighter’ and because I can now say I did it anyway!

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Notation

| | |
|--------------------|---|
| A | Filtrate area |
| ABR | Anaerobic Baffled Reactor |
| AnMBR | Anaerobic Membrane Bioreactor |
| BSA | Bovine serum albumin |
| BOD | Biological oxygen demand |
| COD | Chemical oxygen demand |
| COD _{inf} | COD concentration into reactor |
| CST | Capillary suction time |
| COV | Covariance |
| CSTR | Complete stirred tank reactor |
| c | Compressibility |
| DI | Deionised |
| DO | Dissolved oxygen |
| dP/dt | Membrane fouling rate |
| EGSB | Expanded granular sludge bed |
| EPS | Extracellular polymeric substances |
| EPS _p | Protein fraction of extracellular polymeric substances |
| EPS _c | Carbohydrate fraction of extracellular polymeric substances |
| EPS _{COD} | COD concentration in extracellular polymeric substances |
| F/M | Feed to mass ratio |
| G | Gradient |
| GI | Glucose + Iron |
| GIS | Glucose + Iron + Sulphate |
| GS | Glucose + Sulphate |
| HPLC | High performance liquid chromatography |
| HPsec | High performance size exclusion chromatography |
| HRT | Hydraulic retention time |
| IC | Inorganic carbon |
| J | Permeate flux |
| MBR | Membrane bioreactor |
| MLSS | Mixed liquor suspended solids |
| MLVSS | Mixed liquor volatile suspended solids |

| | |
|--------------------|---|
| MLFSS | Mixed liquor fixed suspended solids |
| P | Pressure |
| P | Transmembrane pressure |
| P ₂₀ | Transmembrane pressure normalised at 20 °C |
| P _T | Transmembrane pressure at test temperature |
| Re | Reynolds number |
| R _m | Filter medium resistance |
| R _t | Total resistance |
| rpm | Rotations per minute |
| SMA | Specific methanogenic activity |
| SMP | Soluble microbial products |
| SMP _c | Carbohydrate fraction of soluble microbial products |
| SMP _p | Protein fraction of soluble microbial products |
| SMP _{COD} | COD concentration in soluble microbial products |
| SRT | Solids retention time |
| t | Time |
| T | Temperature |
| TMP | Transmembrane pressure |
| TOC | Total organic carbon |
| TC | Total carbon |
| TS | Total solids |
| U | Filtrate viscosity |
| UASB | Upflow anaerobic sludge blanket |
| UV | Ultra violet |
| V | Volume |
| VFA | Volatile fatty acids |
| Vol | Volume |
| η | Dynamic viscosity |
| η ₂₀ | Dynamic viscosity at 20 °C |
| η _T | Dynamic viscosity at test temperature |
| α | Specific cake resistance to filtration |
| ρ | □□□□□□□□□□□□□□□□□□□□ density |

INTRODUCTION

1 INTRODUCTION

Anaerobic treatment can be defined as the use of biological processes to convert organic materials into usable energy in the form of methane.

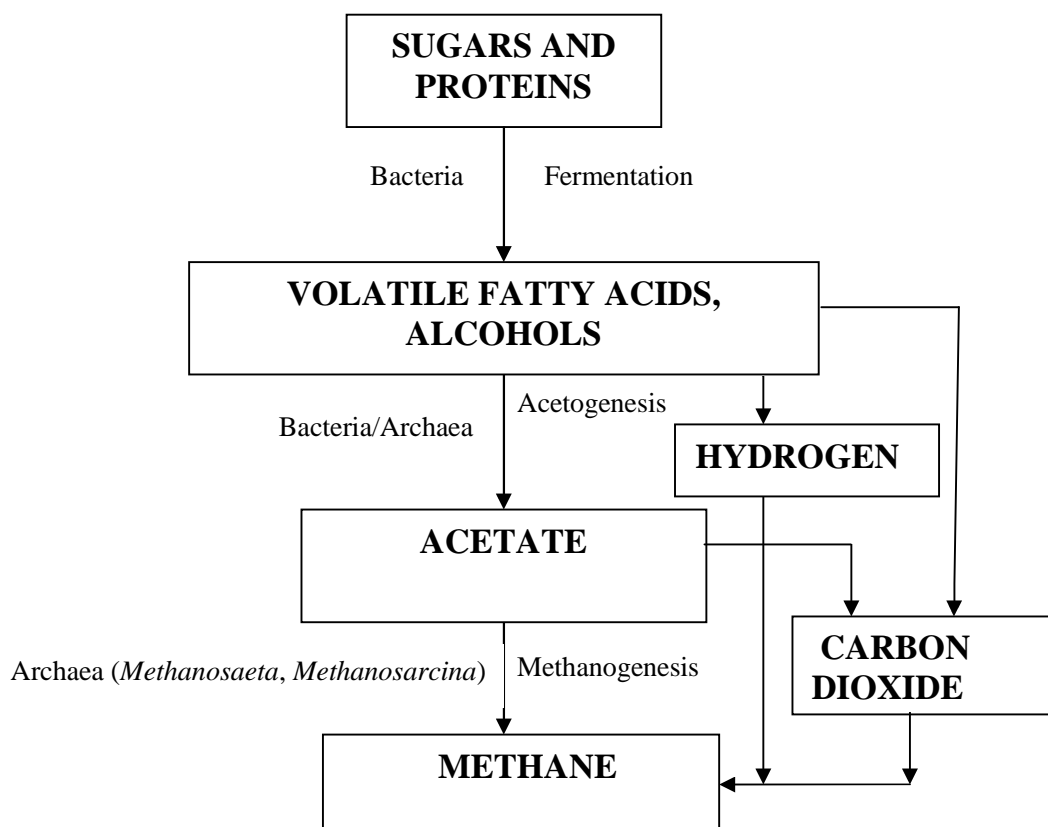


Figure 1.1: The anaerobic digestion process.

The retention of biomass is a critical feature when utilising anaerobic technology in wastewater treatment. Successful retention of biomass in anaerobic digesters is usually achieved by attachment on porous material (anaerobic filter technology) or growth of easy settling microbial granules (UASB and EGSB technology) (Beaubien *et al.*, 1996). However, membrane separation techniques are becoming increasingly popular due to the many advantages these integrated systems have over conventional digesters.

The introduction of membranes into anaerobic bioreactors allows for independent control of hydraulic and solid retention times resulting in higher volumetric loading rates and smaller footprints. Other advantages include good effluent quality and the ability to retain specific anaerobe strains where required (Stephenson *et al.*, 2000; Vallero *et al.*, 2003). Chemical Oxygen Demand (COD) removal efficiencies as high as 99% have been achieved with the use of anaerobic membrane bioreactors. Typical hydraulic retention times range from 12 to 170 hours depending on reactor volumes and waste type. These systems have been successful in treating industrial source wastewaters from landfill leachate ($0.63\text{-}2.2\text{kgCODm}^{-3}$) to brewery wastewater ($80\text{-}90\text{kgCODm}^{-3}$).

Despite its many advantages, the use of anaerobic membrane bioreactors in wastewater treatment is a slow developing technology mainly due to the significant fouling problems observed with continuous operation. Fouling can be defined as the deposition of inorganic deposits, organic deposits and bacterial cells (collectively known as foulants) onto the surface of a membrane (Stephenson *et al.*, 2000). This process is detrimental to the performance and efficiency of an anaerobic membrane bioreactor because it reduces the permeation flux of the system and increases operating costs.

The performance of anaerobic membrane bioreactors is also strongly dependent on other parameters such as biomass and wastewater characteristics as well as environmental conditions.

LITERATURE REVIEW

2 LITERATURE REVIEW

2.1 Anaerobic Systems

2.1.1 Historical Development of the Anaerobic Treatment Process

Anaerobic treatment has been used in the treatment of wastewater for over a century. The simplest and most widely used process is the septic tank. A precursor to this process was reported as early as 1857. According to Buswell (1958), a tank was designed to retain solids by means of sedimentation. A little later, at or around 1860, the 'Mouras' Automatic Scavenger' was designed by a French Engineer, Louis H. Mouras. He built a closed chamber with a water seal in which all faecal matter was rapidly transformed (Seghezzo *et al.*, 1998). In 1910, Winslow and Phelps (1911) used a system known as the biolytic tank. However, anaerobic systems were not regarded as viable for the treatment of wastewater until the development of the Contact Process in 1957 and the Upflow Anaerobic Sludge Blanket reactor two decades later (Seghezzo *et al.*, 1998).

2.1.2 Single Stage Anaerobic Reactors

(i) The Contact Process

This process employs external sludge separation and return. Methods that have been tested or used for sludge separation include vacuum degasification with sedimentation, the addition of organic polymers as well as inorganic flocculants, centrifugation and aeration to stop digestion. The need to return the resulting settled sludge back to the reactor via pumping is a major disadvantage of the contact process due to the higher number of pumps that have to be installed and maintained. The maximum applicable organic loading rate over total reactor volumes used in this process is $10\text{gCODL}^{-1}\text{d}^{-1}$. However, improved contact systems have been developed with the use of granular or dense, well-settling, flocculent sludge, adapting the stirring assembly and intensity to sludge characteristics as well as the use of in-built settlers. This results in higher permissible loading rates and better sludge retention within the reactor

(ii) The Upflow Anaerobic Sludge Blanket (UASB) Reactor

The Upflow Anaerobic Sludge Blanket Reactor was developed in the late 1970s in the Netherlands (Lettinga and Vinken, 1980).

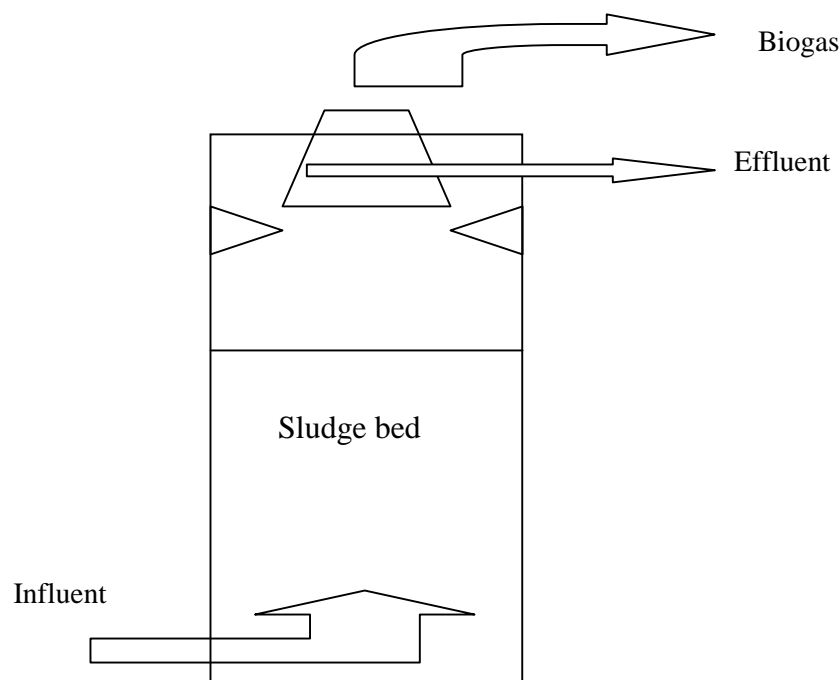


Figure 2.2: Schematic diagram of a UASB reactor. Modified from Seghezzo *et al.*, 1998 and 2002.

An important feature of the UASB reactor is the phase separator which divides the top part of the reactor into the digestion and settling zones (Figure 2.2). Influent wastewater is usually distributed at the bottom of the reactor before it travels upwards through the sludge blanket. The UASB concept relies on the presence of a dense granular sludge bed at the bottom of the reactor. There is some difficulty associated with the formation of granules in this type of anaerobic system. A good inoculum is usually required and growth of these granules will depend on the type of waste to be treated. However, the system does maintain a large active sludge mass, enabling good treatment performance at high organic loading rates. Reactor volumes are reduced and there is usually a resulting increase in the production of quality energy as methane (Seghezzo *et al.*, 1998).

Seghezzo and his co-workers (2002) report that mean specific methanogenic activity (SMA) averaged between 0.1130 and $0.0229 \text{gCOD-gCH}_4^{-1} \cdot \text{VSS}^{-1} \cdot \text{d}^{-1}$ while treating settled sewage at a temperature of 21.6°C in a UASB reactor subject to hydraulic retention times of 3 to 9 hours as well as a solid retention time of 450 days. Higher COD removal efficiencies have been shown to be achievable. Kato *et al.* (1997) achieved efficiencies exceeding 95% at organic loading rates up to $6.8 \text{gCODL}^{-1} \cdot \text{d}^{-1}$ with COD concentrations ranging from 422 to 722mgL^{-1} while treating an ethanol substrate. UASB technology is not recommended for the treatment of wastewaters that produce froth (such as dairy effluents) and wastes with high suspended solids (15% insoluble COD).

(iii) The Expanded Granular Sludge Blanket (EGSB) Reactor

Tracer studies conducted by de Man and his co-workers (1986) illustrated that internal mixing was not optimal in a pilot scale UASB reactor treating sewage at temperatures of 4 to 20°C . The studies suggested that higher treatment efficiencies may be achievable if dead space in the reactor was eliminated or significantly reduced. A better influent distribution system was therefore necessary in order to improve contact between sludge and wastewater and promote efficient use of the entire reactor volume. The Expanded Granular Sludge Bed (EGSB) reactor was developed to provide a solution to the problem (Figure 2.3).

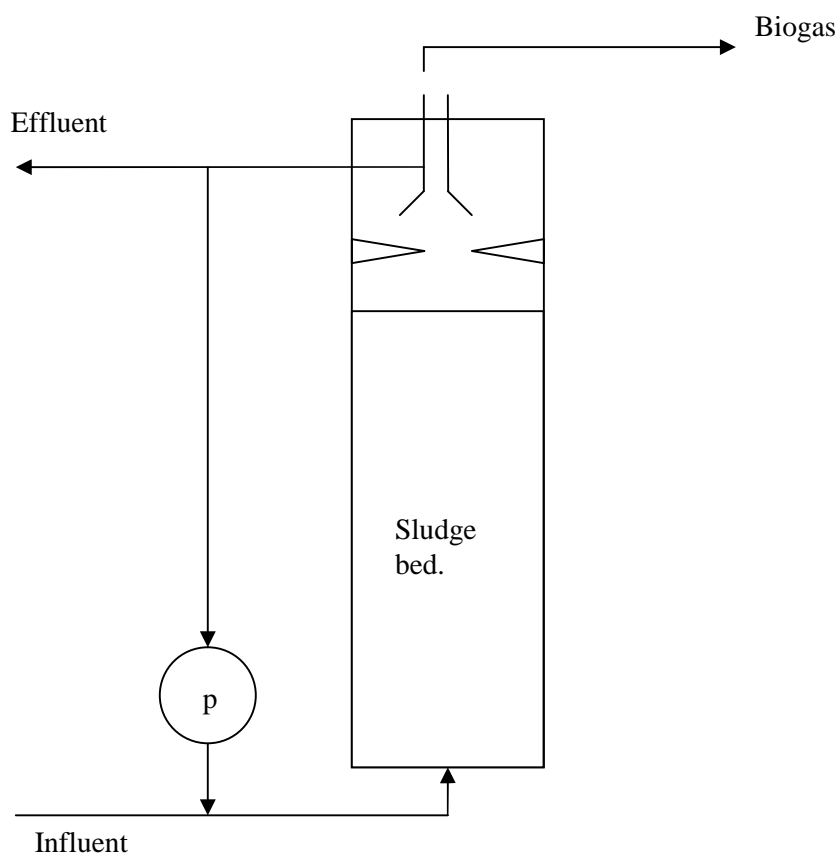


Figure 2.3: Schematic diagram of an EGSB reactor. Modified from Seghezzo *et al.* 1998.

Wastewater enters the reactor at the bottom via the influent distribution system and flows through a sludge bed consisting of anaerobic bacteria (which grow in the form of granules). The height of the reactor can vary between 7 and 14metres. A high superficial liquid velocity ($>4\text{mh}^{-1}$) causes the granular sludge bed to expand, eliminating reactor dead space and promoting better sludge-wastewater contact (Seghezzo *et al.*, 1998). In 1997, Seghezzo conducted studies on the relationship between upflow velocity and substrate consumption and found no relationship between the two. It was observed that granule size and inner structure had a greater effect on substrate consumption. The EGSB reactor behaves as a completely mixed tank (Rinzema, 1988). Higher organic loading rates of up to $40\text{kgCODm}^{-3}\text{d}^{-1}$ can be tolerated in these reactors resulting in higher gas production.

Although EGSB reactors are suitable for treatment of soluble pollutants and dilute wastewaters (where effluent recirculation is not applied), good removal of suspended solids and colloidal matter is yet to be achieved. Kato *et al.* (1997) achieved COD removal efficiencies above 80% at organic loading rates up to $12\text{gCODL}^{-1}\cdot\text{d}^{-1}$ while treating wastes with COD concentrations as low as 100 to 200mgL^{-1} . Biothane systems developed the Biobed EGSB reactor to treat wastewaters from the chemical industry. Total COD removal efficiencies of about 98% were achieved when the reactor was subject to high loading rates of approximately $30\text{kgCODm}^{-3}\cdot\text{d}^{-1}$ (Zoutberg and De Been, 1997).

(iv) The Anaerobic filter

The anaerobic filter is a commonly used system which utilises the anaerobic attached growth process for carbonaceous organic matter removal as well as denitrification of wastewaters. The system generally consists of a column packed with solid media on which anaerobic bacteria grow (Figure 2.4). These anaerobes are not washed away by the upward flow of wastewaters through the column. The system can therefore be used to treat difficult wastewaters under difficult conditions (such as municipal wastewaters at ambient temperatures) due to the long mean cell residence times that can be achieved with short hydraulic retention times. The system also has an additional advantage in that less sludge is produced compared with other anaerobic reactors.

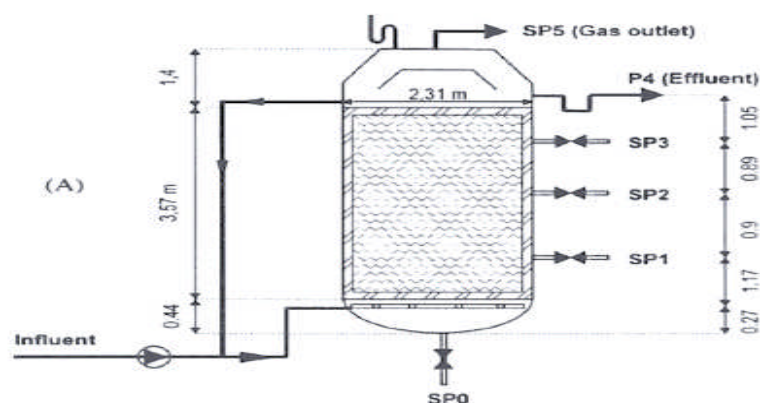


Figure 2.4: Diagram of a Typical Anaerobic Filter Unit (Omil *et al.*, 2003).

2.1.3 Staged Reactor Systems

The staged reactor concept is based on the plug flow treatment system (Van Lier, 1995) and accomplished by the use of sequentially operated reactors or compartments in a single reactor. Sludge present in different compartments of the reactor will usually differ depending on the waste type and specific environmental conditions in the said reactor compartment.

Staged reactors are completely self-regulating and provide higher treatment efficiencies as well as achieve greater process stability. Each stage of the digestive process takes place in a compartment where there is an optimal environment for degradation of compounds or organic matter. Van Lier (1995) demonstrated the need for staging by achieving a high treatment efficiency (effluent $\text{COD} < 0.3 \text{gL}^{-1}$) with a compartmentalized reactor fed with a sucrose-VFA mixture. The system was subject to a loading rate of $120 \text{gCODL}^{-1} \text{d}^{-1}$.

(i) The Anaerobic Baffled Reactor (ABR)

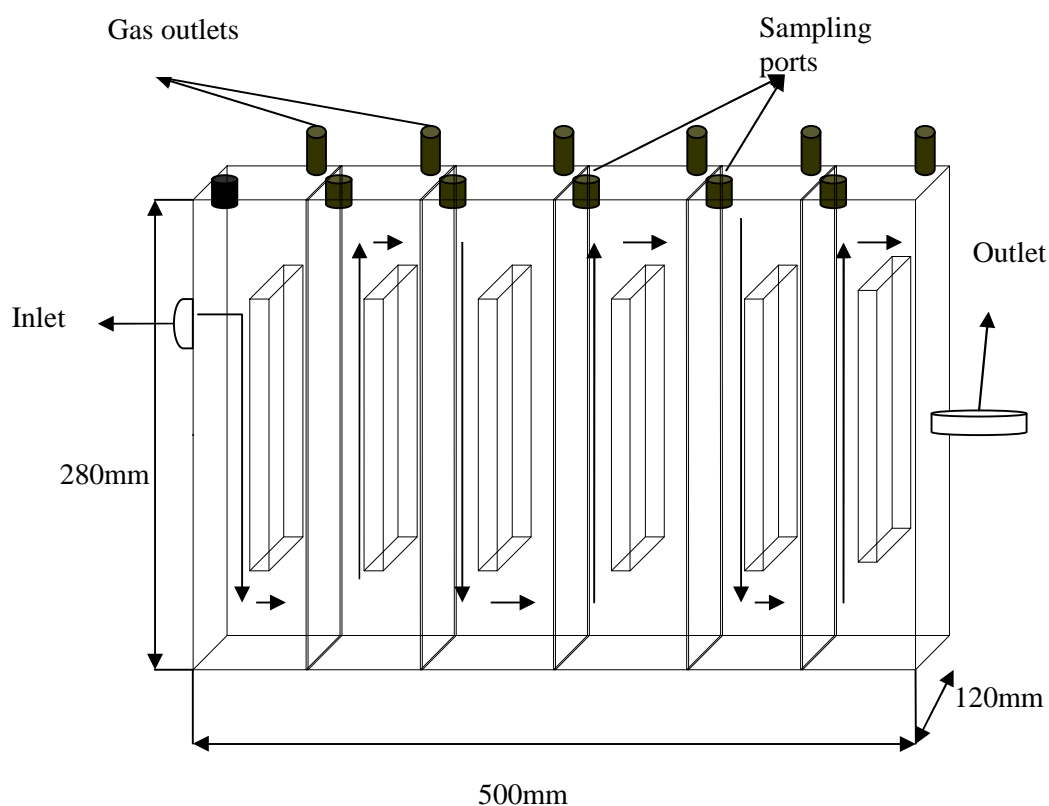


Figure 2.5: Schematic diagram of an anaerobic baffled reactor.

The anaerobic baffled reactor is a recent example of a system that utilises the staged reactor concept (Figure 2.5). Baffles are used to direct the flow of wastewater in an upflow mode through a series of sludge blanket reactors (Metcalf and Eddy, 2002).

The sludge in the reactor will therefore rise and fall while moving through the reactor at a slow rate. Unlike the UASB reactor, granulated sludge is not essential for good performance although it has been observed in the process (Boopathy and Tilche, 1992). Initial loading rates for this type of reactor should be low. Henze and Harremoes (1983) recommend an initial loading rate of 1.2kgCODm^{-3} although reactors subject to higher initial loading rates have been successful. The Anaerobic baffled reactor (ABR) has been used successfully to treat wastewaters with high solids concentration. Boopathy and Sievers (1991) report COD removal efficiencies of 70 and 80% while treating a high strength swine waste with 51.7gL^{-1} total solids. The reactor was subject to a loading rate of $4\text{kgCODm}^{-3}\text{d}^{-1}$ and a hydraulic retention time of 15 days.

Full scale reactors have been installed in Tenjo, Columbia to treat domestic waste. A COD removal efficiency of 70% was achieved with loading rates of $0.4\text{--}2\text{kgCODm}^{-3}$. The cost of installing a baffled reactor in Columbia is approximately 20% less than an equivalent UASB reactor and five times less than a conventional activated sludge plant (Orozco, 1996). Table 2.1 shows the advantages of the ABR over other anaerobic systems (Barber and Stuckey, 1999).

Table 2.1: Advantages of the anaerobic baffled reactor over other anaerobic systems

| Construction |
|---------------------------------|
| 1.Simple design |
| 2.No moving parts |
| 3.No mechanical moving parts |
| 4.Inexpensive to construct |
| 5. High void volume |
| 6. Reduced clogging |
| 7. Reduced sludge bed expansion |

8.Low capital and operating costs

Biomass

1. No requirement for biomass with unusual settling properties.
 2. Low sludge operation
 - 3.High solid retention times
 4. Retention of biomass without fixed media or a solid-settling chamber.
 5. No special gas or sludge separation required.
-

Operation

1. Low HRT
 2. Intermittent operation possible
 - 3.Extremely stable even with hydraulic shock loads
 - 4.Protection from toxic materials in influent
 - 5.Long operation times without sludge wasting
 6. High stability despite organic shocks
-

Table 2.2: Performance of anaerobic digesters

| Anaerobic Digester | Wastewater Type | Volume (L) | Loading Rate (kgCODm ⁻³ d ⁻¹) | Influent COD Concentration (mgL ⁻¹) | Mean feed temperature (°C) | Hydraulic retention time (hours) | COD removal efficiencies | Reference |
|---------------------------|-----------------------------|------------|--|---|----------------------------|----------------------------------|--------------------------|--------------------------------|
| Anaerobic Filter | Domestic Sewage | 160 | 2-10 | 467 | 13-15 | 6 | 35-55% | Derycke and Verstraete, 1986 |
| UASB | Settled sewage | 500 | 2-15 | 152.6 | 21.6 | 2-9hours | 70-80% | Seghezzo <i>et al.</i> , 2002. |
| | Municipal landfill leachate | 40 | 2-4 | 1500-3200 | 13-23 | 13-35 | 65-75% | Kettunen and Rintala, 1998 |
| EGSB | Dilute brewery wastewater. | 225.5 | 0.9-1.4 | 100-200 | 30 | 1.3 | 70-91% | Kato <i>et al.</i> , 1997 |
| Anaerobic Baffled Reactor | Degritted Sewage | 3200 | - | 350-1200 | 30-35 | 20 | 70-90% | Dama <i>et al.</i> , 2002 |

2.1.4 Other Anaerobic Processes

Other anaerobic processes that have been utilised in the treatment of wastewater include the covered anaerobic lagoon process and complete mix process. A comprehensive list of anaerobic treatment processes as well as complete descriptions is given in Metcalfe and Eddy (2002).

2.1.5 Granulation in Anaerobic Bioreactors

Sludge granules are defined as well balanced micro-ecosystems that include all bacterial species required for the degradation of organic substrates to which they are exposed. These granules form biomass with specific properties suitable for upflow anaerobic reactors. The quality of these sludge granules is dependent on factors such as settleability, mechanical strength, composition and distribution of microbial populations, porosity, pore size distribution and substrate/product permeability (Alphenaar, 1994).

According to Speece (1997), the formation of dense granular sludge in high rate anaerobic digesters is favoured under conditions of near neutral pH, a plug flow hydraulic regime, a zone of high hydrogen partial pressure, a non-limiting supply of $\text{NH}_4\text{-N}$ and limited amounts of amino acid (Alphenaar, 1994). Several theories and models have been postulated to describe and explain the granulation process in anaerobic bioreactors (Table 2.3). A complete description of these theories can be found in Hulshoff Pol *et al.* (2002).

Table 2.3: Theories and models of granulation

| Theory/Model | Predominant factors influencing granule formation | Reference |
|---|---|--|
| Rod type granule/filamentous Granule | sludge bed erosion and expansion, selection pressure and sludge residence time. | De Zeeuw (1987) |
| Selection pressure theory | selection pressure. | Hulshoff Pol <i>et al.</i> (1983) |
| Growth of colonised suspended solids | suspended solids. | Pereboom (1994), Yoda <i>et al.</i> (1989) |
| Bridging microflocs by methanotrix filaments | morphology and surface properties of methanotrix sp. | Dubourguier <i>et al.</i> (1987) |
| The spaghetti theory | upflow velocity, turbulence and hydraulic shear force produced by biogas. | Wiegant (1987) |
| Cape town hypothesis | hydrogen partial pressure. | Sam-Soon <i>et al</i> (1987) |
| Multi-layered granules with <i>Methanotrix</i> aggregates as nucleation centres | hydrodynamic behaviour of the reactor, supply of substrate and product removal. | McLeod <i>et al.</i> (1990), Fang (2000) and Vanderhaegen <i>et al.</i> (1992) |
| Nucleation formation and nucleus growth | selection pressure, acetic acid concentration and EPS production. | Chen and Lun (1993) |
| Four step model | physico-chemical property of bacterial species and EPS production. | Schmidt and Ahring (1996), Costerton (1990) |
| Theory/Model | Predominant factors influencing granule formation | Reference |
| Surface tension model | surface thermodynamics of bacterial cells. | Thaveesri <i>et al.</i> (1995) |
| Crystallised nuclei formation | surface charges and surface thermodynamics of bacterial cells. | Zhu <i>et al.</i> (1997) |

It is widely believed that the initial stage of the granulation process is similar to bacterial biofilm formation on solid surfaces. All the theories and models stated in Table 2.3 with the exception of the Cape Town hypothesis are based on the importance of the bacterial species-*Methanosaeta concilii* (*Methanothrix soehngenii*) in the granulation process. The Cape Town hypothesis suggests a different bacterial species-*Methanobacterium* strain AZ as the key microbe in the granulation process.

The granulation process usually begins with the attachment of bacterial cells to an inert carrier which forms the nucleus of the granule. Thick biofilm is then formed on clusters of these nuclei. The addition of inert support media to anaerobic bioreactors has been widely studied. Hulshoff Pol (1989) and Yoda *et al.* (1989) both report shortened granulation times and accelerated start-up when hydro-anthracite and zeolite are respectively added to UASB reactors. According to Verrier *et al.* (1988) and Munoz *et al.* (1993), the addition of support particles to anaerobic digesters also results in increased methane production. Materials used as inert carriers should be spherical, have a high specific surface area and good hydrophobicity as well as a specific gravity similar to anaerobic sludge (Yu *et al.*, 1999).

2.1.6 The Role of Extracellular Polymeric Substances (EPS) in Anaerobic Systems.

Extracellular polymeric substances are high molecular weight compounds (such as polysaccharides, proteins, lipids and DNA) produced by bacterial cells as a by-product of bacterial metabolic processes. EPS will usually form a hydrated gel-like substance in or around biofilm.

It is thought that EPS plays an important role in aggregate formation and cohesion. Approximately 50% of total EPS content of a granule is present in a 40µm thick zone on the surface, the remainder being dispersed around the rest of the aggregate (de Beer *et al.*, 1996). In flocs however, majority of the EPS content present occurred in the centre with little or no EPS on the surface.

A higher EPS content will usually result in better quality sludge. Quarmby and Forster (1995) showed the significance of EPS in determining the strength of granules while investigating the structure of granules in UASB reactors.

Granules generally have higher concentrations of EPS ($1\text{--}1.6\text{mg.gVSS}^{-1}$) than flocs which usually have EPS concentrations of approximately 0.3mg.gVSS^{-1} . Flocs have a high susceptibility to floatation probably due to the lack of EPS coating on the surface. The hydrophilic nature of EPS prevents the attachment of gas bubbles.

Schmidt and Ahring (1994) report that granules exposed to methanogenic and acetogenic substrates have lower amounts of polysaccharides and proteins in the EPS matrix than those grown on more complex substrates. However, EPS lipid content was lower with complex substrates. EPS content of sludge is also affected by temperature conditions in the bioreactor. Sludge incubated under mesophilic conditions has a higher EPS content than sludge incubated under thermophilic conditions (Schmidt and Ahring, 1994).

2.1.7 Volatile Fatty Acids in Anaerobic Systems

Anaerobic conversion of organic matter occurs in stages (Figure 1.1). The hydrolysis of higher molecular mass compounds into monosaccharides, amino acids and other compounds is followed by acidogenesis where these relatively simpler compounds are converted into short chain fatty acids, the most common of which is acetic acid. The products of this stage of anaerobic digestion are collectively known as volatile fatty acids (VFAs). These compounds are converted to methane and carbon dioxide by methanogens during methanogenesis.

For anaerobic digestion to continue adequately, both acidogenesis and methanogenesis have to be in dynamic equilibrium. High concentrations of VFA can lead to anaerobic system failure as only a limited number of substrates are thermodynamically favourable for conversion to methane via methanogenesis. VFAs (especially propionic acid) are also generally toxic to acidogens in high concentrations (Yang *et al.*, 2004). The removal of these compounds via methanogenesis is therefore essential.

Acidogenesis and methanogenesis are carried out by symbiotic microorganisms which are divided into two main groups (acidogens and methanogens). These groups of bacteria differ in their physiology, biokinetics, and growth environment (Yang *et al.*, 2004). Yang *et al.* (2003) suggests that successful optimisation of the anaerobic treatment process is dependent on optimisation of the acidogenesis stage. Optimal conditions for acidogenesis (during treatment of a swine wastewater) and production of acetic and butyric acid were also suggested at 2.1 to 2.4 days HRT and a temperature of $34.5 \pm 0.5^\circ\text{C}$ (Yang *et al.*, 2004).

2.1.8 Low Strength and Complex Wastewaters

Low strength wastewaters are wastes with a chemical oxygen demand of less than 2000mgL^{-1} . These wastewaters usually contain easily biodegradable compounds such as short- chain fatty acids, alcohols and carbohydrates.

The application of UASB technology to the treatment of low strength wastewaters faces many limitations, some of which have already been overcome. The most important of these problems is the low amount of recoverable energy produced by the process in the form of methane. The anaerobic process is only favourable if additional energy in the form of heat is not required. Some full-scale installations are currently operating in tropical regions precisely for this reason. Ambient temperatures are higher (usually varying between 30 and 35°C) and heating is almost never necessary (Foresti, 2002). Other problems faced in the anaerobic treatment of dilute wastes include poor substrate movement into biofilm and sludge washout. In practice, these problems have been overcome with the use of efficient mixing, optimal liquid upflow velocities (V_{up}) of 2.5 - 5.5 m h^{-1} and effluent recirculation.

Kato (1994) reports that a COD removal efficiency of 80-90% is achievable when treating dilute wastewaters in UASB and EGSB reactors subject to organic loading rates of 0.7 - $1.2\text{gCODL}^{-1}\text{d}^{-1}$.

Complex wastewaters are defined as substrates containing large fractions of suspended solids as well as a wide variety of compounds (Zeeman and Sanders, 2001).

In treating this type of waste, the most widely applied reactors are UASB reactors and CSTRs (Continuous Stirred Tank Reactors). The CSTR operates without biomass retention and is usually utilised in the digestion of slurries. For domestic sewage and similar wastewaters, the UASB reactor is most frequently applied. In general, increased complexity of the waste will result in poorer treatment efficiencies and a requirement for lower organic loading rates in UASB reactors (Kato, 1994).

Domestic sewage is a complex wastewater and more often than not, of low strength. Although, this type of waste has a very predictable quality, there is not much insight into the use of anaerobic technology in its treatment. A number of UASB reactors are currently operational in tropical regions. Wiegant (2001) reports that hydraulic design criteria, superficial biogas velocity and solid retention times govern the design of these reactors. He further states typical values for design criteria as shown in Table 2.4.

Table 2.4: Design criteria for UASB reactors in tropical regions.

| Design criteria | Typical values |
|--------------------------------------|----------------|
| Height (m) | 4-4.5 |
| Feed Inlet Distance (m) | 1.9-2.00 |
| Upflow velocity (m.h ⁻¹) | 0.6-0.75 |
| Hydraulic retention time (h) | 5-6 |

COD removal efficiencies of 65-80% have been obtained with UASB reactors treating domestic wastes at temperatures above 20°C when subject to organic loading rates lower than 3kgCODm⁻³d⁻¹ (Rodriguez *et al.*, 2001; Florenico *et al.*, 2001; Passig *et al.*, 2000; Torres and Forresti, 2001; Chernicaró and Nascimento, 2001). The need for good quality methanogenic sludge as an inoculum during start-up periods is considered crucial to the efficient treatment of domestic waste. However, Passig *et al.* (2000) reports that the use of an inoculum may not be necessary at all though this may prolong start-up periods for as long as six months.

2.1.9 Anaerobic Treatment under Psychrophilic Conditions.

Many are still sceptical about the use of anaerobic treatment in treating sewage at low temperatures. The factors that affect anaerobic treatment of wastewater are summarised in the Table 2.5.

Table 2.5: Summary of factors affecting anaerobic wastewater treatment

| Factor | Effect |
|-----------------------------|--|
| Flow and strength variation | Poor effluent quality. However, buffer tanks can be used to quench flow and strength changes |
| Temperature | Slow growth of bacteria, low methanogenic activity, slow hydrolysis, increased gas solubility and inhibition by high acetate concentration |
| Sulphate | Inhibition of methanogenesis process, lower methane production |
| Suspended solids | Slow hydrolysis and mass transfer kinetics, reduction of specific methanogenic activity and disintegration of granules. |

(Kalogo and Verstraete, 2001)

Of the factors stated in Table 2.5, a high concentration of suspended solids ($0.3\text{-}2\text{gL}^{-1}$) is an important difficulty in the treatment of sewage. Under low temperatures, suspended solids are hydrolysed very slowly, accumulating in the reactor and decreasing reactor volume available for active biomass sludge. This gives rise to low COD conversion efficiencies (Kalogo and Verstraete, 2000). There is a corresponding decrease in the proportion of active biomass with a decrease in the ratio of soluble COD to volatile suspended solids. De Baere and Verstraete (1982) suggest that a value of 10 (soluble COD to volatile suspended solids ratio) is required to keep anaerobic sludge active. Zeeman and Lettinga (1999) developed a model that can be used to calculate HRT where SRT, sludge concentration and proportion of influent SS removed and hydrolysed are known.

$$HRT = \left(\frac{C \times SS}{X} \right) \times R \times (1 - H) \times SRT$$

where C= COD concentration in the influent (gCODL^{-1}) and SRT in days.

Reactor volume can then be calculated if the daily influent flow (Q) is known.

$$V = HRT \times Q$$

This model shows that increasing SS concentration of the influent will change the needed HRT.

Average sewage temperatures range from 4 to 20°C and will only exceed 12°C for about six months annually in temperate regions (Derycke and Verstraete, 1986). These temperatures fall substantially below the optima for methanogenesis (35 to 55°C). However, according to Kato (1994), anaerobic bacteria can adapt quite easily to low temperatures and high rate UASB reactors have been utilised under psychrophilic conditions.

Biological reaction rates are much slower under psychrophilic conditions. A lower operational temperature will result in a decrease in microbial growth rates as well as substrate utilisation rates (Van den Berg, 1977; Lin *et al.*, 1987). According to Rebac (1998), a decrease in temperature affects the physico-chemical properties of wastewaters. The solubility of biogases such as methane and hydrogen sulphide increases thereby creating a requirement for a reactor with a slightly lower pH environment to ensure good treatment efficiencies. It is also possible that additional energy may be required for mixing. Increased liquid viscosities will result in slower settling of particles and decreased liquid-solid separation.

Laboratory UASB reactors have been used to treat raw domestic sewage and results obtained by Lettinga and his co-workers (1983) showed adequate performance even at low temperatures. COD reduction reached 65-85% at 20°C and 55-70% at 13-17°C. De Man *et al.* (1988) also showed that domestic sewage can be successfully treated under low temperature conditions (12-18°C) with HRTs of 7-12 hours. COD removal efficiencies of 40-60% were found to be achievable. More recently, other reactor configurations have shown higher removal efficiencies. Removal efficiencies of 80% have been obtained with the use of a granular bed reactor treating sewage from a separated sewer system (De Man *et al.*, 1988). Agrawal and his co-workers (1997) also achieved a COD removal efficiency of 70% using a combination of UASB reactors, and an aerobic post treatment system known as the 'hanging sponge cubes' to treat raw domestic sewage at temperatures of 9-32°C. Higher upflow velocities improve sludge-wastewater contact and result in higher removal efficiencies.

2.1.10 Advantages and Disadvantages of Anaerobic Wastewater Treatment

Initially, the main problem with anaerobic treatment was the long hydraulic retention time needed to achieve satisfactory performance. The hydraulic retention time in anaerobic systems has been considerably shortened by construction of new reactors with high biomass retention. Table 2.6 summarises the main advantages and disadvantages of the anaerobic digestion process.

Table 2.6: Advantages and disadvantages of the anaerobic process.

| Advantages | Disadvantages |
|--|---|
| High Efficiency: Good efficiencies are achievable even at high loading rates. | Low pathogen and nutrient removal: Anaerobic reactors are only partially successful in pathogen removal. |
| Simplicity: Reactors are simple to construct and operate | However, helminth eggs are effectively trapped in the sludge bed. Post treatment is usually required for complete nutrient removal. |
| Flexibility: Anaerobic treatment can be applied on large or small scale | Long start up: Due to slower growth rates of methanogenic organisms, start up times may be longer when compared to aerobic processes. |
| Low space requirements: smaller reactor volumes are required | Possible bad odours: Hydrogen sulphide is produced during anaerobic processes. |
| Low energy consumption: Energy consumption is usually low compared to aerobic methods. Energy is also produced in the form of biogas. | Necessity of post treatment: Post treatment is usually required to reach discharge standards for organic matter, nutrients and pathogens. |
| Low nutrient and chemicals requirement: Adequate pH can be maintained without the addition of chemicals. Micronutrients are also available in sewage, while toxic compounds are absent. | |
| Low sludge production due to slow bacteria growth rates. The sludge is well stabilised and has good dewatering characteristics. It can be preserved for long periods of time without a significant reduction in activity, allowing its use as inoculum for start-up of new reactors. | |

(After Seghezze *et al.*, 1998)

2.2 The Anaerobic Membrane Bioreactor.

In conventional anaerobic digesters, biomass and hydraulic retention times are coupled, limiting organic loading rates and operating biomass concentrations (Pillay *et al.*, 1994). Membrane technologies such as reverse osmosis, ultrafiltration and microfiltration are increasingly used to achieve biomass retention and for a variety of wastewater types (Fakhru'l-Razi, 1994).

Various systems have been developed and used in many wastewater treatment applications. Dorr-Oliver developed the MARS (Membrane Anaerobic Reactor) process which employs an ultrafiltration membrane in a flat sheet module combined with anaerobic digesters. Li *et al.* (1985) carried out a review on the many applications for which this process has been successful and found that the maximum loading rate to which it has been subject was $15\text{gCODL}^{-1}\text{d}^{-1}$ and a COD removal efficiency of 95% was achieved.

Use of unsupported tubular ultrafiltration membranes (MEMTUR) at low inlet temperatures led to the development of the anaerobic digestion ultrafiltration (ADUF) process. The ADUF process involves the use of an anaerobic digester coupled with a tubular ultrafiltration membrane module. Fakhru'l-Razi (1994) achieved a COD removal efficiency of 96.3% with the use of the ADUF process in the treatment of a high strength industrial wastewater. The system was subject to a maximum organic loading rate of $19.7\text{kgCODm}^{-3}\text{d}^{-1}$, a hydraulic retention time of 3.98 days and a solid retention time of 58.8 days. This process has been applied at both pilot and full scale.

The CUMAR (Cross flow ultrafiltration membrane anaerobic reactor) system consists of a cross-flow ultrafiltration membrane unit attached to a completely mixed suspended growth anaerobic digester (Ince *et al.*, 1994). A COD removal efficiency of 97 to 99% was observed while treating a brewery waste. A maximum organic loading rate of $28.5\text{kgCODm}^{-3}\text{d}^{-1}$ was applied to the system.

The SAMBar (Submerged Anaerobic Membrane Bioreactor) system was developed by Vallero *et al.* (2003) in order to achieve high rate sulphate reduction under conditions of high salinity. A maximal sulphate reduction efficiency of 85% was achieved when the system was subject to organic loading rates of $14\text{gCODL}^{-1}\text{d}^{-1}$ and a hydraulic retention time of 8 to 36 hours.

Other anaerobic membrane bioreactor systems include the MCAB (Membrane Coupled Anaerobic Reactor) system and CFMF (Cross flow microfiltration) process.

2.2.1 Membranes and Process Configuration

Anaerobic MBRs may incorporate external side-stream or submerged membranes. Generally, most systems reported in literature to date have incorporated side stream external membranes with completely stirred tank reactors (CSTR) (Table 2.7, Table 2.10). However, two phase reactors have been used in a small number of cases. With such configurations, the membrane has been placed after the first phase reactor, the second phase reactor or after both reactors. Yushina and Hasegawa (1994) achieved a COD removal efficiency between 76 and 92% (using this configuration) while treating food processing wastewaters with an influent COD concentration of 900 to 1400mgL⁻¹ at a temperature of 30°C. A less popular configuration is the combination of UASB reactors with external side-stream or submerged membranes. These systems tend to achieve relatively higher COD removal efficiencies regardless of substrate complexity (Liao *et al.*, 2006). Kiriyaama *et al.* (1994) achieved a COD removal efficiency of 61% while treating municipal sewage with a COD concentration of 70mg L⁻¹ at a temperature of 18°C using a UASB system which incorporated a membrane and was subject to a HRT of 0.3days. A higher treatment efficiency of 92% was achieved by Kimura (1991) while treating hydrolysed night soil using a similar system configuration.

Membrane materials of construction vary widely from ceramic to polymeric which in turn has an effect on membrane performance. Ghyyoot and Vestraete (1997) report that although both ceramic and polymeric membranes produce permeates of the same quality, the former is able to maintain a flux which is much higher than that achievable with the latter type of membrane. Shimizu *et al.* (1989) also found that negatively charged membranes were able to achieve a higher flux than non charged or positively charged membranes. In addition, hydrophobicity and material of construction also play a major role in membrane fouling. Fouling of inorganic membranes is generally characterised by struvite in contrast to organic membranes which tend to foul with both struvite and organic matter (Kang *et al.*, 2002; Liao *et al.*, 2006)

Membranes can generally be classified into three broad groups- microfiltration, ultrafiltration and reverse osmosis (RO) membranes. This categorisation is based on molecular weight cut off and pore size of the membranes. Microfiltration and Ultrafiltration membranes are more commonly used with anaerobic membrane bioreactors. Microfiltration membranes generally have pore sizes of $>0.05\ \mu\text{m}$ and will retain particulate matter. Ultrafiltration membranes on the other hand have pore sizes of $0.002\leq 0.05\ \mu\text{m}$ (Liao *et al.*, 2006) and are useful in retaining colloids and macromolecules as well as particulate matter.

Table 2.7: Examples of membrane performance while treating wastewaters`in Anaerobic MBRs(Modified from Liao *et al.*, 2006).

| Wastewater Type Treated in Anaerobic MBR | Operating Temperature | Membrane Material | Configuration | Pore Size (µm) | Molecular Weight Cut off (Daltons) | Filtration Area (m ²) | Membrane Flux (Lm ⁻² h ⁻¹) | Transmembrane Pressure | Reference |
|--|-----------------------|--------------------|----------------------|----------------|------------------------------------|-----------------------------------|---|--------------------------|--------------------------------|
| Brewery | 35 | Polyethersulphone | External side-stream | 0.2 | - | 0.44 | 7-50 | 140-340 kPa | Strohwald and Ross, 1992 |
| Molasses | 20 | Polypropylene | Submerged | 10 | - | 0.051 | 10-80 | - | Hernandez <i>et al.</i> , 2002 |
| Wool scouring | 40-47 | Poly acrylonitrile | External side-stream | - | 13000 | 3.1 | 17-25 | 2-2.2 kgcm ⁻² | Hogetsu <i>et al.</i> , 1992 |
| Wheat starch | 40 | - | External side-stream | - | 18000 | 144 | 14-25 | 690 kPa | Butcher, 1989 |
| Sewage sludge | 22-50 | Ceramic | External side-stream | 0.1 | - | 0.05 | 200-250 | 200 kPa | Ghyoot and Verstraete, 1997 |
| Sewage sludge | 30-35 | Polyethersulphone | External side-stream | - | 60000 | 0.3 | 19 | 375 kPa | Ghyoot and Verstraete, 1997 |
| Acetate | 35 | Zirconia Oxide | External side-stream | 0.005-0.08 | - | - | 40-70 | 50 kPa | Elmaleh and Abdelmoumni, 1997 |
| Glucose and peptone | 35-38 | Ceramic | External side-stream | 0.2 | - | 0.4 | 12.5-125 | 0.4 kPa | Shimizu <i>et al.</i> , 1992 |
| Domestic wastewater | 12.5-28 | Polyethylene | Submerged | 0.03 | - | 0.3 | 5-10 | 10-60 kPa | Wen <i>et al.</i> , 1999 |
| Sewage | 26 | Polyethylene | External side-stream | 0.1 | - | 54 | 24 | 1.1 kgcm ⁻² | Kataoka <i>et al.</i> , 1992 |
| Sewage | 10-28 | Ceramic | External side-stream | - | 13000 | 13.6 | 15-20 | 1-21 kgcm ⁻² | Tanaka, 1987 |
| Heat treated liquor | 35-38 | Ceramic | Submerged | 0.1 | - | 1.06 | 3-8 | 200 mmHg | Kayawake <i>et al.</i> , 1991 |

2.2.2 Loading rates

Cadi *et al.* (1994) reports that an increase in organic loading rate will produce a proportional increase in withdrawal protein concentration, an increase in substrate utilisation rate and a decrease in COD removal. The system studied was a laboratory scale anaerobic digester coupled with two tubular microfiltration modules, treating a synthetic wastewater containing starch as its sole carbon source. During the study, the system was subject to organic loading rates of 7 to 24gCODL⁻¹d⁻¹. At the maximum OLR of 24gCODL⁻¹d⁻¹, COD removal yield was approximately 87% and permeate protein concentration stabilised at 300mgL⁻¹. A decrease in removal efficiency of only 7% was observed when loading rate was increased from 7.7 to 24.2kgCODm⁻³d⁻¹, showing that COD removal is relatively stable over a range of loading rates. COD removal yields of 95 and 97% were obtained with the MARS and ADUF processes respectively when both systems were fed with whey and brewery wastes at loading rates of 15gCODL⁻¹d⁻¹ (Li *et al.*, 1985), (Strohwald and Ross, 1992). Cadi *et al.* (1994) also reports that at low organic loading rates, specific removal rates increased proportionally but stabilised at 0.6gCOD_r.gVSSd⁻¹ at higher loading rates (14 to 24gCODL⁻¹d⁻¹).

2.2.3 Gas Production

Anaerobic treatment generates energy in the form of methane. Methane yield is dependent on the wastewater source as well as the operating conditions of the process.

Biogas yields decline with increased loading rates. This is due to more favourable conditions for acidogenic bacteria than methanogenic bacteria at higher organic loading rates (Fakhru'l-Razi and Noor, 1999). Ince *et al.* (1998) observed a decrease in methane yield from 80% to 65% while treating a brewery waste with a maximum organic loading rate of 28kgCODm⁻³d⁻¹. The same trend is seen with longer hydraulic retention times (Cadi *et al.*, 1994) and decreasing temperature which results in lower methanogenesis rates (Hogetsu *et al.*, 1992). A summary of the factors that affect biogas production are given in Table 2.8.

Table 2.8: Factors that affect biogas production

| Factor | Effect | |
|--------------------------|---|------------------------------|
| Loading rate | Biogas yields decline with increased loading rates. This is due to more favourable conditions for acidogenic bacteria than methanogenic bacteria at higher organic loading rates. | Fakhru'l-Razi and Noor, 1999 |
| Hydraulic retention time | Longer hydraulic retention times cause a fall in biogas production. | Cadi <i>et al.</i> , 1994 |
| Temperature | Lower temperatures will also cause a decline in biogas production as rate of methanogenesis falls. | Hogetsu <i>et al.</i> , 1992 |

2.2.4 Biomass

Ince *et al.* (1995) examined sludge from a brewery and found the dominant species of micro-organisms to be *Methanococcus* followed by *Methanosarcina*, short rods, medium rods, filaments and long rod species. Continual analysis of the microbial population in the membrane bioreactor revealed a shift in the dominant group from *Methanococcus* at start up to short rod species at the end of the study. Although the proportion of methanogens in total bacteria increased from 6.8% to 9.5%, there was no adverse affect on the performance of the system. COD removal efficiency remained over 97% during steady state operation at a maximum organic loading rate of $28.5\text{kgCODm}^{-3}\text{d}^{-1}$.

Examination of the biomass characteristics in anaerobic membrane bioreactors by colony forming curve analysis show that bacteria are generally slower growing when treating sewage than for some industrial wastes (Kataoka *et al.*, 1992). Klass (1984) attributes this slow growth to the large amounts of cellulosic materials usually present in sewage. Hernandez *et al.* (2002) also showed that the presence of immersed membranes in anaerobic digesters results in improved granular sludge quality (sludge showed greater homogeneity in structure and activity).

2.2.5 Flux and Fouling

Flux is defined as the quantity of material passing through a unit area of membrane per unit time. It is determined by the driving force as well as the total resistance offered by the membrane and the interfacial region adjacent to it. Flux decline in membrane bioreactors is usually due to fouling, a term which describes the process by which substances present in the wastewater are deposited or adsorbed into or onto the membrane surface causing pore restriction or complete pore blocking.

(i) Flux and Fouling in the Anaerobic Membrane Bioreactor

Beaubien *et al.* (1996) demonstrated two clear modes of operation in anaerobic membrane bioreactors, low pressure and high pressure. Under low transmembrane pressures (less than 80kPa), permeate fluxes are strongly dependent on applied pressure and suspended solids concentration. Permeability decreased rapidly between 0 and 2.5kgm^{-3} and moderately for concentrations higher than 2.5kgm^{-3} . This is in contrast to the high pressure mode ($> 100\text{kPa}$) where flux is independent of pressure but strongly influenced by shear stress. Also, crossflow velocity did not affect permeation rates at low transmembrane pressures but was significant at high pressures. Beaubien *et al.* (1996) also defined an optimal pressure at which optimal membrane performance is observed. This pressure allows maximal permeation while keeping fouling of the membrane minimal. For an anaerobic membrane bioreactor operating at a suspended solids concentration of 10kgm^{-3} and a crossflow velocity of 2.63ms^{-1} , the optimal pressure was found to be 80kPa while the maximal permeate flux was $19\mu\text{m.s}^{-1}$.

Choo and Lee (1996) found that permeation flux dropped by more than 90% within 20 days of continuous operation of an anaerobic membrane bioreactor treating an alcohol distillery waste. This drop in flux was attributed to the external fouling of the membrane. This external fouling was found to be closely related to the strong adhesion of cells to the membrane surface, the compacting of the cake layer and the precipitation of struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) at the membrane surface. Choo and Lee (1998) also carried out further studies into the hydrodynamic behaviour of anaerobic biosolids in anaerobic membrane bioreactors.

It was observed that flux decline could be divided into three phases: the exponential flux decay within an initial period of time, usually less than three days; the sluggish gradual flux decline (3-9 days); the pseudo steady state (> 9days). During the exponential decline phase, polarisation and deposition of biosolids on the membrane surface was found to be the major cause of flux decline. Size distribution of biosolids shifted from about $\square 6\mu\text{m}$ to about $3\mu\text{m}$ after 12 days of operation. Specific cake resistance also increased from 3.9 to $6.4 \times 10^{15} \text{ mkg}^{-1}$, illustrating greater compactness of the cake layer due to size reduction. These changes in biosolid size and distribution were found to be mainly responsible for flux loss.

Detailed fouling analysis conducted by Choo and his co-workers (1999) attributed most of the fouling (while treating a distillery waste) to fine colloids. Although fine colloids accounted for 80% of the total resistance to filtration, they constituted only 5% of the total solids. Choo *et al.* (1999) also investigated the effect of membrane material and pore size on internal fouling. It was found that at higher pore sizes, macro organics foul internal pores while lower pore sizes have too high a natural resistance to filtration. Studies by Kang *et al.* (2002) also showed that there is a marked difference in fouling characteristics when organic and inorganic membranes are combined with anaerobic bio-reactors. The key factor in flux decline with organic membranes (such as polymeric membranes) was found to be due to the rough and fibrous nature of these membranes. Internal struvite precipitation was however significant in fouling with inorganic (ceramic) membranes.

Strohwald and Ross (1992) investigated the effects of cross-flow velocity and pressure on membrane performance. No changes in flux were observed when trans-membrane pressure was increased from 140 to 340kPa while treating waste with a mixed liquor concentration of 30gCODL^{-1} . Several factors contribute to the lowering of membrane permeability with increasing suspended solids concentration. Adsorption, pore plugging and concentration polarisation (the tendency of solute to accumulate at membrane-solution interface within a concentration boundary layer or stagnant liquid film) all affect membrane performance at trans-membrane pressure lower than that leading to gel formation.

Fouling in membrane bioreactors can be suppressed by in-treatment to remove foulants, flux reduction and turbulence promotion to reduce the thickness of hydrodynamic boundary layers (Stephenson *et al.*, 2000). Fouling in polymeric and ceramic microfiltration membranes (where inorganic precipitates is the most significant foulant) can be controlled by backfeeding acidic wastewater through the membrane module as well as coupling the membrane with a dialysis/zeolite unit, thereby reducing struvite formation (Choo *et al.*, 1999). Choo and his co-workers also showed that control of deposition of organics and fine colloids can be achieved by addition of powdered activated carbon into the bioreactor. Nitrogen gas sparging as well as high pressured biogas recirculation has been successful in reducing fouling in submerged systems containing polymeric (Fawehinmi *et al.*, 2004) and ceramic membranes (Kayawake *et al.*, 1991).

A summary of typical operating conditions for anaerobic membrane bioreactors is given in Table 2.9: below.

Table 2.9: (Metcalf and Eddy, 2002)

| Parameter | Unit | Value | |
|-------------------------------|--|-----------|---------|
| | | Range | Typical |
| COD loading | kgCODm ⁻³ d ⁻¹ | 2-24 | 8 |
| Solid retention time (SRT) | days | 12-160 | 50 |
| Mixed Liquor Suspended Solids | gL ⁻¹ | 8-50 | 20-25 |
| Solids Yield | gVSSg ⁻¹ COD ⁻¹ | 0.04-0.12 | 0.08 |
| Final Flux | Lm ⁻² h ⁻¹ | 5-26 | 18 |
| Specific Flux | Lm ⁻² h ⁻¹ bar ⁻¹ | 2.5-21 | 14 |

Table 2.10: Examples of anaerobic membrane bioreactor performance

| Wastewater Type | Reactor Type | Vol. (L) | HRT (days) | Temperature (°C) | Loading rate. (kgCODm ⁻³ d ⁻¹) | Influent COD concentration (mgL ⁻¹) | COD removal efficiency (%) | Biogas yield (m ³ CH ₄ kgCOD ⁻¹) | Reference |
|-----------------------------|--------------|----------|------------|------------------|---|---|----------------------------|--|------------------------------|
| Synthetic | CSTR | 120 | 4 | 35 | 19.7 | 84010 | 96 | 0.27 | Fakhru'l-Razi, 1994. |
| Municipal landfill leachate | - | 40 | 0.5-1.5 | - | 1.4-4 | 630-2200 | 50-75 | 0.32 | Kettunen and Rintala, 1998. |
| Palm oil mill | CSTR | 50 | 3 | 35 | 21.7 | 68000 | 92 | 0.28 | Fakhru'l-Razi and Noor, 1999 |
| Brewery wastewater | - | 120 | 2.5-4.2 | - | 28.5 | 80000-90000 | 99 | 0.28-0.35 | Ince <i>et al.</i> , 2000. |
| Distillery wastewater | CSTR | 4 | 13 | 54 | 3.0≤3.5 | 40000 | 90 | 0.0014 | Kang <i>et al.</i> , 2002 |
| Slaughter house wastewater | CSTR | 7 | 1.2 | 30 | 4.3 | 5200 | 90 | - | Fuchs <i>et al.</i> , 2003 |
| Heat treated liquor | CSTR | 200 | 0.6 | 37 | 15.4 | 10300 | 81 | - | Kim and Somiya, 2001 |
| Domestic Sewage | Hybrid | 18 | 0.25 | 20 | 0.4-10 | 100-2600 | >92 | - | Wen <i>et al.</i> , 1999 |
| Municipal Sewage | UASB | 77000 | 0.3 | 12 | 0.65 | 300 | 58 | - | Kinyama <i>et al.</i> , 1992 |

| Wastewater Type | Reactor Type | Vol. (L) | HRT (days) | Temperature (°C) | Loading rate. (kgCODm ⁻³ d ⁻¹) | Influent COD concentration (mgL ⁻¹) | COD removal efficiency (%) | Biogas yield (m ³ CH ₄ kgCOD ⁻¹) | Reference |
|------------------------------|--------------|----------|------------|------------------|---|---|----------------------------|--|-----------------------|
| Dilute Synthetic Wastewaters | - | 3 | 0.125 | - | - | 460 | >90 | - | Hu and Stuckey, 2006. |

(ii) Flux and Fouling in the Aerobic Membrane Bioreactor

Like the anaerobic MBR, fouling in aerobic MBRs takes place by adsorption and deposition resulting in internal and external clogging of membrane pores. Fouling tends to be specific to the membrane material and can be related to key components in the feed such as proteins, colloidal and particulate matter (Stephenson *et al.*, 2000).

There is a school of thought that attributes membrane fouling in aerobic MBRs to extracellular polymeric substances for the most part. Stec and Field (1995), Chang and Lee (1998) and Nagaoka *et al.* (1999) have all linked filtration and hydraulic resistance to EPS levels in activated sludge. Other researchers have focused on fouling by proteins and colloidal matter. Kelly *et al.* (1993) proposes that deposited protein aggregates serve as nucleation sites for non-aggregated dissolved proteins on the membrane surface. Pouet and Grasmicj (1995) also found that fouling of a ceramic microfiltration membrane was mainly due to a colloidal fraction with particle size greater than 1µm. Boubahila *et al.* (2001) and Defrance *et al.* (2000) both agree that the colloidal fraction of activated sludge contributes significantly to fouling. Studies by Lesjean *et al.* (2005) indicate that there is a linear relationship between membrane fouling rates and soluble polysaccharides in activated sludge. However, the same study provides no clear correlation between proteins, mixed liquor suspended solids and membrane fouling rates. Rosenberger and Kraume (2002) and Fan *et al.* (2006) also showed no correlation between MLSS and fouling when membranes are exposed to aerobic sludge. These observations contradict other published literature on the subject. Magara and Itoh (1991), Manem and Sanderson (1996), Maedaeni *et al.* (1999) and Le Clech *et al.* (2003) all agree that membranes foul quicker at higher sludge concentrations.

While activated sludge fractions contribute significantly to membrane fouling, other properties have been found to be just as important. For example, high surface porosities are detrimental to membrane performance (Stephenson *et al.*, 2000). Ghosh and Cui (1999) also showed that the submerged system is capable of higher mass transfer rates and higher permeabilities than the side-stream system.

Fluxes in aerobic MBRs range from 5 to 300 Lm⁻²h⁻¹. Side-stream systems can be subjected to higher operating fluxes than submerged systems although greater shear is required at the membrane surface to control fouling. In general, ceramic membranes are less susceptible to fouling and can therefore be operated at higher fluxes for extended periods of time (Trouve *et al.*, 1994; Stephenson *et al.*, 2000)

2.3 Discussion

The use of anaerobic technology in the treatment of wastewater is a complex and sensitive process. The process is dependent on operating conditions such as temperature, pH, hydraulic retention time, sludge retention time and loading rates as well as wastewater and biomass characteristics. Optimal conditions for good substrate degradation include operating at mesophilic temperatures (35 to 50°C), near neutral pH, good biomass retention and longer sludge retention times. Anaerobic digestion is inefficient when used in the treatment of complex and low strength wastewaters (under psychrophilic conditions) due to slow suspended solids hydrolysis, changes in pH and wastewater characteristics such as viscosity and solubility. Inefficient substrate degradation results in lower methane production and therefore lower re-usable energy. The anaerobic process can only compete with conventional aerobic wastewater treatment methods if the process is not energy intensive and therefore does not create additional operating costs. In addition, few anaerobic bacteria have been found to be psychrophilic (grow and metabolise at temperatures up to 20°C) (Romesser *et al.*, 1979; Conrad *et al.*, 1989; Kotsyurbenko *et al.*, 1995). So far, it is not clear whether anaerobic digestion of low strength and complex wastes may be improved either by developing bacterial populations tolerant to lower temperatures or by forcing mesophilic bacterial populations to adapt to colder conditions.

The integration of membranes and anaerobic reactors may provide a solution to some of the critical problems experienced when utilising anaerobic technology in the treatment of low strength and complex wastewaters at low temperatures. The anaerobic membrane bio-reactor is a credible alternative to UASB and EGSB technology as it completely uncouples hydraulic and sludge retention times (preventing sludge and biomass washout).

However, interaction between membrane material and sludge results in fouling which can reduce permeation flux and therefore, efficiency of the system.

Much research has been conducted into the mechanics of coupling membranes with biological reactors resulting in two major membrane configurations (side-stream and submerged). Recent research into the subject of anaerobic membrane bio-reactors has also focused on optimal operating conditions when these systems are used in the treatment of industrial and synthetic wastewaters. However, there is still a gap in the information available on fouling within these systems and their use in the treatment of domestic and municipal wastes (examples of low strength and complex wastewaters).

The anaerobic membrane bioreactor is an economically attractive alternative to the aerobic membrane bioreactor due to the potential for electricity consumption by membranes, capital and operating costs to be offset by methane production.

AIMS AND OBJECTIVES

3 AIMS AND OBJECTIVES

The primary aim of this study was to develop and optimise the anaerobic membrane bioreactor for the treatment of municipal wastewaters at ambient or below ambient temperatures. In order to achieve this objective, the study concentrated on;

- Establishing the characteristics and properties of anaerobic biomass and granular sludge.
- Attempting to immobilise and acclimatise anaerobic biomass (within the anaerobic digester) to low-temperature conditions with the use of submerged and side-stream membranes.
- Assessing the effect of biomass characteristics and properties on membranes and membrane filtration.
- Establishing the effect of biomass and wastewater characteristics on process performance and fouling within the membrane bio-reactor.
- Investigating fouling amelioration and the effect of gas sparging on fouling.
- Determining the effect of process conditions such as pH and temperature as well as membrane configuration on process efficiency.

MATERIALS AND METHODS

4 MATERIALS AND METHODS

This PhD project was divided into four stages- Dead end filtration trials and characterisation of anaerobic sludge, bench-scale tests, critical flux tests and pilot scale tests.

4.1 Dead End Filtration Trials and Characterisation of Sludge

Filtration trials were carried out using an unstirred dead end filtration cell (KST 47 Model supplied by M-Tech Diagnostics Ltd, UK) (Fig1). The cell was run with two virgin cellulose acetate membranes with a pore size of 0.45µm and 0.2µm respectively. Membranes with the smaller pore size were used in the filtration of SMP and the larger pored membranes in the filtration of sludges. The cell was connected to a receiver (to impose pressure) and a beaker placed on top of an electronic weighing balance collected the filtrate mass. A computer was connected to the electronic balance to record filtrate mass values at one second intervals. Filtrate volume was calculated using Equation 4-1.

$$\rho = \frac{m}{V} \quad \text{Equation 4-1}$$

Where

ρ = density in kgm^{-3} ;

m = mass in kg;

V = Volume in m^3 .

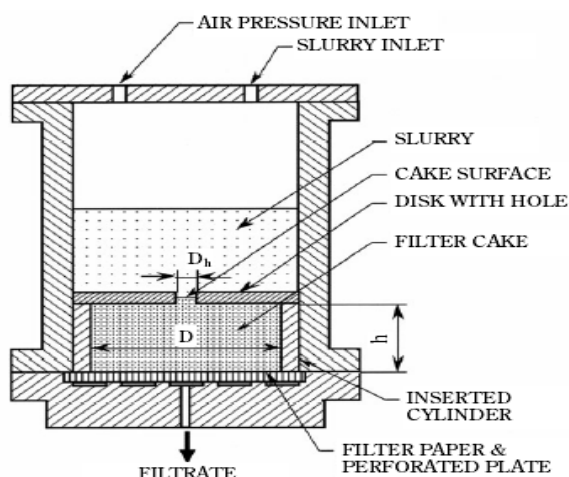


Figure 4.6: Diagram of Dead End Filtration Cell

Three anaerobic and aerobic sludges were analysed over a one month period for viscosity, particle/granule size, cake resistance, total solids as well as EPS and SMP concentration and filtration characteristics. The three anaerobic sludges analysed during these experiments came from different sources. Two of the sludges were obtained from effluent treatment plants treating wastewaters from different paper mills while the third was obtained from a UASB reactor treating a sugar refinery wastewater. All of the anaerobic sludges used during this set of experiments were granular. The aerobic sludges were obtained from membrane bio-reactors and an activated sludge plant set up at Cranfield university sewage works. All sludges utilised in this set of experiments were acclimatized at temperatures of 10 to 15°C after removal from reactors without active degradation of substrate.

Fouling mechanisms were determined using filtration models (Appendix B) after dead end filtration. The fouling contribution of soluble microbial products was also determined by the evaluation of rejection factors Equation 5-6.

4.2 Bench Scale Tests

4.2.1 Anaerobic Membrane Bioreactors (AnMBRs)

Four 0.5L anaerobic membrane bioreactors (A, B, C and D) were run simultaneously in order to study and compare membrane fouling characteristics. Each anaerobic membrane bioreactor (AnMBR) contained a tubular polysulphonic non-virgin membrane (supplied by Triqua BV, the Netherlands) with a pore size of $0.2\mu\text{m}$ and an effective filtration area of 0.001m^2 . All four AnMBRs were incubated in a thermostatic water bath to maintain a constant operating temperature.

Before venting the biogas produced in each AnMBR to the atmosphere, hydrogen sulphide gas and carbon dioxide were stripped off with the use of a 1M zinc acetate solution and 1M sodium hydroxide solution respectively (Figure 4.7). Trans-membrane pressure (TMP) on each membrane was measured with the use of four pressure transducers (mounted on each effluent line) and continuously recorded on a computer.

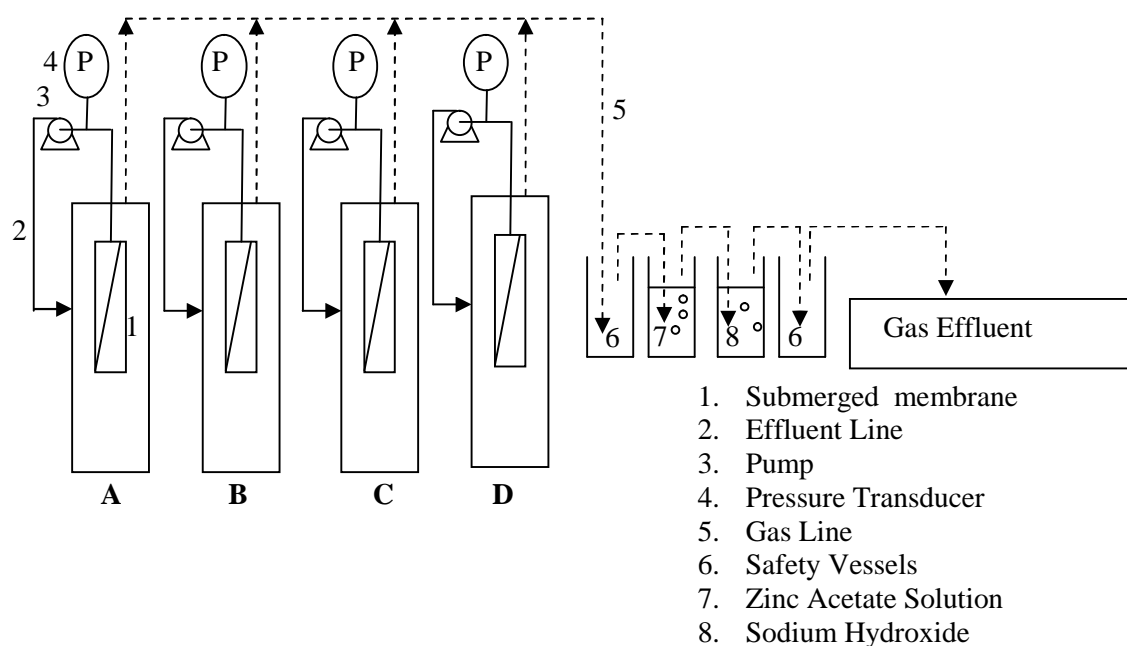


Figure 4.7: Schematic Diagram of Bench-Scale Experimental Set-Up



Figure 4.8: Picture showing Four Bench Scale Anaerobic Membrane Bioreactors in Water Bath.

(i) Inoculum, Medium and Wastewater Composition

All four AnMBRs were inoculated with 4g of crushed granular anaerobic sludge (Eerbeek, the Netherlands) containing sulphate reducers and methanogens. Several compounds were utilised in making up substrates for each of the AnMBRs in order to simulate real wastewaters. Glucose was used to simulate carbohydrates, sulphate to simulate sulphate rich wastewaters and iron to simulate wastewaters with high metal concentrations. A basal medium and trace element solution prepared according to Vallero *et al.* (2005) was added to the AnMBRs (at a rate of 2.22mLgCOD^{-1}) Each of the AnMBRs contained 2.14gCODL^{-1} at start-up with those AnMBRs containing sulphate having a COD to sulphate ratio of 1. The COD to iron ratio in those AnMBRs containing iron was 10.

Table 4.11: Wastewater composition of each AnMBR.

| | |
|-------|----------------------------|
| AnMBR | Synthetic Waste |
| G | Glucose |
| GS | Glucose and Sulphate |
| GI | Glucose and Iron |
| GIS | Glucose, Iron and Sulphate |

(ii) Experimental design

Three sets of investigations were carried out with the same experimental set-up. The first experiment was carried out at a temperature of 30°C, the second at 20°C and the third at 30°C with gas sparging through the bottom of each AnMBR. Before inoculation at the start of each experiment, sludge utilised was acclimatized at the required temperature. During each of the investigations, the AnMBRs was batch fed every two days (the interval for batch feeding was chosen after measurement of the total amount of time taken for complete glucose depletion) with the same substrate present at start-up.

(iii) AnMBR Sample Analysis

Samples were taken daily from the AnMBRs for COD, Volatile Fatty Acids (VFA), EPS, SMP and Total Solids (MLSS) Analysis. VFA concentrations were determined using a gas chromatograph (Hewlett Packard HP 5890A, Palo Alto, USA) and TMP as well as calculated specific cake resistance values used as an indication of the fouling extent on the membrane surface. Statistical analytical techniques were used to correlate all independent sets of data obtained during the experiments.

4.2.2 Crossflow Membrane Filtration Rig

Short term fouling tests were carried out at different crossflow velocities with six anaerobic and aerobic sludges. A 1L tank was attached to a side-stream crossflow microfiltration unit (

Figure 4.9), pressure transducers and a computer (to automatically record TMP values at one second intervals). TMP behaviour was observed over a period of three hours while the flux to which the membrane was subject was increased by fixed amounts (step height) at regular intervals (step durations).

Critical Flux was determined using the flux step method as described by Le Clech *et al.* (2002) and Vallero *et al.* (2003).

This method describes the critical flux as the highest flux for which there is no change in TMP or TMP increase rate remains stable. TMP increase rate can be defined by Equation 4-2.

$$\frac{dP}{dt} = \frac{TMP_f - TMP_i}{t_f - t_i} \quad \text{Equation 4-2}$$

Where:

TMP_f = final TMP at end of flux step;

TMP_i = initial TMP at the beginning of flux step;

dP/dt = fouling rate or TMP increase rate over s flux step duration;

t_f = time at end of flux step;

t_i = time at beginning of flux step.

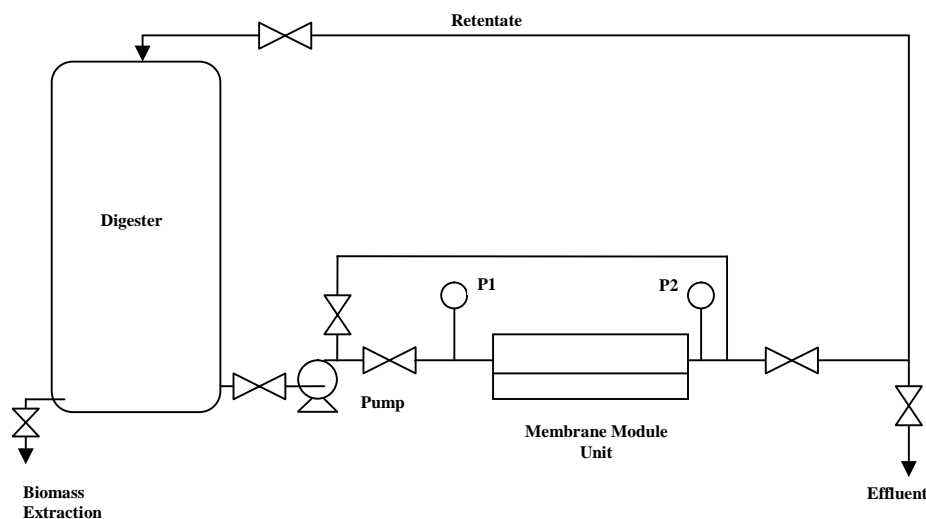


Figure 4.9: Schematic Diagram of Cross-flow Microfiltration Rig

A flux step height of $4.5\text{Lm}^{-2}\text{h}^{-1}$ and step duration of 15 minutes was applied to the system. The module unit of the rig contained a non-virgin flat sheet membrane (Kubota,UK) with a pore size of $0.1\mu\text{m}$ and total filtration area of 0.26m^2 . Prior to each critical flux test, the module unit was dismantled and cleaned by flushing with distilled water and new flat sheet membranes of the same pore size and area were utilised. Fouling rates and critical flux were determined using Equation 4-2. All experiments were carried out at a crossflow velocity of 0.7ms^{-1} except during experiments to test the effect of crossflow velocity on critical flux.

Table 4.12: List of Sludges and Bench Scale Tests

| Source | Type of Sludge | Nature of Sludge | Bench scale Test | System used for test |
|--|------------------------------|------------------|--|-------------------------------|
| Smurfit Townsend Hook, Tate and Lyle, UK | Anaerobic | Granular | Effect of physical characteristics of sludge on specific cake resistance and membrane fouling | Dead end filtration cell. |
| Cranfield University WwTW | Aerobic | Flocculent | Effects of physical characteristics of sludge on specific cake resistance and membrane fouling | Dead end filtration cell. |
| Smurfit Townsend Hook, Tate and Lyle, UK | Anaerobic | Granular | Effect of mixed liquor characteristics on critical flux. | Crossflow microfiltration rig |
| Cranfield University WwTW, UK | Aerobic | Flocculent | Effect of mixed liquor characteristics on critical flux. | Crossflow microfiltration rig |
| Eerbeek, the Netherlands | Anaerobic (used as inoculum) | Granular | Influence of operating conditions and microbial substances on performance in an active system | Bench Scale AnMBR. |

4.3 Pilot Scale Tests

4.3.1 Cranfield University Sewage Treatment Works and Pilot Plant Hall

The sewage influent flow to the Cranfield university sewage works varies widely between $300\text{m}^3\text{d}^{-1}$ and $700\text{m}^3\text{d}^{-1}$. The sewage undergoes primary sedimentation and gravity de-sludging in a pyramid-square tank (8.6m x 8.6m x 7.8m) fitted with v-notch weirs and scum boards. Primary settled sewage collected at mid-height from this sedimentation tank provides the influent (200 to 700mgCOD.L^{-1}) to the pilot plant hall.

4.3.2 Pilot Scale Anaerobic Membrane Bioreactor

Pilot scale tests were conducted using a 40L anaerobic membrane bioreactor installed in the pilot plant hall (Figure 4.10, Figure 4.11). This hybrid AnMBR was designed to incorporate side-stream and submerged membranes (allowing both independent and simultaneous use of each type of membrane configuration) as well as a double wall containing temperature regulated re-circulated water (in order to maintain constant operating temperatures). Nitrogen gas was sparged intermittently through a diffuser mounted at the bottom of the AnMBR to reduce membrane fouling, promote efficient mixing and eliminate dead zones. Gas was also sparged through the bottom of the side-stream external membrane module to aid circulation of the mixed liquor (gas lift mode).

Biogas produced by the AnMBR was vented to the atmosphere after stripping hydrogen sulphide and carbon dioxide gasses with the use of 1M zinc acetate and 1M sodium hydroxide solutions respectively. Trans-membrane pressure (TMP) on both the side-stream and submerged membranes was measured with the use of pressure transducers (RS Components, Corby) mounted on each effluent/permeate line and continuously recorded on a computer via the Pico data logging system.

The system was run for 4 months with complete solids retention as well as a constant hydraulic retention time (HRT) of 6 ± 0.4 hours (except where specific fouling experiments were being carried out).

The system was initially run at an operating temperature of $35\pm 1^{\circ}\text{C}$ without a membrane module to allow acclimatization of anaerobic granular biomass used as inoculum. After an initial period of 14 days, submerged and side-stream membranes were installed to allow withdrawal of permeate without loss of solids. The system was then allowed to acclimatize further until stabilisation round about day 60. Operating temperature was then dropped to $22\pm 0.5^{\circ}\text{C}$ and $12\pm 0.5^{\circ}\text{C}$ on day 70 and day 98 respectively. Fouling experiments were carried out at each of these operating temperatures with each membrane type whether in side-stream or submerged configuration.

All fouling experiments were conducted in the shortest amount of time possible to avoid changes in biomass characteristics unless where required. The system was also subject to gas sparging in the form of nitrogen to determine the response of biomass and the resulting effect on membrane fouling in the system.



Figure 4.10: Pictures of pilot scale anaerobic membrane bio-reactor.

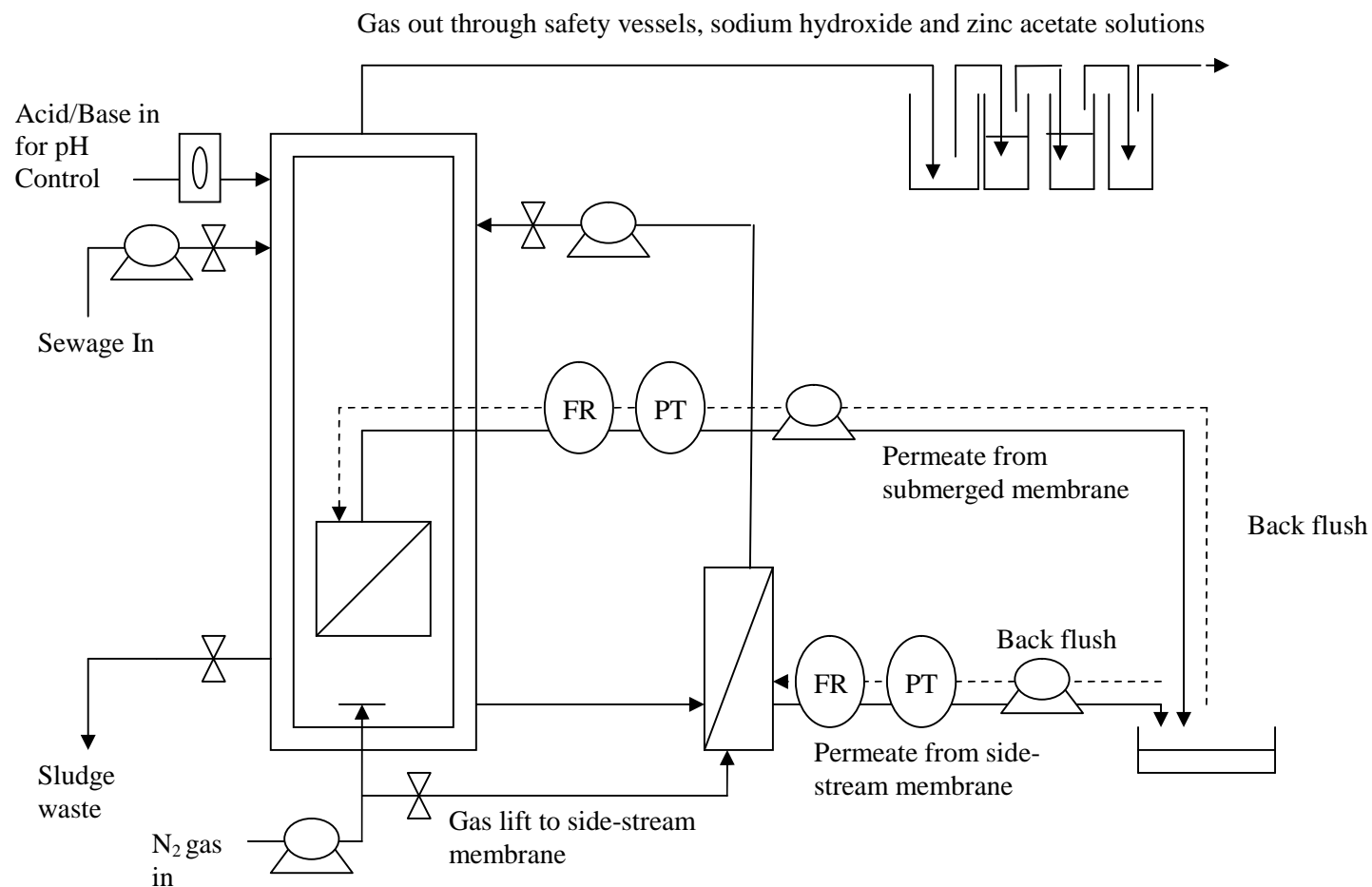


Figure 4.11: Schematic Diagram showing Pilot-Scale Hybrid Anaerobic Membrane Bio-reactor

(i) Membranes, Modules and Configuration

Two membrane configurations were utilised during the course of the experiments (submerged and side-stream). The submerged module consisted of 8 hollow fibre membrane cartridges (supplied by Mitsubishi Rayon) with a total filtration area of 0.9m^2 . Each membrane cartridge had an outer diameter of 0.5mm and a pore size of $0.1\mu\text{m}$.

Two membrane modules were operated in side-stream configuration. A summary of side-stream membrane and module characteristics is given in Table 4.13.

Table 4.13: Table showing characteristics of two side-stream membranes and modules

| Membrane Type | Supplier | Material | Module Length (mm) | Bore Size (mm) | Pore Size (μm) | No of Channels | Total Filtration Area (m^2) |
|---------------|---------------|---------------|--------------------|----------------|-----------------------------|----------------|--|
| X-Flow | Zenon | Polysulphonic | 1000 | 8 | 0.03 | 7 | 0.175 |
| Tubular | Milleniumpore | Polyethylene | 1000 | 8 | 0.1 | 12 | 0.502 |

All membranes utilised were non-virgin membranes. Effluent was continually withdrawn from all membranes except during critical flux and short-term fouling tests. Submerged membranes were back flushed with permeate when trans-membrane pressure (TMP) exceeded 0.75bar. All membranes were removed for chemical cleaning when TMP reached a value of 1.5bar, at which point lumen clogging occurred. Chemical cleaning was carried out ex-situ by back flushing membranes with a 1gL^{-1} solution of Sodium hypochlorite (NaOCl) for 1hour. The membrane was then back flushed for another hour with a solution of citric acid (3gL^{-1}) to remove all traces of Sodium hypochlorite.

(ii) Sample Collection and Analysis

Samples were collected weekly from the AnMBR during all sets of experiments. All analytical tests were carried out within 5 hours of sample collection.

Samples were analysed for chemical oxygen demand (COD), sulphate, ammonia and nitrate concentration using spectroquant photometric test kits as well as a NOVA 60 Merck spectrophotometer supplied by Merck (VWR International Ltd, Poole, UK). Other analytical tests carried out are described below.

4.4 Analytical Methods

Samples were collected weekly from all systems during all sets of experiments. All analytical tests were carried out within 5 hours of sample collection. Samples were analysed for chemical oxygen demand (COD), sulphate, ammonia and nitrate concentration using spectroquant photometric test kits as well as a NOVA 60 Merck spectrophotometer supplied by Merck (VWR International Ltd, Poole, UK). Other analytical tests carried out are described in the following sections.

4.4.1 TS, MLSS and MLVSS

Total solids (TS) concentration, mixed liquor suspended solids concentration (MLSS), mixed liquor volatile suspended solids (MLVSS) and mixed liquor fixed solids concentration (MLFSS) were determined using standard methods as described in ALPHA (1998).

TS concentration was determined using standard method 2540B. This method was used for analysis of smaller bench scale AnMBRs (500-1000mL). A well mixed sample was pipetted into a dry pre-weighed evaporating dish before being dried overnight in an oven at a temperature of 105°C. The evaporated sample is then cooled and re-weighed. TS concentration was then calculated using Equation 4-4.

$$TS = \frac{(A - B) \times 1000}{\text{Sample volume (mL)}} \quad \text{Equation 4-3}$$

Where:

A = weight of evaporating dish + dried residue, g;

B = weight of dish, g.

MLSS concentration was determined using standard method 2540D. A 20mL sample of mixed liquor was passed through dried, pre-weighed Whatman GC/F glass filters of 70mm diameter (Fisher Scientific, Loughborough) under vacuum (Speedivac 2 rotary pump, D. Benway Ltd, UK). Filtered samples were then dried overnight at a temperature of 105°C in an oven (Gallenkamp Hotbox OVB 350, Walton on Thames). Samples were weighed after cooling in a desiccator and MLSS concentration (gL^{-1}) calculated using Equation 4-5.

$$MLSS = \frac{(C - D) \times 1000}{\text{Sample volume (mL)}} \quad \text{Equation 4-4}$$

Where:

C = weight of filter paper + dried residue, g;

D = weight of filter paper, g.

MLVSS and MLFSS concentrations give a rough approximation of the amount of organic matter present in the solid fraction of wastewater and were determined using standard method 2540E. The residue from methods 2540B or 2540D were ignited to constant weight (approximately 4 hours) at 550°C before being cooled in a dessicator and weighed. MLVSS and MLFSS concentrations were then calculated using Equation 4-6 and 4-7 respectively.

$$MLVSS = \frac{(E - F) \times 1000}{\text{Sample volume (mL)}} \quad \text{Equation 4-5}$$

$$MLFSS = \frac{(G - F) \times 1000}{\text{Sample volume (mL)}} \quad \text{Equation 4-6}$$

Where:

E= weight of residue + filter paper before ignition, g;

F = weight of residue + filter paper after ignition, g;

G = weight of filter paper, g.

4.4.2 Capillary Suction Time

Capillary Suction Time (CST) is a measure of sludge dewaterability. It was determined using the Triton CST filterability tester (model 2000) supplied by Triton Electronics Ltd, Essex, UK. The test was carried out at room temperature using an 18 mm sludge reservoir containing a 6.4mL sample of sludge. Water was extracted from the sludge by capillary suction. The time taken for the liquid front to move past a first electronic contact (R1) to a second contact (R2) is measured automatically and gives the capillary suction time in seconds (ALPHA, 1998) (Figure 4.12).

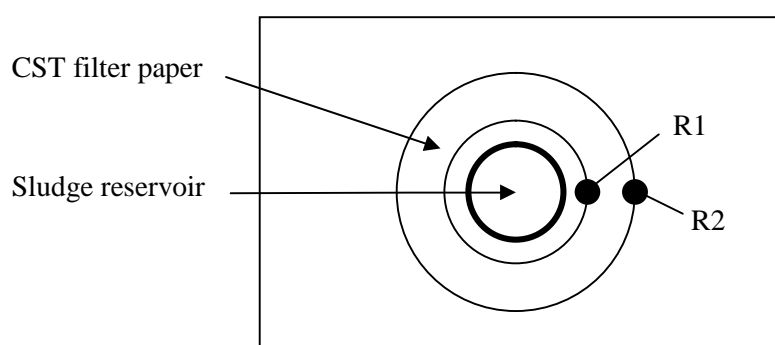


Figure 4.12: Representation of the Triton 2000 Capillary Suction Time (CST) Test Apparatus.

4.4.3 Sludge Viscosity

Viscosity is a measure of a fluid's resistance to flow. Sludge viscosity was measured with the use of the DV-E viscometer supplied by Brookfield Viscometers Limited, Harlow. The DV-E viscometer includes a rotating spindle which was immersed in the sludge or mixed liquor sample. The viscous drag of the fluid against the spindle is measured with a rotary transducer. Sludge viscosity was determined for shear rates of 0.4 s^{-1} to 22 s^{-1} .

4.4.4 Particle Size Distribution

Sludge and mixed liquor particle size was determined using the Mastersizer 2000 supplied by Malvern Instruments Ltd, Worcestershire, UK.

The Mastersizer 2000 uses laser diffraction to determine the light scattering pattern of sludge particles dispersed in deionised water (DI). Particle size can then be calculated using Mei theory (Mei *et al.*, 2003) which predicts the way light is absorbed and scattered by spherical particles.

All sludge and mixed liquor samples were analysed using the same standard operating procedure. The optical properties of the sludge material were set at default (refractive index 1.52, absorption 0.1, stirrer speed of 1800rpm) appropriate for the majority of naturally occurring samples. Samples were added to a DI water reservoir until laser obscuration (fraction of light “lost” by scattering and adsorption from the analyser beam) was between 10% and 20%. Final results were expressed in terms of volume and equivalent spheres. The percentage volume of particles was plotted against particle size (μm) and 10, 50 and 90 percentiles were reported along with the specific surface area of the sludge particle ($\text{m}^2.\text{g}^{-1}$).

4.4.5 Specific Cake Resistance to Filtration

Analyses of cake resistance to filtration were performed using the methodology developed by Coakley and Jones (1956). Sludge samples were placed in a filter cell and filtered across a $0.2 \mu\text{m}$ membrane under pressures of 0.5 to 1.5bar. Fluid and particle separation can be described by Equation 4-8.

$$\frac{t}{V} = \frac{UC\alpha}{2A^2P}V + \frac{UR_m}{AP} \quad \text{Equation 4-7}$$

Where:

t = filtration time, s;

V = filtrate volume, m^3 ;

C = Solids content, mixed liquor suspended solids (MLSS) or total solids (TS) concentrations, $\text{kg}.\text{m}^{-3}$;

α = specific cake resistance to filtration, $\text{m}.\text{kg}^{-1}$;

A = filtrate area, m^2 ;

P = pressure, Pa;

U = Filtrate viscosity, Pa.s;

R_m = filter medium resistance, m⁻¹.

If Equation 4-8 represents a straight line on an x-y graph, then plots of experimental results with t/V on the Y-axis and V on the X-axis allow the calculation of specific cake resistance from Equations 4-9.

$$\alpha = \frac{2PA^2G}{UC} \quad \text{Equation 4-8}$$

Where:

G = Gradient of the t/V against V line.

4.4.6 SMP and EPS Extraction and Determination

(i) SMP and EPS Extraction

EPS was extracted using a modified heating extraction method (Table 4.14) based on Zhang *et al.* (1999).

Table 4.14: SMP and EPS Extraction

| Procedure | |
|-----------|--|
| 1 | 50 ml of well mixed sludge samples were placed in 250 ml plastic Nalgene bottles. |
| 2 | The samples were centrifuged (5000 rpm – 5 min) (Rotanta 96R, Hettich-Zentrifugen, Tuttlingen, Germany), and supernatant collected and filtered through 0.45 µm filters (GF 52, Schleicher & Schuell, London, UK) to recover SMP. This fraction was then analysed for carbohydrates, proteins and COD. |
| 3 | Capsule bound material was then recovered by hand shaking remaining solids with 50 ml of DI water. |
| 4 | The mixture was then placed in the oven at 105°C for 60 minutes. |
| 5 | After cooling at room temperature for 30 minutes, the mixture was centrifuged at 7,500 rpm for 5 minutes, and the supernatant filtered through 0.45 µm filters to recover EPS. EPS was then analysed for carbohydrates, proteins and COD. |

(ii) Carbohydrate Measurement

Carbohydrate concentrations in both EPS and SMP were determined using methods introduced and described by Dubois *et al.* (1956) and Le Clech *et al.* (2002) respectively. 0.4mL of 5% (w/w) phenol (Sigma, UK) and 2 mL of sulphuric acid were added to 0.4mL supernatant samples in a test tube. Samples were left at room temperature (18-20°C) for 10 minutes. The contents of each tube was then transferred to cuvettes and analysed on a Jenway UV/VIS spectrophotometer (Model 6505 S) against a blank at a wavelength of 480 nm. Carbohydrate concentrations were determined from a calibration curve (see Figure A.1 in Appendix A) obtained with glucose standards (Sigma, UK).

(iii) Protein Measurement

EPS and SMP Protein concentration was determined using the diagnostic kit no. 690 (Sigma, UK). A sample volume of 0.2mL was mixed with 2.2mL of Biuret reagent and allowed to acclimatise at room temperature (18-20°C) for 10 minutes in test-tubes. 0.1mL of Folin and Ciocalteu's phenol reagent was then added to the sample. The sample was then left at room temperature for 30 minutes. The content of each test-tube was transferred to cuvettes and analysed on a Jenway UV/VIS spectrophotometer (Model 6505 S) against a blank at a wavelength of 595 nm. Protein concentrations were determined from a calibration curve (see Figure A.2 in Appendix A) developed with bovine serum albumin (BSA) protein standards (Sigma, UK).

4.4.7 Total Organic Carbon (TOC), Total Inorganic Carbon (IC) and Total Carbon (TC)

TOC, IC and TC measurements were carried out using a Shimadzu TOC-V analyzer supplied by Shimadzu UK Ltd, Milton Keynes, UK. The equipment uses the combustion/non-dispersive infrared gas analysis method to determine the total inorganic carbon and total carbon content of samples. All samples were syringe filtered through 0.45µm filters and run against 0-100 mg.L⁻¹ calibration curves prepared from potassium hydrogen phthalate (for total carbon measurements) and sodium carbonate and sodium hydrogen carbonate (for inorganic carbon measurements). TOC concentration was calculated as the difference between TC and IC concentrations.

4.4.8 High Performance Size Exclusion Chromatography (HPSEC)

All samples were syringe-filtered through 0.45 μ m filters prior to HPSEC analysis. HPSEC analysis was carried out using High Pressure Liquid Chromatography (HPLC) equipment supplied by Shimadzu VP series, Milton Keynes, UK. The equipment included a 30cm long BIOSEP-SEC S3000 column with an inner diameter of 7.8mm. The mobile phase utilised for all measurements was a 0.01 M sodium acetate solution injected at a flow rate of 1 mL.min⁻¹. All measurements were carried out at a wavelength of 254nm. Standard elution times for proteins with known molecular weights were determined using protein standards (Sigma, UK) (Table 4.15).

Table 4.15: Elution Times for Proteins of Specific Molecular Weights

| Molecular Weight kDa | Elution time (min) |
|----------------------|--------------------|
| 12.4 | 8.72 |
| 29 | 8.55 |
| 66 | 7.12 |
| 150 | 6.81 |
| 200 | 6.38 |
| 443 | 5.83 |
| 669 | 5.69 |

4.4.9 Bio-Gas Analysis

Bio-gas analysis was carried out using the Sensidyne gas detection system provided by Cole Parmer, UK. The system incorporated a gas pump and graduated detection tubes. The gas pump was used to draw a set sample of biogas through sulphur dioxide, hydrogen sulphide, ammonia, and general hydrocarbon detection tubes. The tubes showed discolouration on contact with specific gasses. The concentration of these gasses was then read directly from the tubes.

4.4.10 Temperature Correction for TMP

In order to make fouling rates determined under varying operating conditions comparable, TMP was corrected for temperature.

The relationship between viscosity of a fluid and its temperature can be described by Equation 4-10 (Gunder, 2001).

$$\eta = 1.793.e^{(-0.043.T^{0.864})} \quad \text{Equation 4-9}$$

Where:

η = dynamic viscosity of fluid, mPa.s;

T = temperature of fluid, °C.

Combining Equation 4-10 and classical resistance theory produces Equation 4-11 (which can be used to calculate corrected TMP values):

$$TMP_{20} = TMP_T \cdot \frac{\eta_{20}}{\eta_T} = TMP_T \cdot \frac{\eta_{20}}{1.793.e^{(-0.043.T^{0.864})}} \quad \text{Equation 4-10}$$

Where:

J = permeate flux, L.m⁻².h⁻¹;

TMP₂₀ = TMP at ambient temperature of 20°C, mbar;

P_T = measured TMP at temperature T, mbar;

η_{20} = permeate dynamic viscosity at ambient temperature of 20 °C, mPa.s;

η_T = permeate dynamic viscosity at temperature T, mPa.s.

4.5 Statistical Analysis

Statistical tests were carried out on all sets of data to determine correlations between variables using the statistica software package (StatSoft Inc., 2000). Functions utilised during data analysis included correlation tests for development of correlaton matrices as well as linear and non-linear regression.

The correlation test assigns a coefficient between 1 and -1 to depict relationships between individual arrays or sets of data (a coefficient of 0 infers a lack of relationship between data sets) and incorporates the covariance of data sets. Covariance is the average of the products of deviations for each data point pair. All correlation coefficients were determined using Equation 4-12.

$$\rho_{x,y} = \frac{COV(X,Y)}{\sigma_X \sigma_Y} \quad \text{Equation 4-11}$$

Where:

$$COV(X,Y) = \frac{1}{n} \sum_{i=1}^n (x_i - \mu_x)(y_i - \mu_y) \quad \text{Equation 4-12}$$

And

COV (X,Y) = covariance of data sets X and Y;

σ = standard deviation of each data set;

ρ = correlation coefficient.

Linear regression analysis was carried out by using the "least squares" method to fit a line through experimental data. This type of regression analysis can be described by Equation 4-14 where there are multiple ranges of x values.

$$y = G_1x_1 + G_2x_2 + G_3x_3 + \dots + b \quad \text{Equation 4-13}$$

Equation 4-13 is reduced to Equation 4-14 where there is a single range of x values.

$$y = Gx + b \quad \text{Equation 4-14}$$

Where:

y = range of dependent values;

x = range of independent values;

G = slope of straight line;

b = intercept of straight line.

Non-linear regression techniques determine the equation that best describes the relationship between sets of independent and dependent data that are not best described by Equation 4-13 and Equation 4-14.

It also utilises the least squares method but is used to fit a curves through data. The relationship between any pair of data sets may be described by exponential, logarithmic or polynomial lines or derivations of all three.

RESULTS

5 RESULTS: DEAD END FILTRATION TRIALS AND CHARACTERISTICS OF ANAEROBIC SLUDGES

5.1 Scope

Physical characteristics of sludge have been shown to affect digester optimisation and performance as well as bio-fouling in membrane bio-reactors. Bio-fouling can be defined as the deposition of bacterial cells and microbial products onto the surface of a membrane (Stephenson *et al.*, 2000). These microbial products include soluble microbial products (SMP), a general term used to describe soluble compounds produced by bacterial cells as a result of metabolism and other cellular processes (Stephenson *et al.*, 2000).

There is still a lot unknown about the mechanisms behind anaerobic membrane bio-fouling. This chapter attempts to provide some insight into how the physical characteristics of sludge affect its behaviour in the membrane bio-reactor as well as bio-fouling mechanisms when membranes are exposed to anaerobic sludge. Results were also compared with aerobic sludge to establish any differences between the two types of sludge.

5.2 Results

5.2.1 Characteristics and Fluid Hydrodynamics of Anaerobic Sludge

(i) Viscosity

All three anaerobic sludges were granular and exhibited non-Newtonian properties as shown by the non-linear response of viscosity to shear rate (Figure 5.13). A fluid may be said to have non-Newtonian properties when a finite stress is required for deformation to occur (Tilton, 1997). These time dependent fluids are also known as yield stress materials.

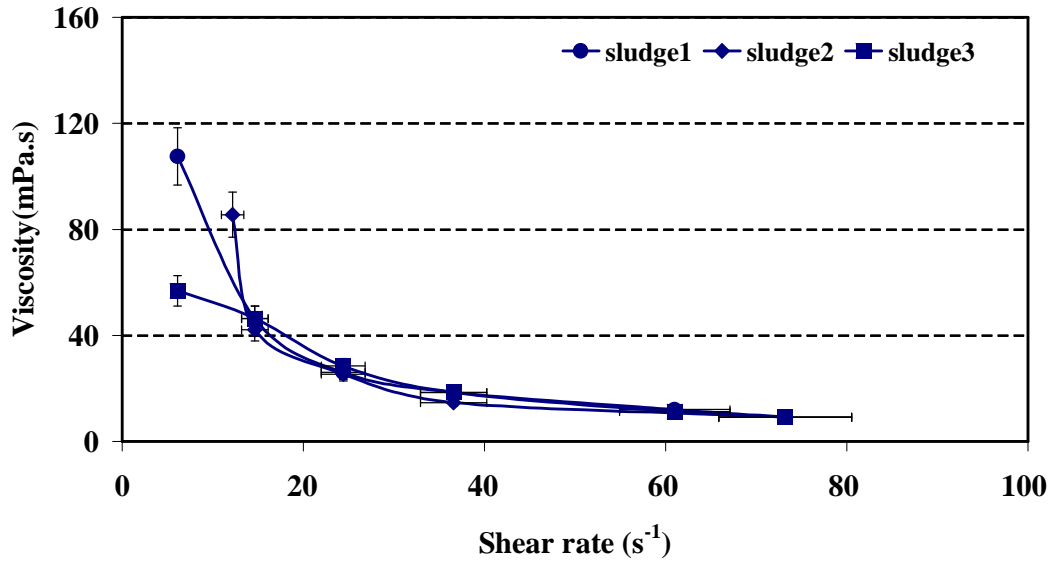


Figure 5.13: Viscosities of Three Anaerobic Sludges at Different Shear Rates

All three anaerobic sludges had viscosities that measured between 9 at high shear rates of 80s^{-1} and 110mPa.s at low shear rates of 8s^{-1} . These values are significantly higher than values reported in literature on the aerobic and anaerobic sludges. Pevere *et al.*, (2006) in trying to estimate the limit viscosity of anaerobic granular sludges found that apparent viscosity measured between 3 and 5.5mPa.s at shear rates in the range of 200s^{-1} to 1000s^{-1} . Le Clech (2002) also found that an aerobic sludge with a MLSS concentration of 8gL^{-1} had a dynamic viscosity of 4.6 to 16.7mPa.s at shear rates of 7 to 122s^{-1} . Germaine (2004) also measured dynamic viscosity of aerobic sludges at a shear rate of 12.24s^{-1} and found that values varied between 3 and 40mPa.s depending on phase of growth of microbes present in the sludge.

Further investigation confirms that all three anaerobic sludges in this study are shear-thinning and exhibit pseudoplastic behaviour (Figure 5.14). Pseudoplastic fluids without yield stresses produce rheograms where the slope decreases with increasing shear rate (Figure 5.1). Deformation of these fluids typically obeys a power law model (Equation 5-1, Figure 5.14) over a range of shear rates.

$$\mu = K\gamma^{n-1} \quad \text{Equation 5-1}$$

Where:

μ = viscosity in mPa.s,

K = consistency index in $\text{g.cm}^{-1}.\text{s}^{(2-n)}$,

n = dimensionless power law exponent.

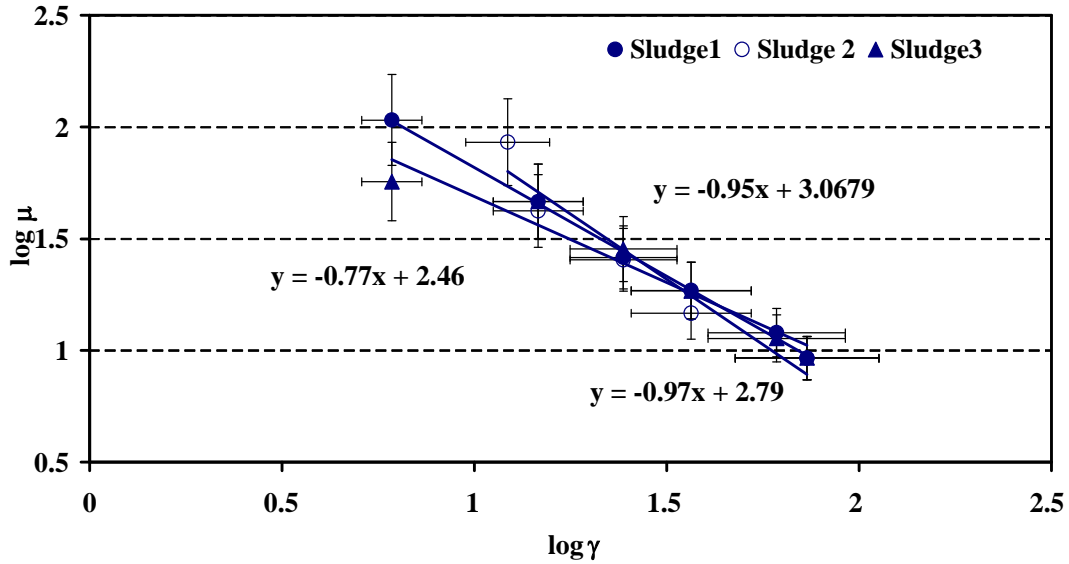


Figure 5.14: Rheological Chart Depicting Pseudoplasticity of Anaerobic Sludge

Power law exponents for all three anaerobic sludges analysed varied between 0 and 0.23 while consistency indices did not exceed $1200\text{g.cm}^{-1}.\text{s}^{2-n}$ (Table 5.16).

The promotion of turbulence to inhibit the thickness of hydrodynamic boundary layers is important in reducing fouling in membrane bio-reactors (Stephenson *et al.*, 2000). The critical Reynolds number at which hydrodynamic boundary layers become turbulent is 500,000 and can be described by Equation 5-2 (Tilton, 1997)

$$\text{Re}_L = \rho V^{2-n} L^n / K \quad \text{Equation 5-2}$$

Where:

Re_L = Reynolds number,

ρ = density of sludge (kg.m^{-3}),

K = consistency index ($\text{kg.m}^{-1}.\text{s}^{-2+n}$),

V = velocity in m.s^{-1} .

For each of the sludges tested, the minimum particle velocity required to create a turbulent boundary layer across a surface of 1m in length can be calculated by re-arranging Equation 5-2 to obtain Equation 5-3

$$\sqrt[2-n]{\frac{\text{Re}_L K}{\rho L^n}} = V \quad \text{Equation 5-3}$$

The kinetic Energy of each sludge granule or particle while in turbulence can then be calculated thus;

$$E = \frac{mv^2}{2 \times 1000} \quad \text{Equation 5-4}$$

Where:

E = kinetic energy of each particle/granule in KJ,

m = mass of each particle in kg.

Table 5.16 shows the results obtained for each of the sludges tested. More energy will be required to create turbulence in the case of sludge 3 than with the other two sludges if all other conditions in the immediate membrane environment remain the same. Particles present in sludge 3 will require a minimum velocity of 343.8ms^{-1} and minimum energy input of 59.1KJ to create a turbulent boundary layer in comparison to sludges 1 and 2 which would require minimum velocities of 242.8 and 135.7ms^{-1} as well as minimum energy inputs of 29.5 and 9.2KJ respectively.

Table 5.16: Table showing Power Law Exponents, Consistency Indices and Particle Kinetic Energy for all Three Anaerobic Sludges

| Sludge | Source | n | $K(\text{g.cm}^{-1} \cdot \text{s}^{-2+1})$ | $V(\text{m.s}^{-1})$ | E (KJ) |
|--------|------------|------|---|----------------------|--------|
| 1 | Paper mill | 0.03 | 1169 | 242.8 | 29.5 |
| 2 | Paper mill | 0.05 | 288 | 135.7 | 9.2 |

| Sludge | Source | n | $K(\text{g.cm}^{-1}.\text{s}^{-2+1})$ | $V(\text{m.s}^{-1})$ | E (KJ) |
|--------|-------------|------|---------------------------------------|----------------------|--------|
| 3 | Sugar plant | 0.23 | 617 | 343.8 | 59.1 |

It therefore follows that where sludges exhibit non-Newtonian properties as was the case with the sludges analysed, it is not the viscosity itself that determines sludge and fouling behaviour in a membrane bio-reactor but how this parameter changes with shear rate and other conditions. Consistency indices and power law exponents are also important in determining the fouling nature of sludges and mixed liquors. All three anaerobic sludges in this study for example, had a dynamic viscosity of approximately 8mPa.s at a shear rate of 75s^{-1} but showed different evolutionary characteristics at lower shear rates. The said sludges would also be expected to exhibit differing hydrodynamic characteristics when in contact with membranes as shown in Table 5.16.

(ii) Particle Size, EPS and SMP

SMP protein present in anaerobic sludge 1 measured over 900mgL^{-1} but dropped to approximately 340mgL^{-1} within one week (Figure 5.15). Latter SMP levels remained relatively stable over the one month period (never exceeding 370mgL^{-1}). EPS protein concentrations on the other hand, continually increased from 8.2mg.gTS^{-1} to a maximal value of 28.1mg.gTS^{-1} . Both SMP and EPS contained large amounts of protein and relatively small amounts of carbohydrates. Protein fractions of both EPS and SMP measured approximately 8 to 10 times carbohydrate fractions over the one month period. These trends were generally true for all other anaerobic sludges tested (Figure 5.16 and Figure 5.17). At the start of the tests, both sludges 2 and 3 had SMP protein concentrations of 944.6 and 930.4mg.L^{-1} respectively, dropping to approximately 300 and 340mgL^{-1} within one week. EPS protein levels also measured between 8 and 28mgTS^{-1} for sludge 2 and between 4 and 27mgTS^{-1} for sludge 3.

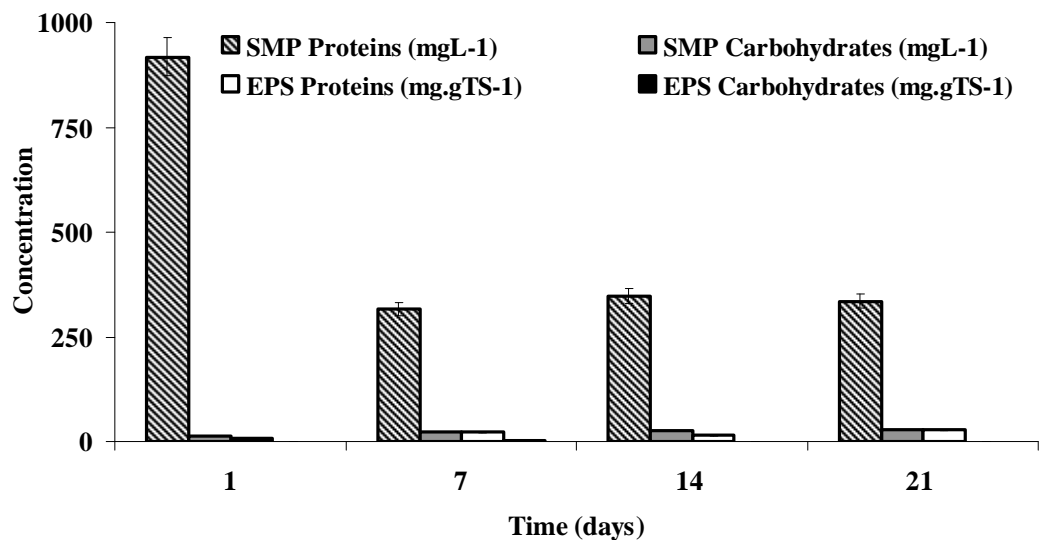


Figure 5.15: Evolutions of EPS and SMP Concentration in Anaerobic Sludge 1 over a One Month Period.

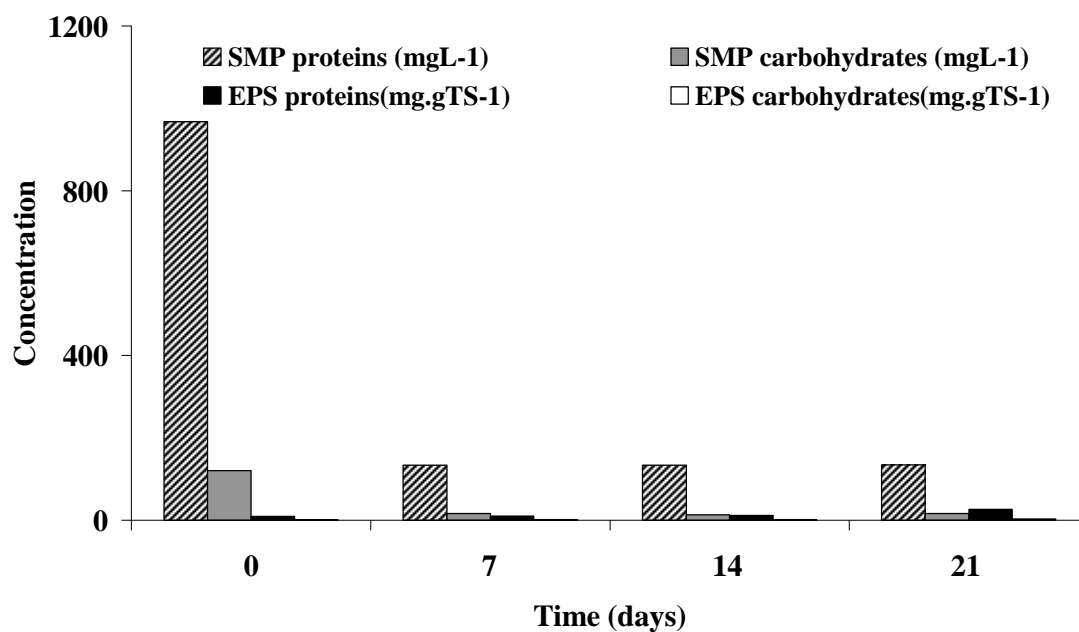


Figure 5.16: Evolutions of EPS and SMP Concentration in Anaerobic Sludge 2 over a One Month Period.

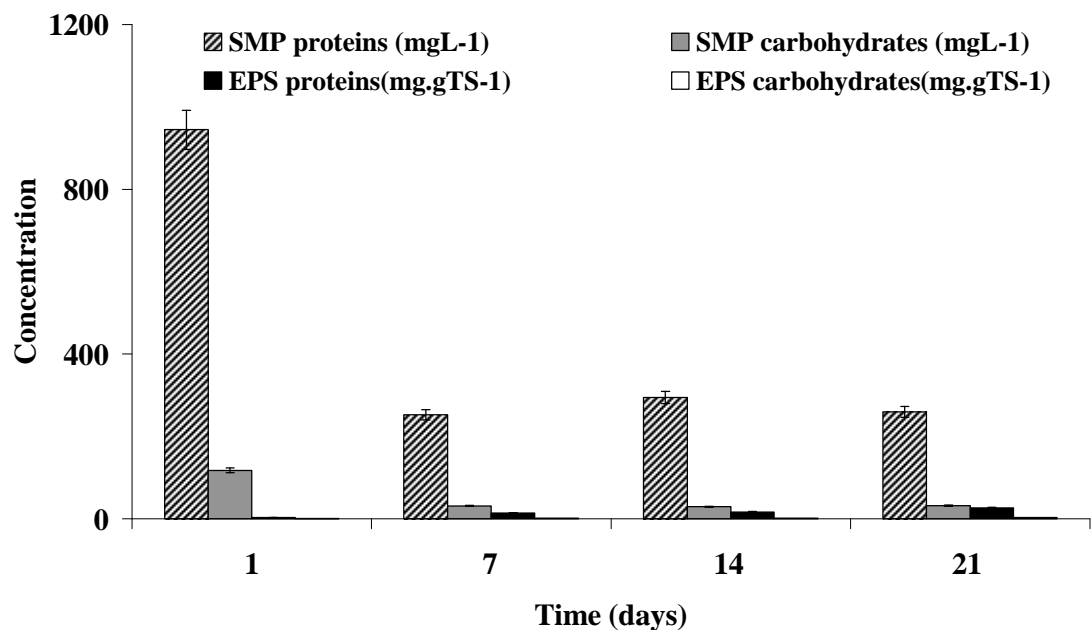


Figure 5.17: Evolutions of EPS and SMP Concentration in Anaerobic Sludge 3 over a One Month Period.

The increase observed in EPS levels is probably associated with the proliferation/growth of granules present in the sludge (Figure 5.18). This is supported by results showing that increased levels of EPS protein resulted in larger anaerobic sludge granules (Figure 5.19). Mean granule size for all three sludges varied between 129.01 μ m and 946.69 μ m throughout the period (Table 5.17). Maximum granule diameter did not exceed 1500 μ m.

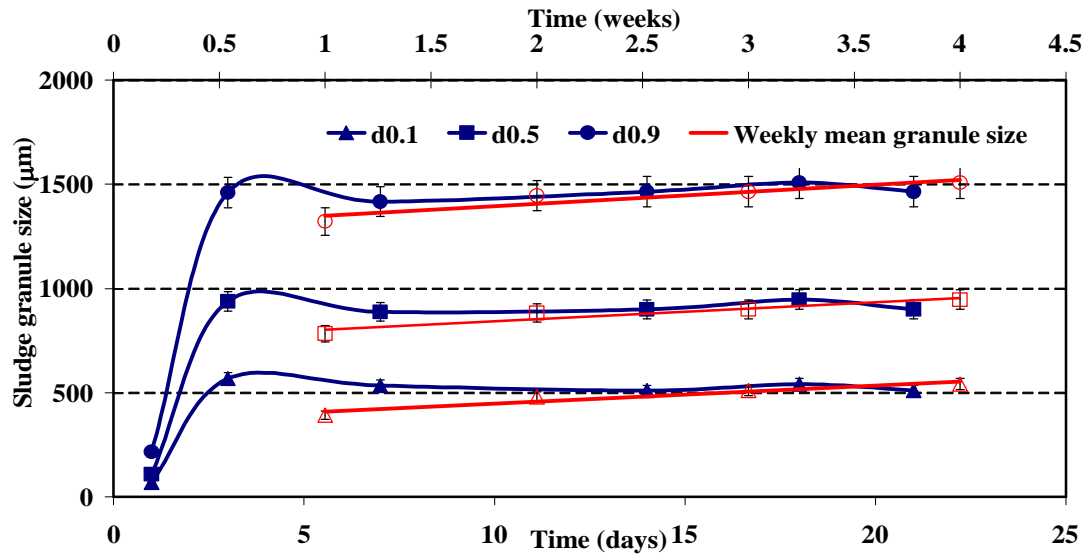


Figure 5.18: Evolution of Granule/Particle Size with Time (Using Anaerobic Sludge 3 as an example).

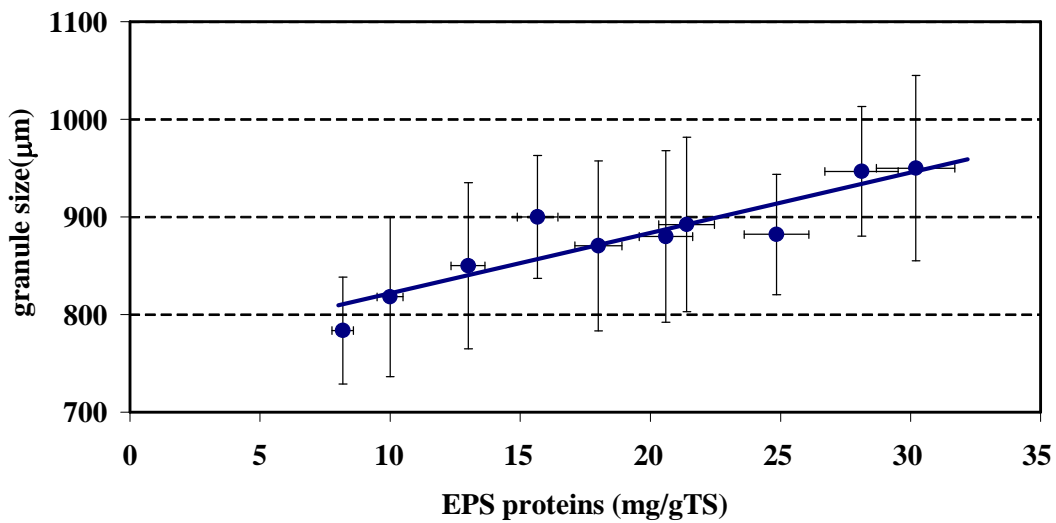


Figure 5.19: Granule Size as a Function of EPS Protein from Anaerobic Sludge (Using Anaerobic Sludge 1 as an example).

(iii) Specific Cake Resistance and Compressibility

Specific cake resistance is a power law function of the imposed pressure drop;

$$\alpha = \beta(\Delta P)^c$$

Equation 5-5

Where:

c = cake compressibility,

β = constant dependent primarily on size and shape of sludge granules.

All three anaerobic sludges formed a compressible cake with a specific cake resistance of $1 \times 10^{13} \text{ m.kg}^{-1}$ to $1 \times 10^{16} \text{ m.kg}^{-1}$ during filtration. Several factors were found to affect cake compressibility including granule size and sludge source (Table 5.17). Sludge 1 and 2 showed similar compressibility of 0.45 and 0.44 respectively while compressibility for sludge 3 was much higher at 0.63 (Figure 5.20, Table 5.17). The β factor for this particular sludge (15.52) was also very different from sludge 1 and 2 with the latter sludges having values between 13.5 and 14 (Figure 5.20, Table 5.17).

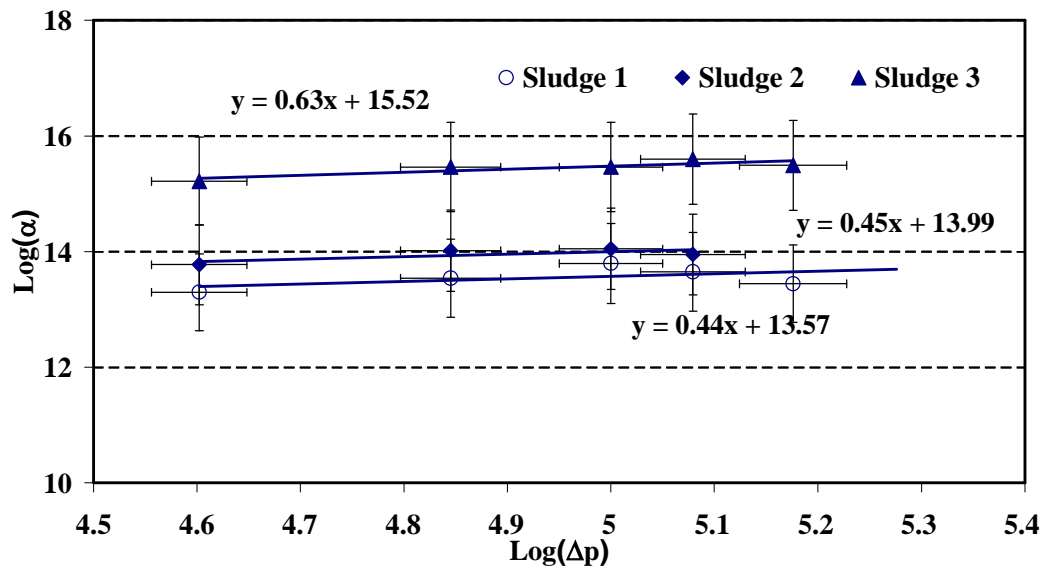


Figure 5.20: Compressibility Chart for Three Anaerobic Sludges with Different Characteristics.

Table 5.17: Table showing Relationship between Sludge Characteristics and Compressibility.

| Sludge | Source | c | β | Viscosity (mPa.s) | $d_{0.5}$ | EPS_C | EPS_P |
|--------|-------------|------|---------|----------------------|-----------|---------|---------|
| 1 | Paper mill | 0.44 | 13.57 | 135.91 | 129.01 | 0.53 | 22.55 |
| 2 | Paper mill | 0.45 | 13.99 | 59.64 | 330.76 | 4.98 | 26.37 |
| 3 | Sugar plant | 0.63 | 15.52 | 72.98 | 946.691 | 0.65 | 27.47 |

(iv) Interactions between Normalised Characteristics of Anaerobic Sludge

Table 5.18: Correlations Matrix showing Relationships between normalised Anaerobic Sludge Characteristics.

| | α | $d_{0.5}$ | CST_n | Viscosity | SMP_p | SMP_c | EPS_p | EPS_c | TS |
|-----------|----------|-----------|---------|-----------|---------|---------|---------|---------|--------|
| α | 1.0000 | | | | | | | | |
| $d_{0.5}$ | 0.2344 | 1.0000 | | | | | | | |
| CST_n | 0.7870 | 0.8866 | 1.0000 | | | | | | |
| Viscosity | 0.6112 | -0.2258 | 0.2379 | 1.0000 | | | | | |
| SMP_p | -0.2131 | -0.9104 | -0.8012 | 0.3122 | 1.0000 | | | | |
| SMP_c | 0.1037 | 0.9752 | 0.7775 | -0.4251 | -0.9385 | 1.0000 | | | |
| EPS_p | 0.2806 | 0.8746 | 0.9983 | 0.2466 | -0.8122 | 0.7685 | 1.0000 | | |
| EPS_c | 0.0947 | -0.0756 | 0.0598 | 0.0578 | -0.3241 | -0.0133 | 0.1176 | 1.0000 | |
| TS | -0.8761 | -0.8058 | -0.9760 | -0.3137 | 0.7988 | -0.6998 | -0.9867 | -0.2624 | 1.0000 |

α in m.kg-1; TS in g.L-1; SMP in mg.L-1; EPS in mg.gTS-1; CST_n in s.gTS-1; Viscosity in mPa.s at 12.24 s-1 shear rate; $d_{0.5}$ in μ m.

All significant correlations are marked in bold.

Table 5.18 is a correlations matrix depicting relationships between anaerobic sludge characteristics. In the correlations matrix, values between -1 and +1 have been assigned for pairs of characteristics. The stronger the positive or negative correlation between the pair, the closer the assigned numerical value will be to +1 or -1 respectively. Characteristics that show correlations between -0.1 to 0.1 are assumed to have no significant correlation.

The strongest positive correlations were observed between EPS_p and CST_n (0.9983), SMP_c and $d_{0.5}$ (0.9752), CST_n and $d_{0.5}$ (0.8866), EPS_p and $d_{0.5}$ (0.8746), TS and SMP_p (0.7988), CST_n and α (0.7870), SMP_c and CST_n (0.7775), EPS_p and SMP_c (0.7685) and viscosity and α (0.6112). The high positive correlation between specific cake resistance and CST indicates that more dewaterable cakes have a lower specific cake resistance. EPS_p , mean particle size and SMP_c also affect dewaterability as can be seen from the high positive correlations of these properties to capillary suction time. An increase in these characteristics will produce an increase in time taken to dewater anaerobic sludge and vice versa. EPS_p and SMP_c also showed a high significant correlation to mean particle size inferring that a change in one of these characteristics will contribute to a corresponding change in the other. A higher specific cake resistance will also produce a more viscous sludge as denoted by the assigned value of 0.6112.

EPS_p also showed less significant correlations with viscosity and specific cake resistance with values of 0.2466 and 0.2806 respectively. Viscosity is also affected by SMP_p with an assigned correlation value of 0.3122. Correlations of 0.2344 and 0.2379 were also assigned to $d_{0.5}$ and specific cake resistance as well as viscosity and CST_n respectively.

The highest negative correlations (-0.6 to -1) were assigned to TS and α , TS and $d_{0.5}$, TS and CST_n , TS and SMP_c , TS and EPS_p , SMP_p and $d_{0.5}$, SMP_p and CST_n , SMP_p and SMP_c and SMP_p and EPS_p . A change (increase or decrease) in TS concentration produces an opposite change in specific cake resistance, mean particle size and sludge dewaterability. The same trend is expected when the influence of SMP_p on mean particle size and sludge dewaterability is looked at.

The high correlations noted for SMP and EPS fractions show that the two substances are linked with levels of one substance affecting the other. Less significant correlations of -0.2 to -0.4 were assigned to SMP_p and α , $d_{0.5}$ and viscosity as well as TS and viscosity.

5.2.2 Characteristics and Fluid Hydrodynamics of Aerobic Sludge

(i) Particle Size, EPS and SMP

Maximum EPS and SMP protein concentrations for all aerobic sludges tested were approximately 100mg.gMLSS^{-1} and 60mgL^{-1} respectively (Figure 5.21, Figure 5.22 and Figure 5.23). On the other hand, carbohydrate fractions of both EPS and SMP measured higher than with anaerobic sludge. EPS carbohydrate concentration fell between 80 and 120mg.gMLSS^{-1} while SMP carbohydrates remained relatively stable at 13 to 14mgL^{-1} .

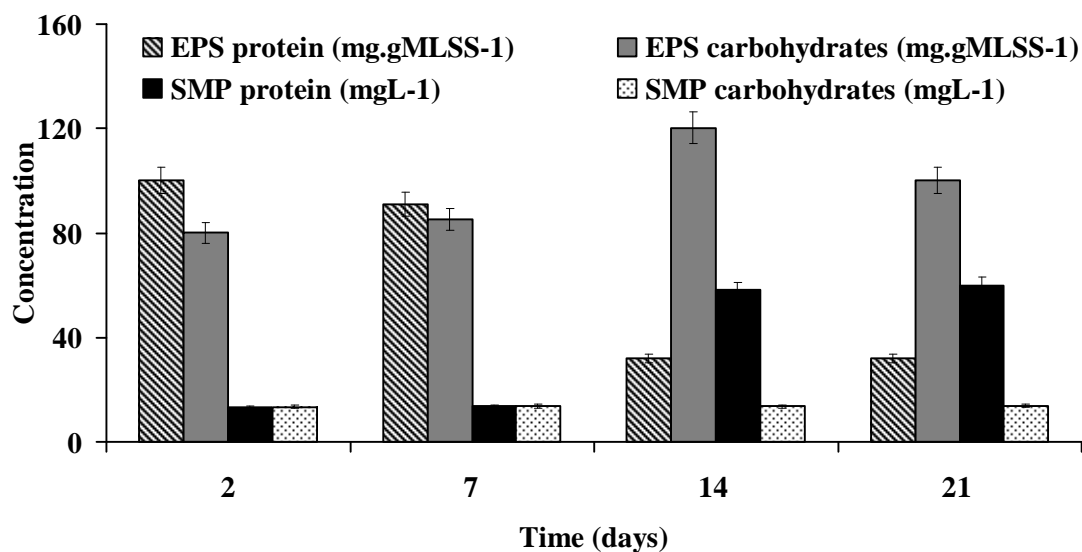


Figure 5.21: Evolution of EPS and SMP concentrations in Aerobic Sludge over a One Month Period.

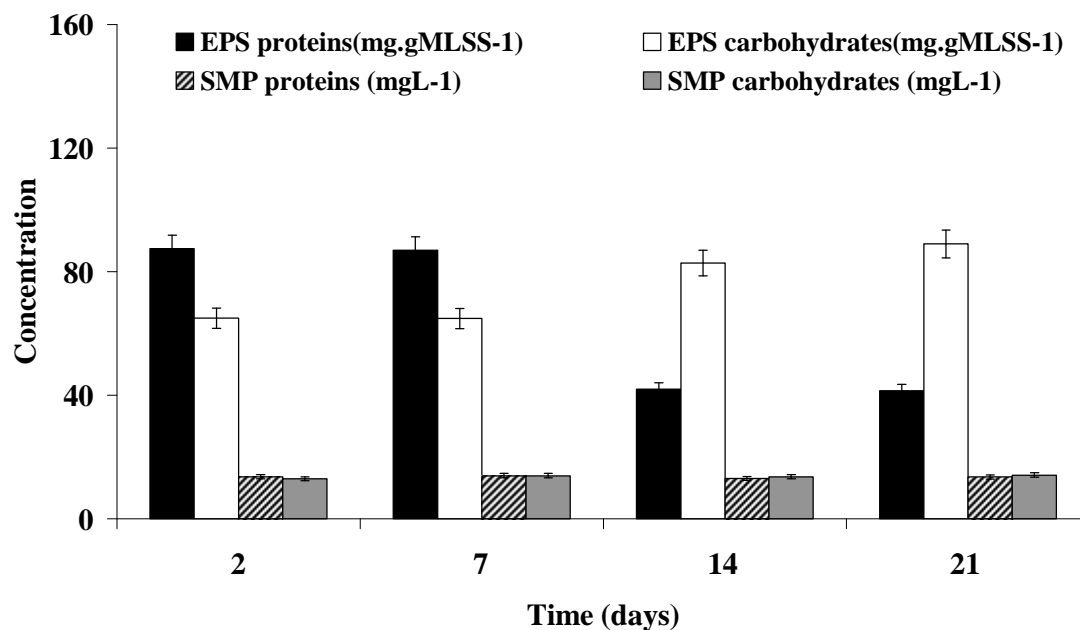


Figure 5.22: Evolution of EPS and SMP concentrations in Aerobic Sludge 2 over a One Month Period.

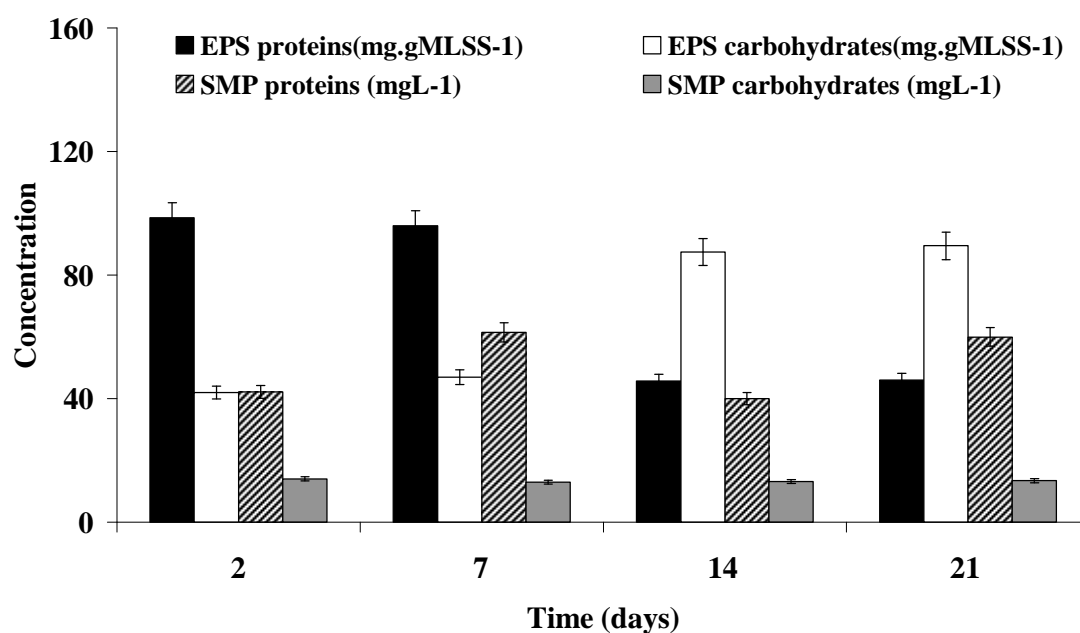


Figure 5.23: Evolution of EPS and SMP concentrations in Aerobic Sludge 3 over a One Month Period.

The maximum particle diameter for all three aerobic sludges did not exceed 160 μm throughout the entire period. Mean particle diameter varied between 35 and 40 μm for all sludges (Figure 5.24). During the one month period, there was little or no change in minimum and the mean particle size. However, maximum particle diameter did decrease for all aerobic sludges tested. Sludge one showed a fall in maximum particle diameter from 135.04 μm to 84.42 μm (Figure 5.24)

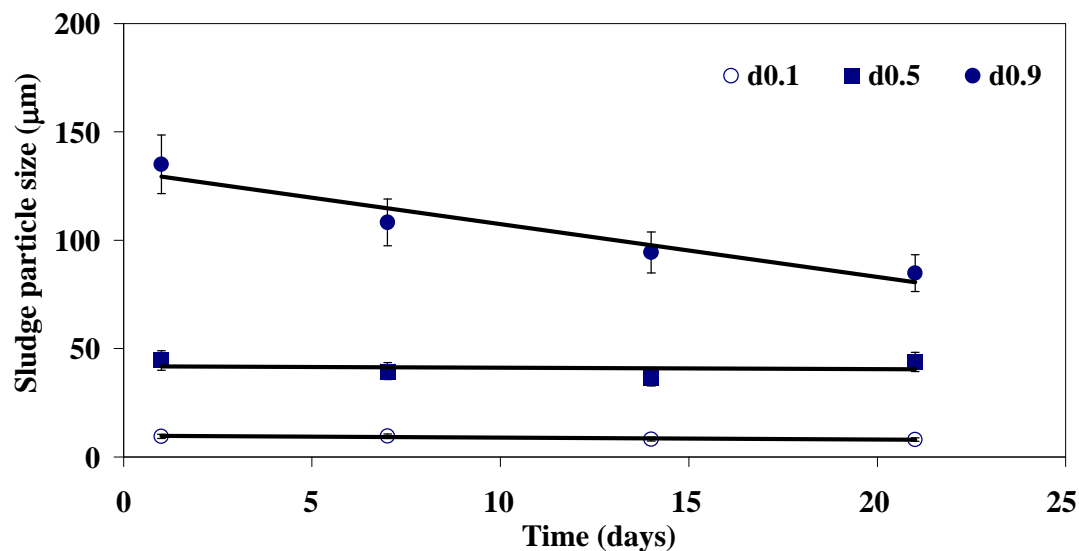


Figure 5.24: Aerobic Sludge Particle Size over a One Month Period (Using Aerobic Sludge 1 as an example).

(ii) Specific Cake Resistance and Compressibility

Specific cake resistance values of the three aerobic sludges analysed never exceeded $1 \times 10^{14} \text{ m.kg}^{-1}$. All three aerobic sludges generally formed cakes with lower specific cake resistances than anaerobic sludges.

The three aerobic sludges also formed compressible cakes. Cake compressibility values obtained in all cases fell between 0.7 and 0.8 (Figure 5.25). All cakes formed by aerobic sludges in this set of experiments were much more compressible than cakes formed by anaerobic sludges ($0.4 < n < 0.65$).

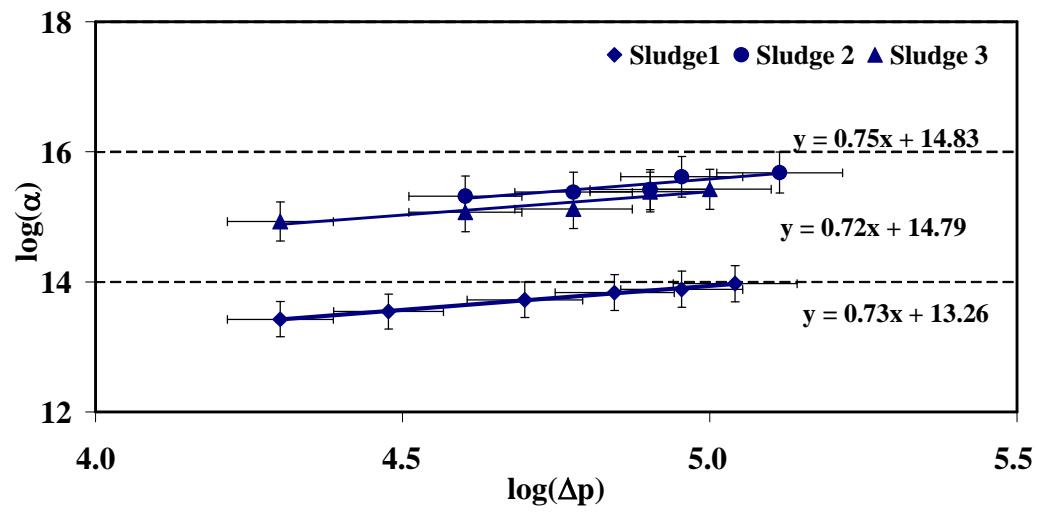


Figure 5.25: Compressibility Chart for Three Aerobic Sludges.

(iii) Interactions between Normalised Characteristics of Aerobic Sludge

Table 5.19: Correlations Matrix showing Relationship between Various Aerobic Sludge Characteristics.

| | α | $d_{0.5}$ | CST_n | SMP_p | SMP_c | EPS_p | EPS_c | MLSS |
|-----------|----------|-----------|---------|---------|---------|---------|---------|--------|
| α | 1.0000 | | | | | | | |
| $d_{0.5}$ | 0.3263 | 1.0000 | | | | | | |
| CST_n | -0.3208 | -0.2284 | 1.0000 | | | | | |
| SMP_p | -0.0953 | 0.0037 | -0.0230 | 1.0000 | | | | |
| SMP_c | 0.5263 | -0.0906 | 0.2615 | 0.0607 | 1.0000 | | | |
| EPS_p | 0.0394 | -0.0062 | -0.7016 | 0.0143 | -0.2576 | 1.0000 | | |
| EPS_c | 0.0614 | -0.1635 | -0.2749 | 0.0765 | 0.4931 | 0.6634 | 1.0000 | |
| MLSS | -0.8587 | 0.3151 | -0.5089 | 0.0612 | -0.3630 | 0.5680 | 0.2409 | 1.0000 |

α in $m.kg^{-1}$; MLSS in $g.L^{-1}$; SMP in $mg.L^{-1}$; EPS in $mg.gMLSS^{-1}$; CST_n in $s.gMLSS^{-1}$; Viscosity in $map's$ at $12.24 s^{-1}$ shear rate; $d_{0.5}$ in μm .

All significant correlations are marked in bold.

The highest positive correlations between aerobic sludge characteristics (0.4 to 1) were assigned to relationships between fractions of EPS and SMP as well as EPS_p and MLSS (Table 5.19). An increase or decrease in MLSS concentration produced a corresponding change in EPS_p. This trend infers that a link does exist between EPS production and biomass.

Less significant correlations of 0.1 to 0.4 were also noted for $d_{0.5}$ and α , $d_{0.5}$ and MLSS, CST_n and SMP_c as well as MLSS and EPS_c. High negative correlations were assigned to MLSS and specific cake resistance (α) as well as MLSS and CST_n with values of -0.8587 and -0.5089 respectively. Specific cake resistance of sludge is highly dependent on its solids concentration with higher MLSS concentration producing cakes with lower specific cake resistances. The lesser value assigned to MLSS and capillary suction time shows correlation between the two characteristics, indicating that an increase in MLSS concentration will cause a reduction in sludge dewaterability. EPS_p also showed a high correlation to capillary suction time and therefore sludge dewaterability with an assigned value of -0.7016.

Negative correlations were also assigned to EPS_c and $d_{0.5}$ (-0.1635), SMP_c and EPS_p (-0.2576), MLSS and SMP_c (-0.3630), EPS_c and CST_n (-0.2749) as well as EPS_c and CST_n (-0.2749). In correlating all of the individual sludge characteristics, SMP_p was excluded because of the minute concentrations present

5.2.3 Comparison of Filtration Characteristics and Fouling Mechanisms for Aerobic and Anaerobic Sludges

(i) SMP and Membrane Fouling

Rejection factors (Equation 5-6) show the proportion of SMP deposited on the membrane surface during filtration in simple terms. Rejection factors were therefore utilised as a suitable indicator of the membrane fouling propensity of SMP.

$$R^* = \frac{C_i - C_f}{C_i} \quad \text{Equation 5-6}$$

Where:

R^* = Rejection factor,

C_i = Initial concentration before filtration,

C_f = Final concentration of filtrate.

Figure 5.26 shows the pressure-rejection profiles for different fractions of SMP from anaerobic sludge. Rejection factors for the total carbon content of the SMP sample varied from 0.4 to 0.7 indicating that 40 to 70% of total carbon content was retained by the membrane. Rejection was highest at 0.7 to 1 bar and lowest at 0.4 to 0.6 bar as well as 1.0 to 1.2 bar. Therefore fouling of the membrane is highest between pressures of 0.7 and 1 bar.

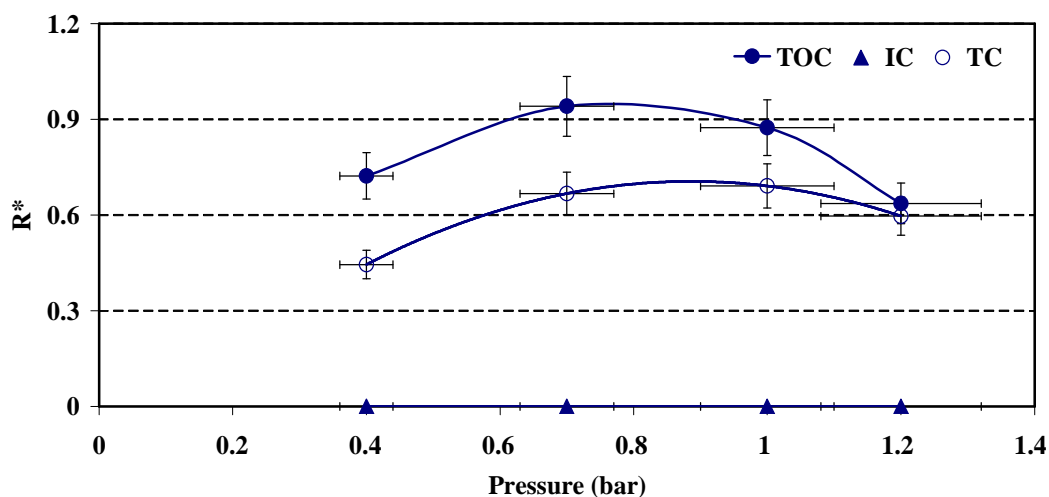


Figure 5.26: Pressure-Rejection Profile for SMP from Anaerobic MBR.

Further investigations into the components of SMP that have the highest fouling propensity show total organic carbon (proteins and carbohydrates) as the principal membrane foulant. Rejection factors for total organic carbon varied from 0.6 to 0.94 indicating that of the total organic carbon fraction, 60 to 94% is retained by the membrane. There was no detectable difference in filtrate concentrations of inorganic carbon so rejection factors were approximately 0 at all pressures showing that the membrane retained little or no inorganic carbon and therefore this fraction of SMP makes little contribution to the fouling of the membrane.

A comparison between the pressure-rejection profiles of SMP from anaerobic and aerobic MBRs (Figure 5.27) highlights differences between fouling mechanisms in the two systems. Membrane fouling continually increased when SMP from the aerobic mbr was filtered under higher pressures. However, membrane fouling with anaerobic SMP was lowest when pressures were less than 0.7 bar or above 1 bar. Rejection factors were generally higher with anaerobic SMP except at high pressures above 1 bar (atmospheric pressure). This observation indicates that anaerobic SMP has a higher membrane fouling propensity than aerobic SMP below atmospheric pressure. However, this trend may be reversed when membranes are subject to higher pressures.

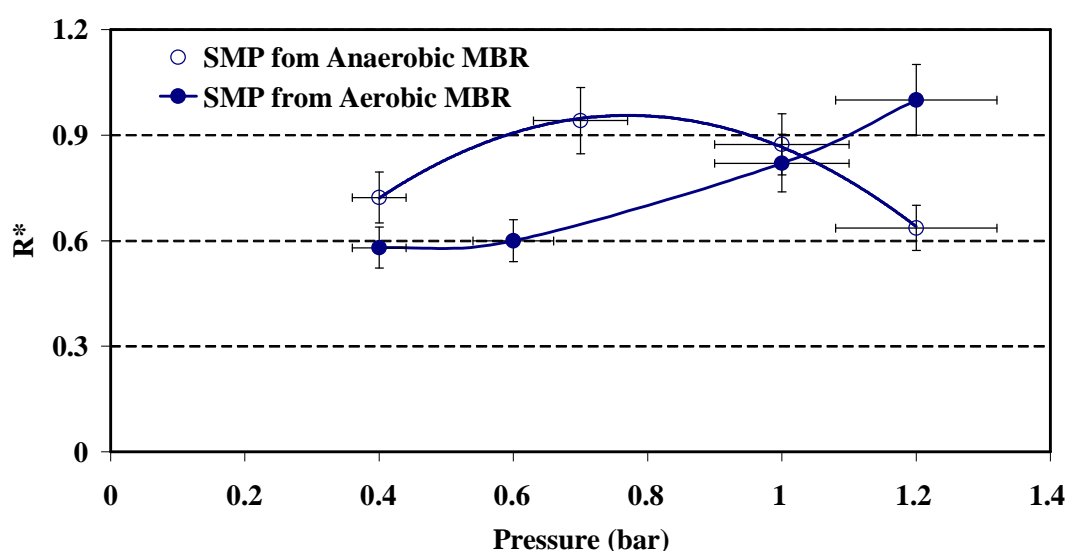


Figure 5.27: Pressure-Rejection Profile for TOC fraction of SMP from Anaerobic and Aerobic MBRs

(ii) Filtration Characteristics of Anaerobic and Aerobic Sludges

Sludges from anaerobic and aerobic membrane bioreactors were analysed to determine which of the linear models presented in appendix A best described fouling within the said systems. Figure 5.28 shows models as applied to experimental filtration of all six sludges.

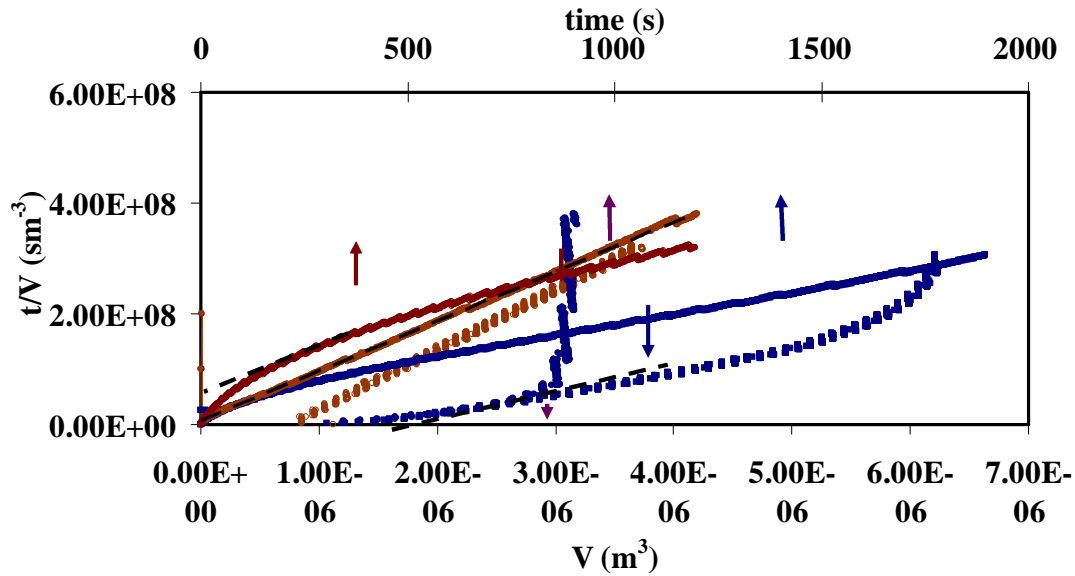


Figure 5.28: Filtration Models as Applied to Experimental Filtration of Six Anaerobic and Aerobic sludges.

Figure 5.29 and Figure 5.30 show individual data obtained for anaerobic (sludge 1) and aerobic sludge (sludge 2) respectively. Data obtained for each type of sludge (anaerobic/aerobic) was representative for all sludges of that type tested during these experiments. The cake filtration model was found to best describe experimental filtration data obtained with anaerobic sludge (Figure 5.29) while the pore blocking model was more applicable to data obtained with aerobic sludge (Figure 5.30). These models were found to be consistent at all pressures tested.

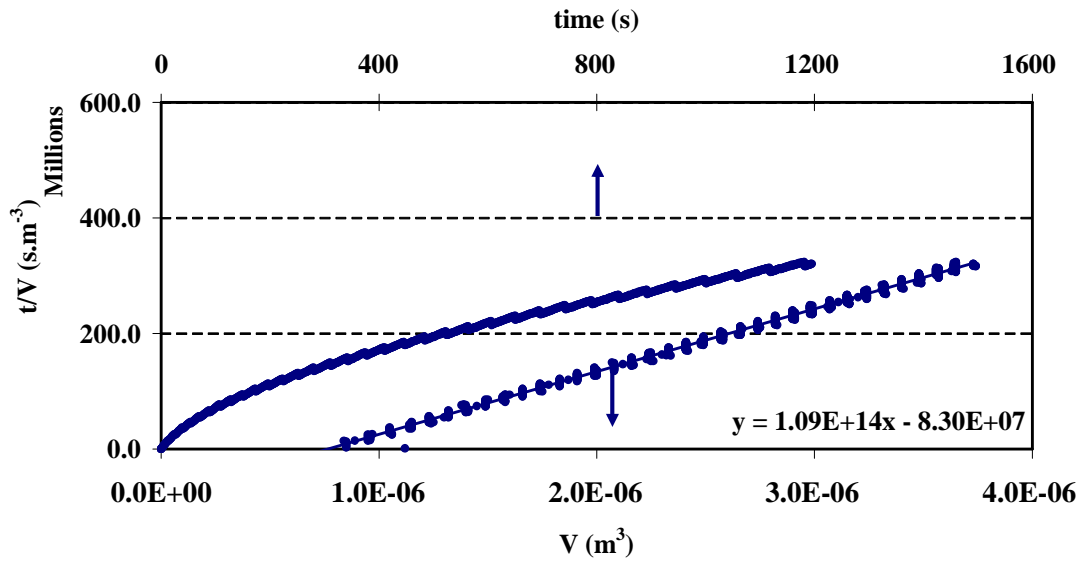


Figure 5.29: Pore Blocking and Cake Filtration Models as Applied to Experimental Filtration of Anaerobic Sludge.

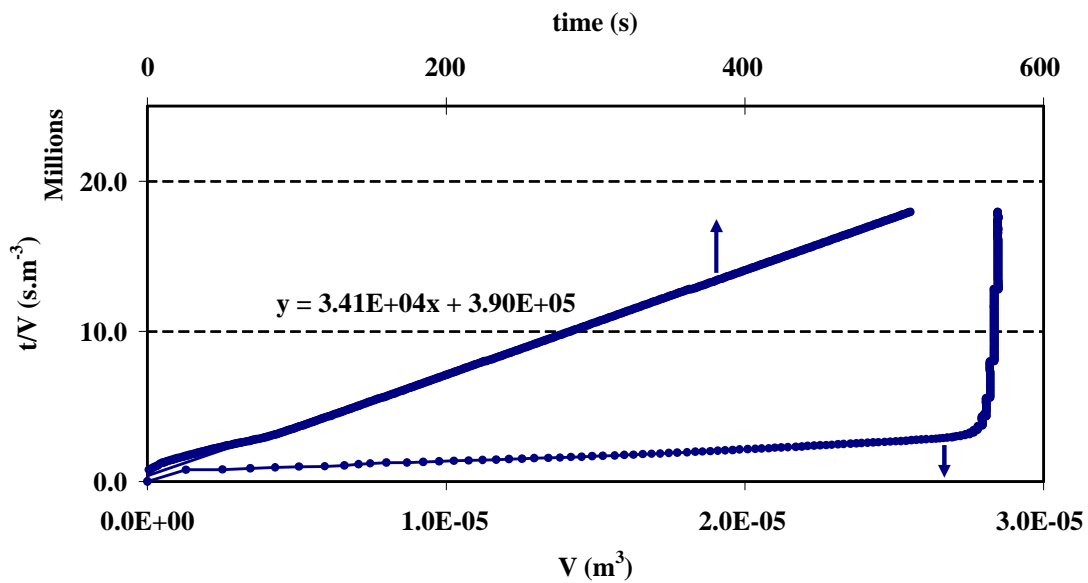


Figure 5.30: Pore Blocking and Cake Filtration Models as Applied to Experimental Filtration of Aerobic Sludge.

5.3 Discussion

Results from this chapter show the wide variation in sludge characteristics depending on source and operating conditions to which it has been subject. The three anaerobic sludges analysed during these experiments not only showed marked differences in physical properties when compared with one another but differed from aerobic sludges as well.

Results from rheological experiments appear to point to the non-Newtonian nature of anaerobic sludges. These sludges are essentially shear-thinning or pseudoplastic fluids which exhibit Newtonian behaviour at very high or very low shear rates (Figure 5.13). Pevere *et al.* (2006) looked into the evolution of viscosity of anaerobic granular sludge and identified their non-Newtonian nature while attempting to link apparent viscosity with other physical characteristics such as total suspended solids, surface charge and sludge origin. Results presented here are comparable to aerobic sludges which have been described by several authors as non-Newtonian. Forster (2002) investigated rheological properties of activated sludges from three different sewage treatment works and determined that the said sewage sludges exhibited yield stresses, a characteristic peculiar to non-Newtonian fluids. His work is further confirmed by work carried out by others including Defrance *et al.* (2000) and Guibaud *et al.* (2004). Xing *et al.* (2001) however defined sludge from an aerobic MBR as a Newtonian fluid.

Despite general agreement on non-Newtonian behaviour of sludges, differences do exist between flow characteristics of anaerobic and aerobic sludges. Consistency indices previously reported in literature (105 to 275.8 g.cm⁻¹.s⁻²⁺¹) by Moeller and Torres (1997) were generally much lower than the values determined for anaerobic granular sludge (288 to 1200 g.cm⁻¹.s⁻²⁺¹) in these experiments. Power law exponents for the three anaerobic sludges analysed also measured between 0.03 and 0.23 in contrast to values between 0.4 and 0.5 for all of the aerobic sludges analysed by Moeller and Torres (1997).

Larger amounts of EPS were found to be present in aerobic sludge per specific mass of biomass in comparison to anaerobic sludge. The proportion of protein compared with carbohydrates present in both EPS and SMP was also much higher for the anaerobic sludges analysed. Table 5.20 makes comparisons between results from this study and other published works on EPS characterisation.

Table 5.20: Summary of Studies on EPS Content of Various Sludges.

| Wastewater Type | Source/Treatment Type | Units | EPS _p | EPS _c | Reference |
|------------------|---|------------------------|------------------|------------------|----------------------------|
| Paper mill | Anaerobic UASB reactor | mg.gTS ⁻¹ | 10-50 | 1-5 | This study |
| Sugar refinery | | | 7-30 | 0.5-3 | |
| Municipal sewage | Aerobic MBR | mg.gMLSS ⁻¹ | 35-90 | 40-90 | |
| Municipal sewage | Conventional aerobic activated sludge plant | | 40-90 | 60-80 | Alvarez (2005) |
| Leachate | Aerobic MBR | mg.gMLSS ⁻¹ | 30-76 | 17-45 | |
| Municipal sewage | | | 75-125 | 1-25 | |
| Chemical | Conventional aerobic activated sludge plant | mg.gVSS ⁻¹ | 45-61 | 13-21 | Sponza (2002) |
| Leather | | | 44-50 | 25-29 | |
| Dye | | | 37-47 | 23-29 | |
| Winery | | | 67-73 | 15-17 | |
| Pulp paper | | | 38-42 | 30-36 | |
| Petrochemical | | | 38-48 | 18-26 | |
| Cannery | Anaerobic UASB reactor | mg.gTS ⁻¹ | 140-142 | 41-46 | Batstone and Keller (2001) |
| Brewery | | | 140-142 | 34-37 | |

Average EPS content of aerobic sludges analysed during this study were very different from other published works on the subject. It is difficult to determine the exact reason for these differences due to wide availability of different methods for quantifying EPS concentration. However, a contributory factor may be the low acclimatisation temperatures to which all the sludges in this study were subject as well as the storage of the same sludges without active degradation of substrate.

This study also appears to show that anaerobic sludges have higher concentrations of SMP in comparison to aerobic sludges. Concentrations for aerobic sludges varied from 10 to 132mgL⁻¹ and 14 to 17mgL⁻¹ respectively for protein and carbohydrate fractions depending on sludge origin. On the other hand, anaerobic SMP concentrations measured 150 to 900mgL⁻¹ for protein and 20 to 100mgL⁻¹ for carbohydrates. The wide variability in concentration values may once again be due to differing sludge sources. Results of this study contradict findings of Kuo *et al.* (1996) and Germirli *et al.* (1993). Kuo *et al.* (1996) found that normalised production of SMP is lower in anaerobic systems than in aerobic systems. Germirli *et al.* (1993) also found that single stage anaerobic systems produced lower residual COD levels in comparison to aerobic systems. High SMP concentrations were noted for each of the anaerobic sludges in this study compared to Chudoba (1985b) who showed that 1g of biomass subject to anaerobic conditions will produce 15.7mgL⁻¹ of residual COD while aerobic biomass produces 15 to 25mgL⁻¹. The high concentrations measured in this study may be attributed to the storage of sludges without active degradation of substrate at low temperatures. It is hypothesised that increased amounts of SMP were excreted for metabolic purposes due to the absence of substrates and nutrients as well as to relieve the stress of being subject to temperatures below ambient. This is in agreement with Kuo (1993) who gave a definitive list of the reasons for SMP production including environmental stress (such as extreme temperatures) and bacterial starvation. Extending this reasoning to the higher amounts of SMP measured for anaerobic sludges in comparison to aerobic sludges in this study, it can be postulated that the aerobic sludges contained less SMP due to the increased adaptability of aerobic biomass to environmental stress such as temperature and pH change.

Specific cake resistance of anaerobic sludges determined by filtration varied from $1 \times 10^{13} \text{ m.kg}^{-1}$ to $1 \times 10^{16} \text{ m.kg}^{-1}$ in comparison to aerobic sludges which never exceeded $1 \times 10^{14} \text{ m.kg}^{-1}$. Specific cake resistance is largely dependent on particle size and can give an indication of the contribution of biomass to membrane fouling under dead end conditions. Specific cake resistance was much higher for anaerobic sludges because these granular sludges contained larger particles (800 to 1000 μm) in comparison to flocculent aerobic sludges (48 to 51 μm). Values indicate a greater resistance to filtration with anaerobic biomass in contrast to statements made by Yin *et al.* (2004) who suggested that the order of magnitude of specific resistance of filtration with respect to different kinds of sludges is aerobic sludge > raw sludge > anaerobic sludge.

Compressibility denotes the rigidity of a cake and how quickly a cake layer can be deformed at high pressures. Values will vary from 0 for very rigid and incompressible cakes to 1 for highly compressible cakes. Cakes formed by anaerobic sludges were less compressible with values of 0.55 ± 0.15 in comparison to aerobic sludges (0.75 ± 0.05). Stephenson *et al.* (2000) suggests the cake layer initially formed during membrane filtration might be useful in trapping organics that would have blocked membrane pores if allowed to reach the membrane surface. Cakes formed by anaerobic sludges are less likely to become deformed at higher pressures than aerobic sludges so the benefits of having a cake layer are not lost under extreme operating conditions such as high pressure. Aerobic sludges on the other hand will become more compact at higher pressures causing greater flux decline.

In general, individual anaerobic sludge characteristics showed a greater correlation to one another in comparison to aerobic sludge. Some of the highest correlations existed between SMP, EPS and particle size showing that these fractions are important in maintaining the structure of anaerobic granules. EPS_p in anaerobic sludge showed a high positive correlation (>0.8) to particle/granule size in contrast to EPS_c which showed no significant correlation. The reverse was seen for aerobic sludge with EPS_p showing no significant correlation and EPS_c showing a negative correlation to particle size inferring that increased levels of this substance may contribute to sludge flocculence. High correlations were also noted for EPS and CST indicating that sludge dewaterability is affected by EPS concentrations.

Correlations were negative for aerobic sludge and positive in the case of anaerobic sludge. It therefore follows that the presence of high amounts of EPS increases sludge dewaterability where the said sludge is aerobic but has the reverse effect in anaerobic sludge. This is in agreement with work carried out by Kieding and Nielsen (1997) who thought that higher levels of EPS resulted in improved sludge stability and solid-liquid separation. Chen *et al.* (2002) on the other hand found that the presence of high levels of EPS in activated sludge was detrimental to sludge dewaterability as it caused an increase in the amounts of bound water contained in the activated sludge which in turn led to poor settleability. However, it is important to note that these correlations are only a simplistic view of the relationships between individual sludge properties.

Analysis of SMP and its impact on filtration showed that total organic carbon (TOC) fractions and little or no inorganics (IC) are retained on the surface of the membrane. A lesser proportion of aerobic SMP was retained compared to anaerobic SMP until pressures exceeded 1 bar. The lower fouling propensity of anaerobic SMP at higher pressures is unanticipated as there should be a quicker build up of foulants on the membrane surface with increased pressure under dead end conditions (the subjection of fluids to higher pressures should normally result in higher fluxes if there is minimal fouling of the membrane). The decrease in fouling propensity at pressures higher than 1 bar indicates that a proportion of SMP which would normally be retained by the membrane is forced through the membrane. As rejection of a particular foulant is directly related to the size of the particles it contains, it may be hypothesised that excessive pressures result in the break up of organic fractions in SMP resulting in smaller molecules which are then able to pass through the cake layer and membrane.

Further analysis of fouling by anaerobic and aerobic sludges shows that both types of sludges are filtered via different mechanisms. Cake filtration best described anaerobic sludge filtration due to the larger size of the particles present in this sludge while the pore blocking model was found to best describe filtration of aerobic sludge. These models however, only describe the initial stages of sludge filtration via membranes. For aerobic sludge, organic colloidal matter travel to the membrane surface before the formation of the cake layer and block pores thereby reducing flux through the membrane.

The low specific cake resistance and high compressibility of aerobic sludge cake formed later in the process results in further flux decline. The reverse process is observed with filtration of anaerobic sludges. A cake layer is formed initially and the high specific cake resistance and low compressibility of this cake allows the trapping of organic colloidal matter (despite the higher concentrations of these substances present in anaerobic sludge) before these substances get to the membrane surface.

The link between sludge characteristics and membrane filtration is complex. Both anaerobic and aerobic sludges showed complex but different interrelationships between individual sludge characteristics. It is therefore difficult to determine the exact impact of each of these characteristics on membrane bio-fouling. However, it is clear that SMP, EPS, particle size, solids concentration and sludge dewaterability have some effect on membrane fouling as they dictate the amount of individual sludge components that are retained on the membrane surface whether in terms of biomass cells or colloidal matter. It is clear from this chapter that the greater proportion of fouling when a membrane is exposed to anaerobic sludge can be attributed to bacterial cells rather than colloidal matter. The reverse can be said for aerobic sludge. Comparisons of anaerobic and aerobic sludge characteristics showed up potential fouling problems such as the higher rejection factors obtained with anaerobic SMP filtration as well as higher cake resistances. However, anaerobic sludge did form a less compressible cake (with lesser amounts of pore blocking) than aerobic sludge, an advantage when considering permeates fluxes in relation to membrane fouling.

Table 5.21: Summary of Findings: Anaerobic vs. Aerobic Sludge

| Property | Anaerobic | Aerobic | Comment |
|--------------------------|---|---|---|
| Viscosity | 3-120mPa.s @ shear rates of 5 to 100s ⁻¹ | 3-40mPa.s @ shear rates of 8 to 122s ⁻¹ | Both anaerobic and aerobic sludges are essentially non-Newtonian fluids. |
| EPS | EPS _p : 3-30 mg.gTS ⁻¹ . EPS _C : 0 to 3.5mg. mg.gTS ⁻¹ . | EPS _p : 40-100 mg.gMLSS ⁻¹ . EPS _C : 40-90mg. mg.gMLSS ⁻¹ . | EPS concentrations per unit mass of sludge higher in aerobic sludge than anaerobic sludge. |
| SMP | SMP _p : 200-1000 mg.L ⁻¹ . SMP _C : 29-120 mg.L ⁻¹ . | SMP _p : 40-90 mg.L ⁻¹ . SMP _C : 10-15 mg.L ⁻¹ . | SMP concentrations higher in anaerobic sludge than aerobic sludge. |
| Particle size | Max: 1300-1510µm Mean: 700-950µm Min: 350-550µm | Max: 80-160µm Mean: 35-40µm Min: 10-20µm | Larger particles present in anaerobic sludge in comparison to aerobic sludge. |
| Specific cake resistance | Min: 1 X 10 ¹³ m.kg ⁻¹ Max: 1 X 10 ¹⁶ m.kg ⁻¹ | Min: 1 X 10 ¹¹ m.kg ⁻¹ Max : 1 X 10 ¹⁴ m.kg ⁻¹ . | Anaerobic sludges generally have higher specific cake resistances than aerobic sludges. |
| Compressibility | Min: 0.4 Max: 0.65 | Min: 0.7 Max: 0.8 | Aerobic sludges more compressible than anaerobic sludges |
| Fouling behaviour | SMP rejection highest below atmospheric pressure. Filtration of sludge is best described by cake filtration | SMP rejection highest above atmospheric pressure Filtration of sludge is best described by pore blocking model | SMP is a foulant in both types of sludges. There appears to be an increased likelihood of irreversible fouling with aerobic sludges. Aerobic sludges block pores intrinsically while anaerobic sludges form a cake on the surface of the membrane. |

6 RESULTS: BENCH SCALE TESTS

6.1 Scope

Conclusions from chapter 2 (literature review) of this thesis show that the anaerobic membrane bioreactor still lags behind its aerobic counterpart because of the complexity of the anaerobic digestion process as well as problems with adaptability and flexibility. In addition, past research has shown significant fouling problems when membranes are exposed to anaerobic biomass.

Fouling in anaerobic membrane bioreactors is still poorly understood. It has been established that struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$), bacterial cells and colloidal matter are major membrane foulants (Choo and Lee, 1996) but there is still limited information on the role of extracellular polymeric substances (EPS) and soluble microbial products (SMP) in bio-fouling of membranes when coupled with anaerobic digesters. EPS are high molecular weight compounds released as a result of cell lysis, growth and decay while SMP is a general term used to describe soluble compounds produced by bacterial cells as a result of metabolism and other cellular processes (Stephenson *et al.*, 2000).

Results obtained in chapter 5 were based on inactive systems where the digesters were not actively breaking down or treating substrates. This chapter will seek to provide some insight into the influence of wastewater composition, presence/absence of gas and temperature on the production of EPS and SMP in AnMBRs as well as how these operating conditions and substances impact on fouling in an operational anaerobic membrane bioreactor.

The chapter will also attempt to link anaerobic sludge and mixed liquor characteristics directly with membrane fouling rates in the short term as well as give further insight into the differences that exist when membranes are fouled by anaerobic and aerobic sludges. Critical flux, specific cake resistance and TMP increase rate were chosen as fouling indicators. Critical flux determines the range of permeate fluxes to which a membrane can be subject before irreversible fouling begins to take place. An increase in fouling propensity is indicated by a drop in critical flux.

Critical flux in a membrane bio-reactor is dependent on hydraulic conditions, nature of membranes utilised as well as the nature of foulants to which the membrane is subject.

6.2 Results

6.2.1 Bench Scale Anaerobic Membrane Bioreactors

(i) Critical Flux Tests

Critical flux of the bench scale AnMBRs was determined using the flux step method as described in chapter 4. A value of approximately $26\text{L.m}^{-2}.\text{h}^{-1}$ was obtained for all four AnMBRs (Figure 6.31). All AnMBRs were therefore operated at fluxes below this value irrespective of configuration, operating conditions and substrate composition.

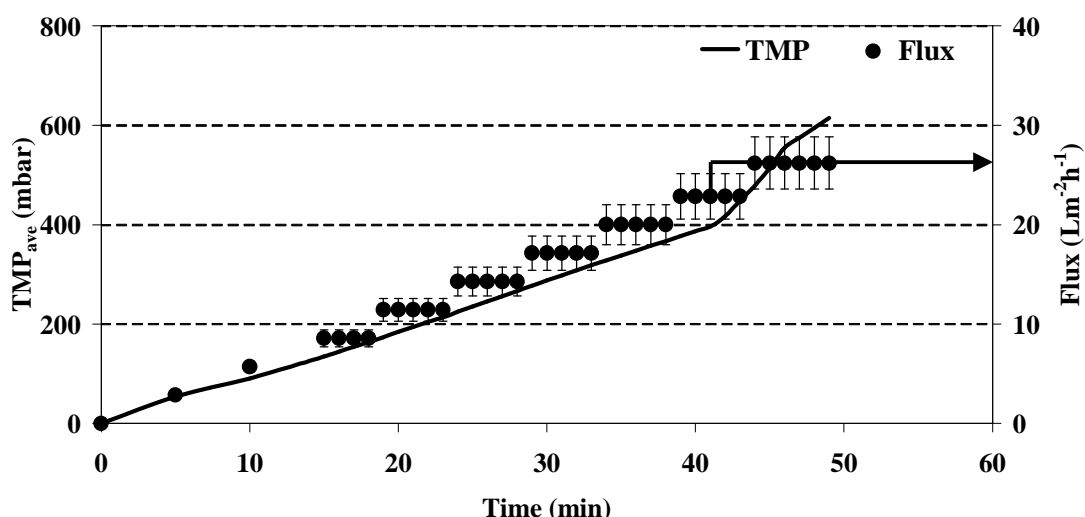


Figure 6.31: Critical flux determination by the flux step method at Total Solids (TS) concentration of 4gL⁻¹

(ii) Performance of AnMBRs

Volatile fatty acid concentration (VFAs) in the permeate varied from 0 to 3100mg.L⁻¹ with the lowest amounts observed during the first 2 to 4 days of experiments (Figure 6.32). The highest amounts of volatile fatty acids were observed when the AnMBRs were subject to an operating temperature of 20oC. VFA concentration under this operating condition increased from 0 to just over 3000mgL⁻¹ within 14days (for all four AnMBRs) compared to a maximum concentration of 1600 mgL⁻¹ observed at 30oC without gas sparging. Similar VFA concentrations were observed in all four AnMBRs irrespective of substrate composition. Gas sparging resulted in increased VFA production with maximum concentrations during latter periods increasing by a approximately 60%.

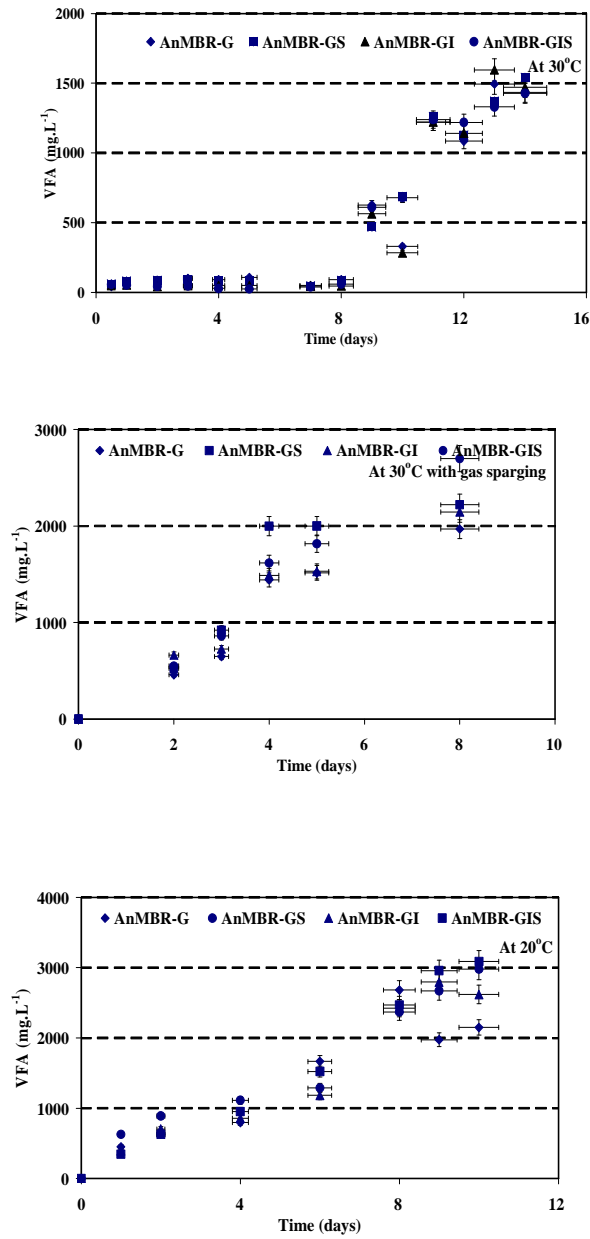


Figure 6.32: VFA concentrations in each of the four AnMBRs when subject to different operating conditions.

A glucose depletion rate of approximately $0.21 \text{ gCOD.gTS}^{-1}.\text{h}^{-1}$ (at steady state) was observed in all four anaerobic membrane bioreactors irrespective of composition. A sulphate reduction rate of 0.018 to $0.03 \text{ gSO}_4^{2-}.\text{gTS}^{-1}.\text{h}^{-1}$ was achieved in those AnMBRs containing sulphate with the lower reduction rates observed in AnMBR GIS (containing iron and sulphate). However, complete breakdown of substrate into methane was slow and incomplete due to limited pH control. An overall COD removal efficiency of approximately 80% was observed in all four AnMBRs (irrespective of influent composition) when operated at 30°C . This figure dropped to 50% at 20°C . The drop in performance and efficiency observed was probably due to the increased concentrations of volatile fatty acids (VFAs) in all four AnMBRs at the lower temperature. The presence of high amounts of volatile fatty acids during the experiments resulted in a large drop in pH (below the optima for methanogenesis, 6.5-7.5) and without adequate pH control, this acid-pH shock led to poor conversion of the said intermediate products to methane.

(iii) Effect of Substrate Composition, Temperature and Gas Sparging on EPS and SMP

Progressively higher amounts of SMP were observed in AnMBRs GS, GI and GIS containing sulphate and iron at 30°C (Figure 6.33). At the higher temperature of 30°C AnMBR GIS showed the highest amounts of SMP with levels of approximately 200 mgL^{-1} , twice the amount present in AnMBR G. The subjection of all four AnMBRs to a lower operating temperature of 20°C resulted in increased SMP levels in all except AnMBR GIS where SMP concentration dropped from 199 to 139 mgL^{-1} . Results obtained from this set of experiments are in line with a previous study carried out by Hao and Lao (1988) who found that SMP concentration varies from 4% to 9% of influent substrate concentration depending on bacterial species and dilution rate. SMP content of each of the four AnMBRs in this study varied from 6.5 to 9.4% of COD present at start up of AnMBRs depending on type of substrate utilised.

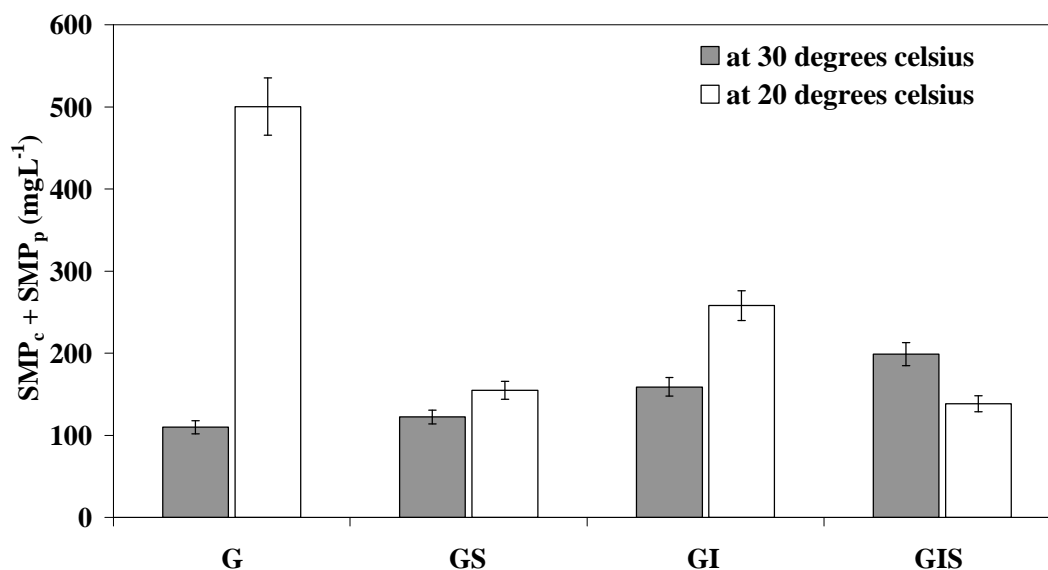


Figure 6.33: SMP content of each AnMBR

The introduction of nitrogen gas into the AnMBRs resulted in increased EPS production in all the AnMBRs except AnMBR GIS where EPS levels dropped from 27 to 14mg.gTS⁻¹ (Figure 6.34). The highest increase in EPS content was observed in AnMBR G where there was a three and a half fold increase from 35mg.gTS⁻¹ to 125mg.gTS⁻¹. It also appears that EPS production increased with temperature where sulphate was present and decreased where sulphate was absent. A drop in EPS content was observed in AnMBR G (35 to 28 mg.gTS⁻¹) and GI (41 to 26 mg.gTS⁻¹) when there was a decrease in temperature from 30 to 20°C. The opposite effect was observed with AnMBR GS (EPS content increased from 30 to 54mg.gTS⁻¹) and GIS (EPS content increased from 25 to 75mg.gTS⁻¹) with the same drop in operating temperature. The increased EPS content noted in AnMBRs GS and GIS may be due to the stimulation of the sulphate reducers' metabolism in the systems GS and GIS as a result of the presence of sulphates in the feed.

The observed drop in EPS content at 20°C in AnMBR G and GI is not surprising as it is well known that the optimal temperature range for methanogenesis is between 30-35°C (Kettunen and Rintala, 1998). Shin *et al.* (2001) extracted EPS amounts of 129 to 171mg.gMLSS⁻¹ while aerobically treating a glucose waste. This is significantly higher than EPS content observed in the four anaerobic membrane bioreactors where maximum amounts did not exceed 123.05 mg.gTS⁻¹.

From the observed results, it can be inferred that EPS levels are affected by the type of biomass (anaerobic or aerobic) present in a system as well as the wastewater type/composition to which it is exposed. EPS production is enhanced by gas sparging even when the said gas is inert probably due to increased biomass-substrate contact. A drop in operating temperature may or may not result in higher EPS levels depending on the type of waste being treated as well as the type of biomass present.

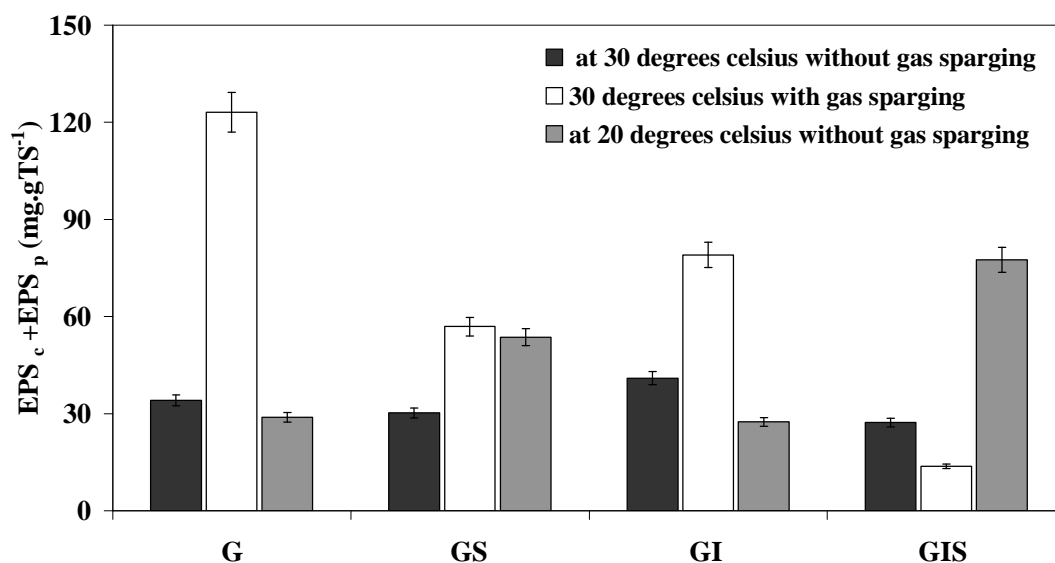


Figure 6.34: EPS content of each AnMBR

(iv) Effect of Substrate Composition, Temperature and Gas Sparging on Fouling Rate

Two major stages of fouling (rapid and slow) were observed during the course of these experiments (Figure 6.35). This agrees with work carried out on permeation flux by Choo and Lee (1998) which established exponential and sluggish stages of flux decline while treating an alcohol-distillery wastewater in an anaerobic membrane bioreactor (subject to an approximate organic loading rate of 1.5kgCODm^{-3} per day).

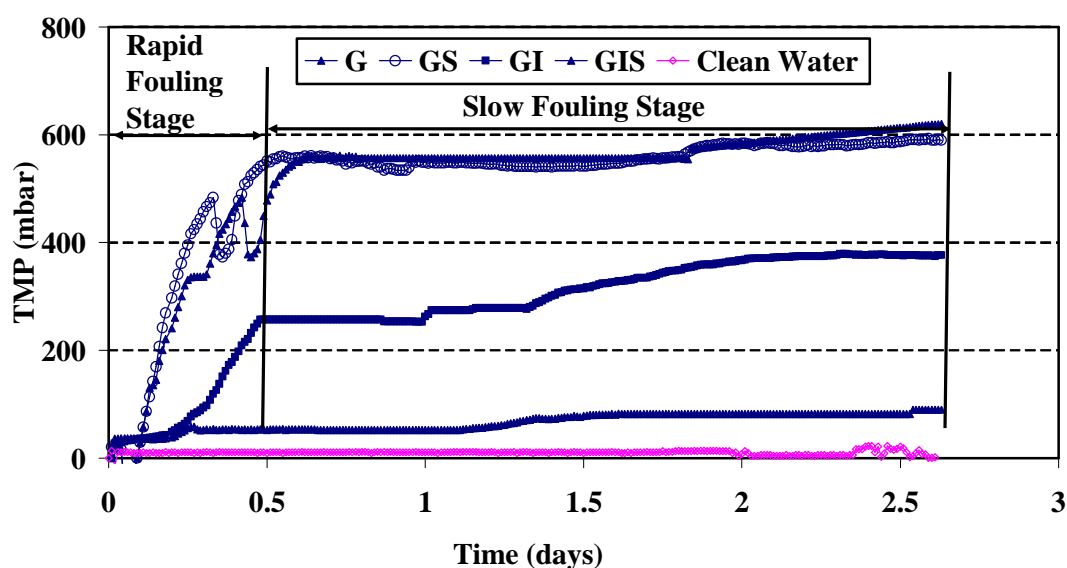


Figure 6.35: Example of TMP chart showing the two fouling stages observed in each of the four AnMBRs.

The rapid fouling stage was characterised by bacterial cell and biosolid deposition. These cells form a cake on the membrane surface. The specific resistance of this cake (α) to filtration increases with the number of cells that are deposited on the membrane surface. Therefore, the constant (α) is useful in determining the fouling rate during this stage. Fouling rates during this stage appear to be highest in the absence of sulphate (Figure 6.36). AnMBR GS and GIS showed the lowest fouling rates during the rapid fouling stage. Gas sparging caused an increase in fouling rates in all four AnMBRs with the highest increase observed in AnMBR G (specific cake resistance varied from 4.64×10^{15} to $2.41 \times 10^{16} \text{ mkg}^{-1}$). A drop in operating temperature from 30°C to 20°C also resulted in lower fouling rates except where iron was present (AnMBRs GI and GIS).

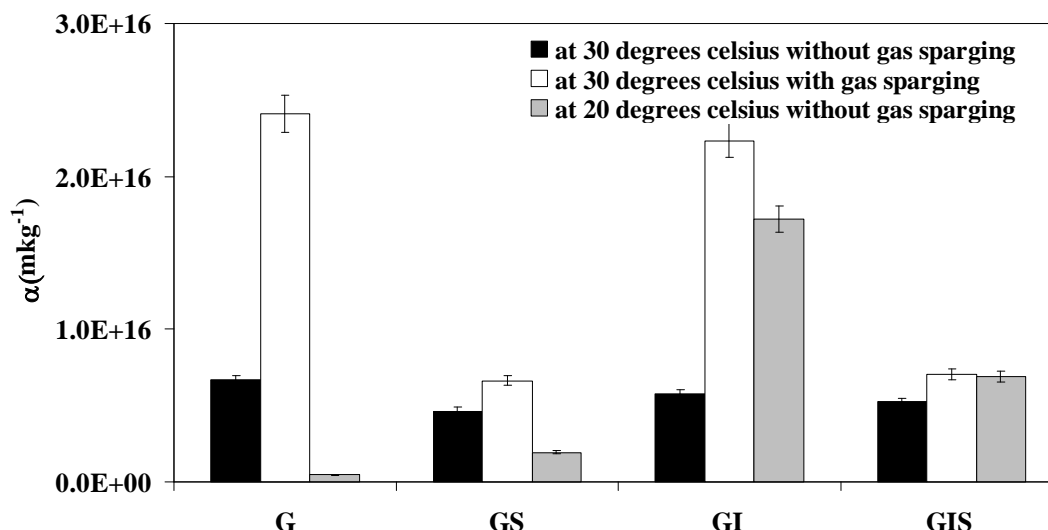


Figure 6.36: Specific cake resistance as a measure of fouling in each AnMBR during the rapid fouling stage.

Figure 6.37 shows fouling rates during the slow fouling stage. Fouling rates during the slow fouling stage appear to be highly dependent on factors such as substrate composition and temperature. When all four AnMBRs were operated at the same temperature (without gas sparging), lower fouling rates were observed in AnMBR GS (11.5 mbard^{-1}) and GIS (8 mbard^{-1}) containing sulphate than in AnMBR G (33 mbard^{-1}) and GI (76 mbard^{-1}) which did not contain sulphate. However, a drop in operating temperature (from 30°C to 20°C) of all four AnMBRs resulted in an increase in fouling rate with the highest fouling rate increase seen in those that contained sulphate (30 to 54 mbard^{-1} for AnMBR GS and 27 to 77.5 mbard^{-1} for AnMBR GIS).

The introduction of gas into all four AnMBRs caused a decrease in fouling during the slow fouling stage probably due to the sloughing of foulants off the membrane surface. The presence of gas also strips some of the H_2S present in the AnMBRs as well as inhibits the build up of sulphide precipitates (a possible foulant) in the reactor mixed liquor.

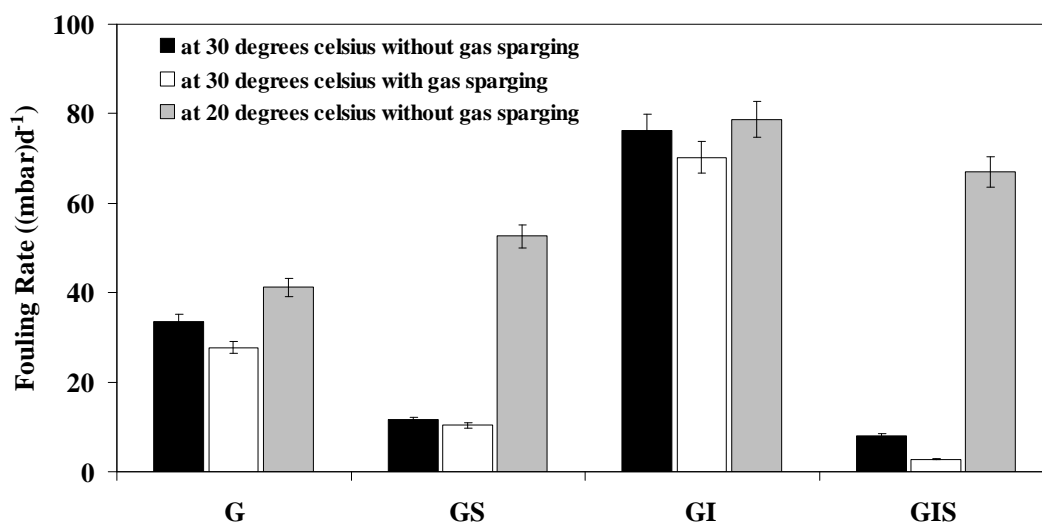


Figure 6.37: Fouling rates during the slow fouling stage in each of the four AnMBRs.

The highest fouling rate ($79\text{mbar}\cdot\text{d}^{-1}$) was observed in AnMBR GI (which contains iron and no sulphate) when it was subject to a temperature of 20°C without gas sparging. The high fouling rate observed in AnMBR GI may be due to the deposition of iron compounds such as carbonates and phosphates into the membrane pores causing pore blockage and intrinsic membrane fouling. The presence of sulphate and iron in AnMBR GIS may have resulted in the production of iron sulphides which are corrosive to the membrane and therefore degrade the membrane surface. The high fouling rate observed in AnMBR GIS may therefore be due to the precipitation of iron sulphides onto the surface of the membrane. However, this was not confirmed experimentally during experiments although black deposits that could not be attributed to biomass were seen on the surface of the membrane in this particular AnMBR.

(v) The Effect of EPS and SMP on Fouling Rates.

Total extracellular polymeric substances (EPS) was found to affect fouling rates during the rapid fouling stage (Figure 6.38). The use of regression techniques established a linear relationship between EPS content and specific cake resistance irrespective of temperature and the presence/absence of gas.

However, at the lower operating temperature of 20°C, the same increases in EPS levels produced much higher increases in fouling rates than at 30°C (Table 6.22). Fouling rates were therefore more sensitive to variations in EPS levels when systems were subject to psychrophilic conditions.

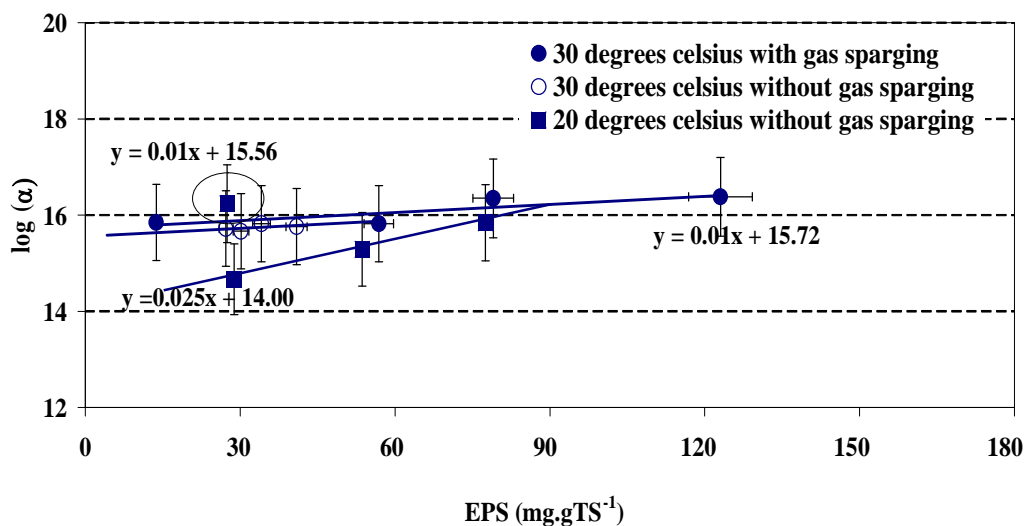


Figure 6.38: Specific cake resistance as a function of EPS content of the AnMBRs.

Table 6.22: Description of Linear Relationship between EPS and Cake Resistance under different operating conditions.

| Operating Temperature | Gas Sparging | Slope |
|-----------------------|--------------|-------|
| 30 | - | 0.01 |
| 30 | Yes | 0.01 |
| 20 | - | 0.025 |

No relationship was found to exist between EPS content in each of the four AnMBRs and fouling rates during the slow fouling stage.

The parabolic relationship (established with regression techniques) between soluble microbial products and fouling rate (Figure 6.39) confirms SMP as a significant foulant during the slow fouling stage. Fouling rates during the slow fouling stage were therefore influenced by the SMP content in each of the AnMBRs. Below SMP concentrations of 125mgL^{-1} , fouling rates follow a linear relationship with SMP concentration irrespective of operating temperature. SMP production then reaches a point where further increases in SMP levels do not produce proportional increases in fouling rates.

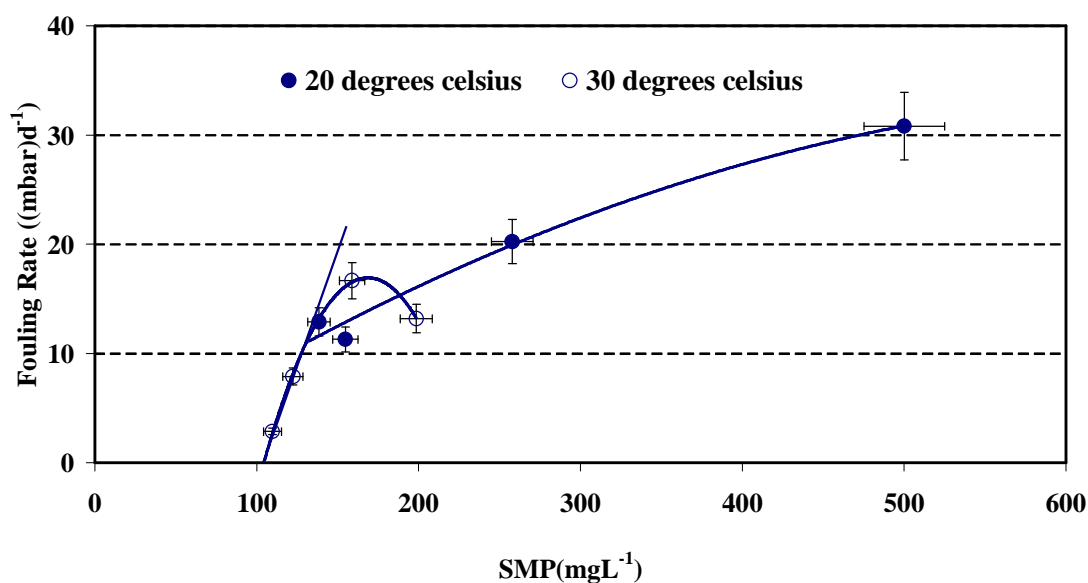


Figure 6.39: Fouling rate as a function of SMP concentration in each AnMBR.

6.2.2 Bench Scale Crossflow Membrane Filtration Rig

(i) Critical Flux and TS Concentration

All anaerobic sludges analysed showed a decrease in critical flux with increase in total solids concentration up to a critical TS concentration. At this point, further increases in TS concentration produced no change in critical flux (Figure 6.40). All the sludges tested had a critical TS concentration of approximately 10gL^{-1} (Figure 6.41). However, despite analysing the anaerobic sludges at similar TS concentrations of 5 to 20gL^{-1} , critical flux values became increasingly divergent as TS concentration approached the critical value of 10gL^{-1} (Figure 6.41). Critical flux measured 31.5 and $27\text{Lm}^{-2}\text{h}^{-1}$ for TS concentrations of 5 and 7gL^{-1} respectively for all anaerobic sludges (1, 2 and 3) tested. These values dropped to 22.5 , 18 and $13.5\text{Lm}^{-2}\text{h}^{-1}$ for sludges 1, 2 and 3 respectively at TS concentrations of 10gL^{-1} . Fouling rates below critical fluxes measured $0\text{mbar}\cdot\text{min}^{-1}$ in almost all cases consistently fell below the limit of detection, becoming increasingly unstable during post critical flux operation (Figure 6.40).

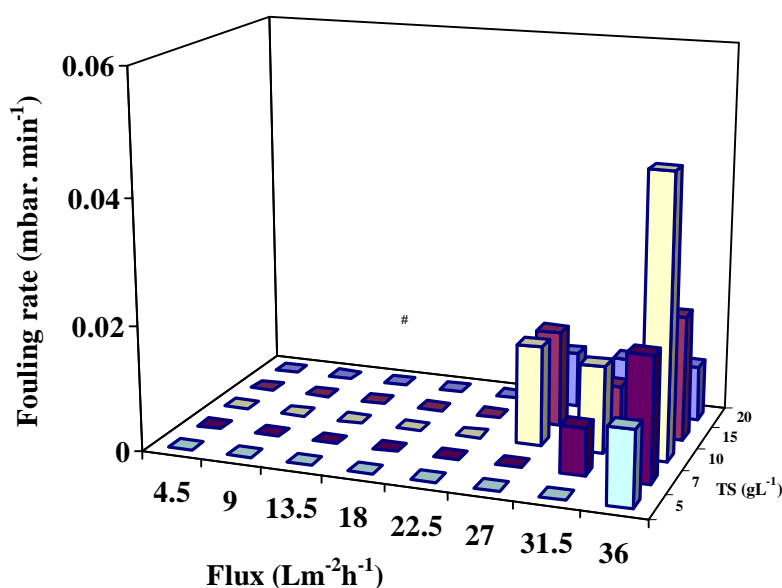


Figure 6.40: Example of Chart showing Effect of TS concentration on Short-Term Fouling Rates and Critical Flux for Anaerobic Sludge.

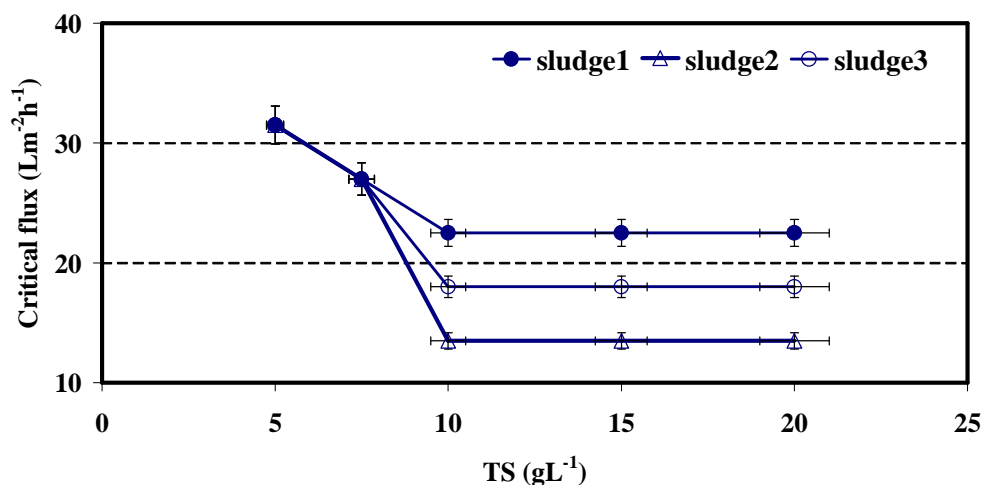


Figure 6.41: Critical Flux as a Function of Total Solids (TS) Concentration for Three Anaerobic Sludges

The relationship between critical flux and EPS was difficult to determine as it required changing EPS concentrations of the sludges analysed. In chapter 5, it was established that EPS concentration varied with time even without active degradation of substrates. In order to determine the effect a change in EPS would have on critical flux, EPS concentration of sludge was measured weekly and critical flux experiments carried out when a significant difference in concentration was observed.

No relationship was found to exist between EPS carbohydrates and critical flux (Figure

6.42,

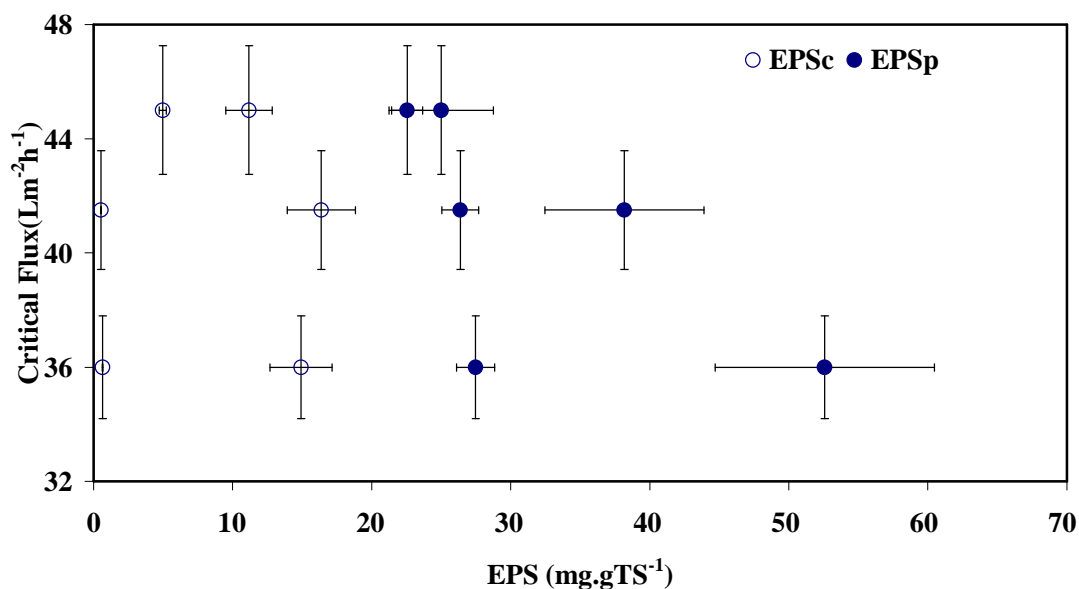


Figure 6.42). However, changes in EPS proteins present in sludge produced significant changes in critical flux (Figure 6.42). In general, higher amounts of EPS proteins produced drops in critical fluxes of anaerobic sludges analysed. At EPS protein levels below 27mg.gTS⁻¹, critical flux remained above 44Lm⁻²h⁻¹. However, the presence of higher EPS protein levels of 27 to 60mg.gTS⁻¹ in sludges resulted in lower critical flux values (36 to 41.5Lm⁻²h⁻¹).

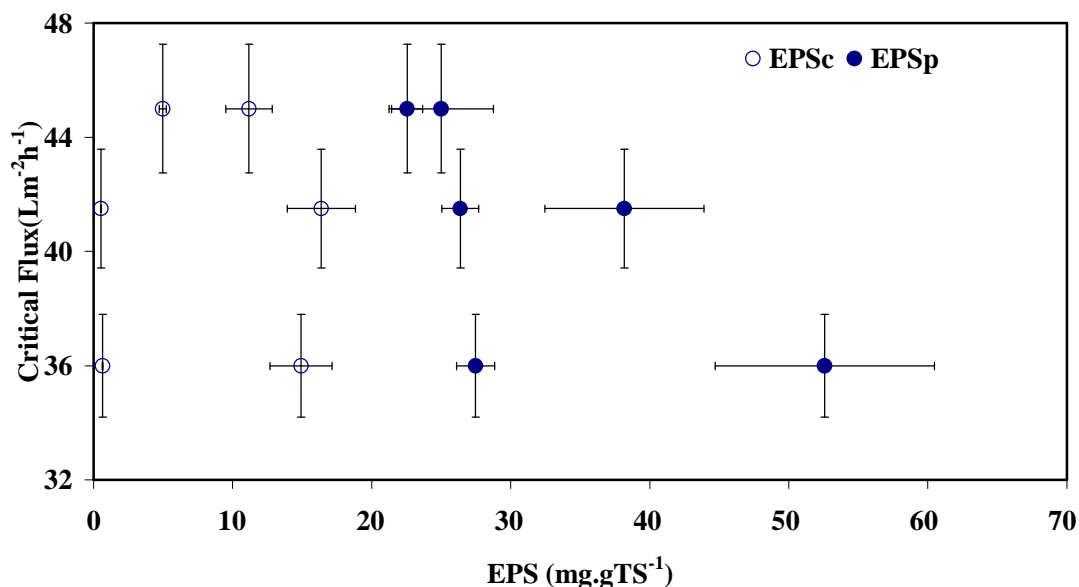


Figure 6.42: Critical Flux as a Function of EPS Concentration for Anaerobic Sludge

For all aerobic sludges tested, critical flux dropped with increasing MLSS concentration. Aerobic sludges were tested at MLSS concentrations of 5.5 to 15gL⁻¹ (Figure 6.43). At the lower end of the spectrum (5.5 to 7gL⁻¹), critical flux was approximately 18Lm⁻²h⁻¹. At 9gL⁻¹, critical flux fell to 13.5Lm⁻²h⁻¹. The lowest critical flux value of 4.5Lm⁻²h⁻¹ is observed at 15gL⁻¹, the highest MLSS concentration at which the three aerobic sludges were tested. No relationship was found to exist between EPS concentration and critical flux for all the aerobic sludges tested (Figure 6.44).

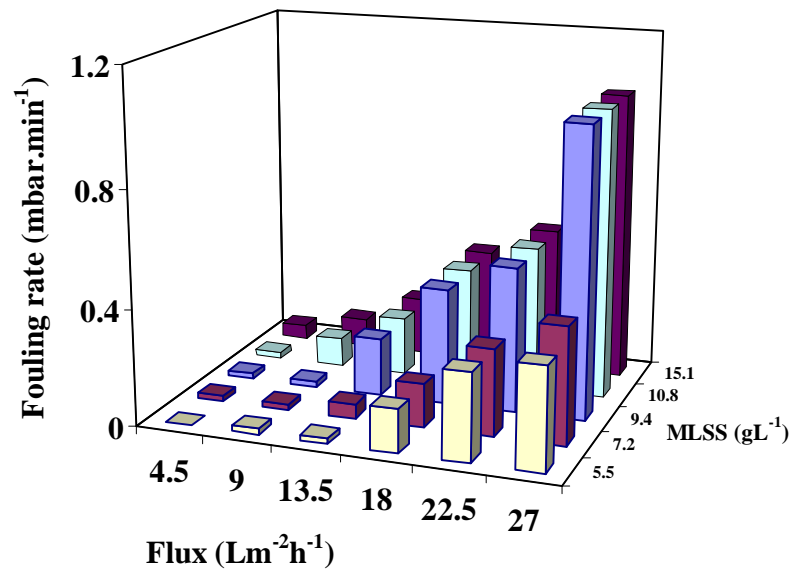


Figure 6.43: Effect of MLSS Concentration on Short-Term Fouling Rates and Critical Flux for Aerobic Sludge

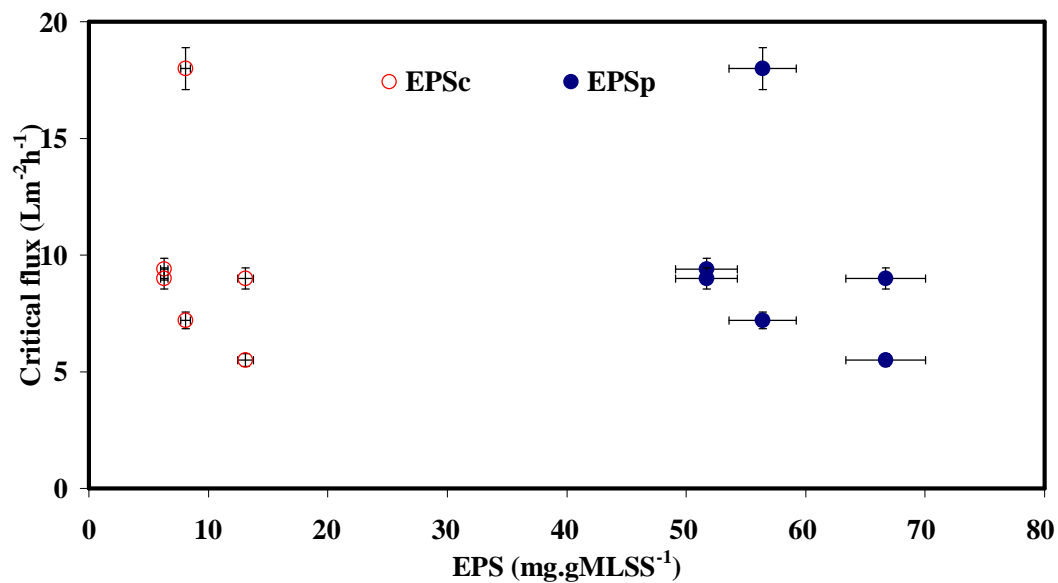


Figure 6.44: Critical Flux as a Function of EPS Concentration for Aerobic Sludge

(ii) Critical Flux and Crossflow Velocity

Subjecting anaerobic sludges to increasing crossflow velocities resulted in reduced critical fluxes (Figure 6.45 and Figure 6.46). Visual inspection of the Perspex membrane module showed that increased crossflow velocity pushed more particulate solids (all anaerobic sludges utilised in these experiments were granular) unto the membrane surface where settling unto the membrane surface then took place. Post critical operation also resulted in increased instability in resulting fouling rates (Figure 6.45). Critical flux values were significantly different for the three anaerobic sludges despite being subject to similar crossflow velocities. Critical flux values measured between 36 and $13.5\text{Lm}^{-2}\text{h}^{-1}$ for sludge1, 22.5 and $9\text{Lm}^{-2}\text{h}^{-1}$ for sludge2 and 18 and $4.5\text{Lm}^{-2}\text{h}^{-1}$ for sludge 3. All sludges were subject to crossflow velocities of 0.65 to 1.4ms^{-1} .

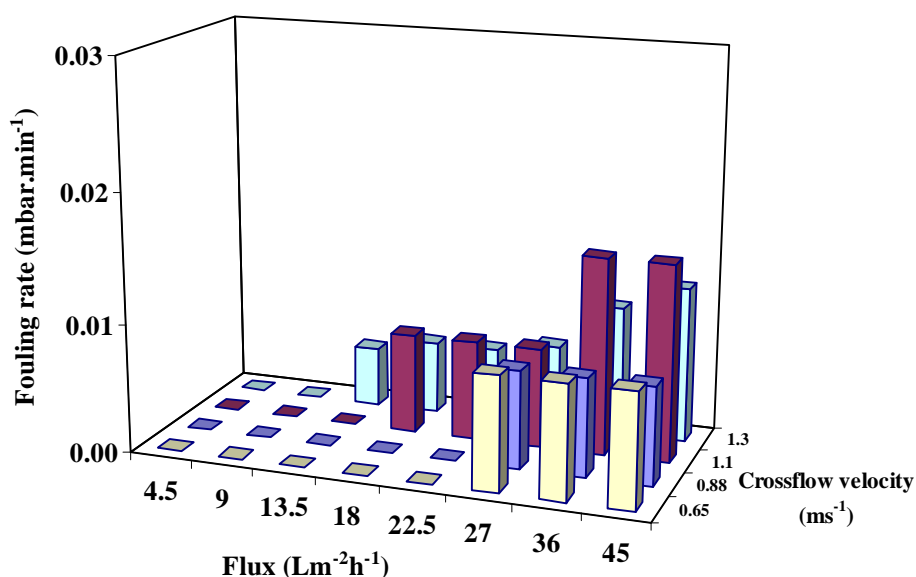


Figure 6.45: Example of Chart showing Effect of Crossflow Velocity on Short-Term Fouling Rates and Critical Flux for Anaerobic Sludge

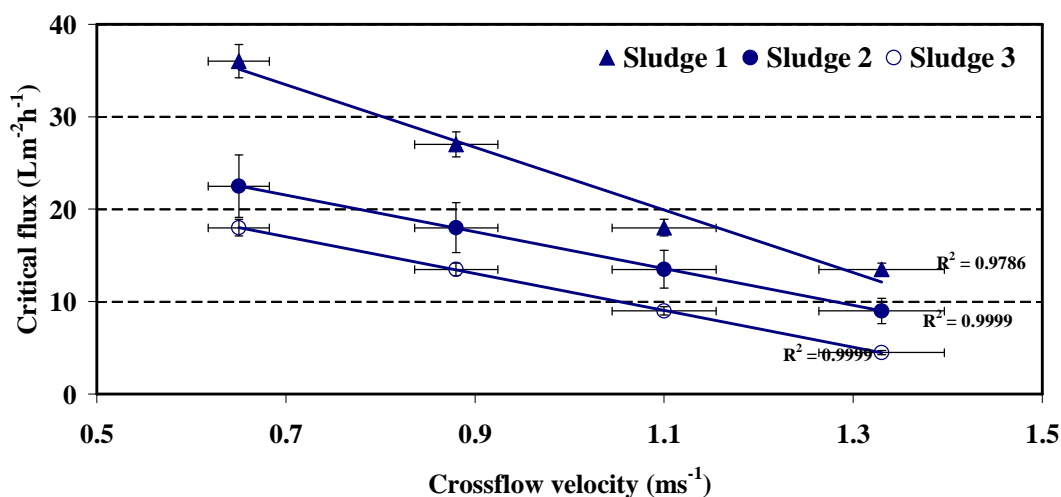


Figure 6.46: Critical Flux as a Function of Crossflow Velocity for Three Anaerobic Sludges

As established during analysis of anaerobic sludges, crossflow velocity has a direct effect on the critical flux of sludge. An opposite effect to that observed with anaerobic sludges was observed with aerobic sludges. Increasing the crossflow velocity caused an increase in critical flux values of all three aerobic sludges tested (Figure 6.47 and Figure 6.48). All aerobic sludges were tested at crossflow velocities of 0.66 to 1.4ms⁻¹ with the maximum critical flux value (18Lm⁻²h⁻¹) obtained for sludge 1 at a crossflow velocity of 1.3ms⁻¹. The lowest critical flux value of 4.5Lm⁻²h⁻¹ was observed with sludge 3 when it was subject to a crossflow velocity of 0.66 ms⁻¹.

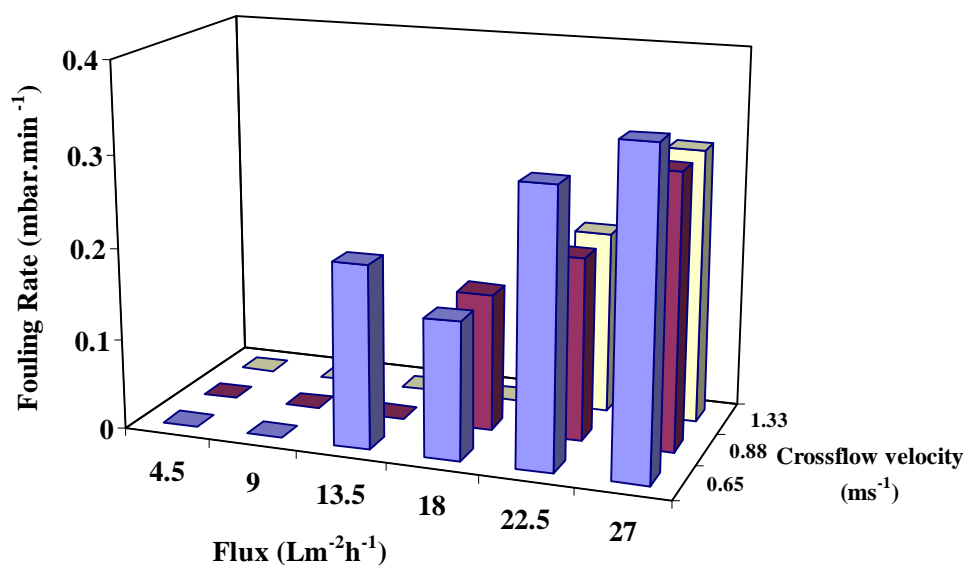


Figure 6.47: Effect of Crossflow Velocity on Short-Term Fouling Rates and Critical Flux for Aerobic Sludge

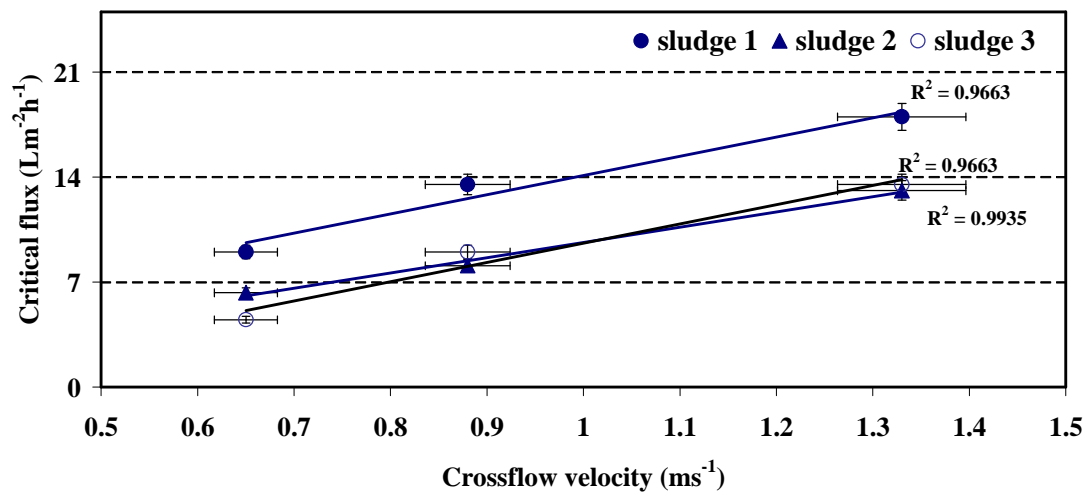


Figure 6.48: Critical Flux as a Function of Crossflow Velocity for Three Aerobic Sludges

(iii) Critical Flux and Mean Granule Size

Sludges 1, 2 and 3 were made up of granular biomass with very different mean sizes. The effect these differences in granule size have on critical flux was investigated while keeping other operating parameters such as TS concentration and crossflow velocity constant. Tests were carried out at a TS concentration of 4gL^{-1} and a crossflow velocity of 0.66ms^{-1} .

Results obtained showed that critical flux decreases with increasing mean granule size (Figure 6.49). At a mean granule size of $148.5\mu\text{m}$, critical flux measured $54\text{Lm}^{-2}\text{h}^{-1}$ for sludge2. This value fell to $36\text{Lm}^{-2}\text{h}^{-1}$ when sludge3 with a higher mean granule size of $911\mu\text{m}$ was subject to the same test. Sludge 1 had a mean granule size of $628\mu\text{m}$. Critical flux for this sludge was $45\text{Lm}^{-2}\text{h}^{-1}$.

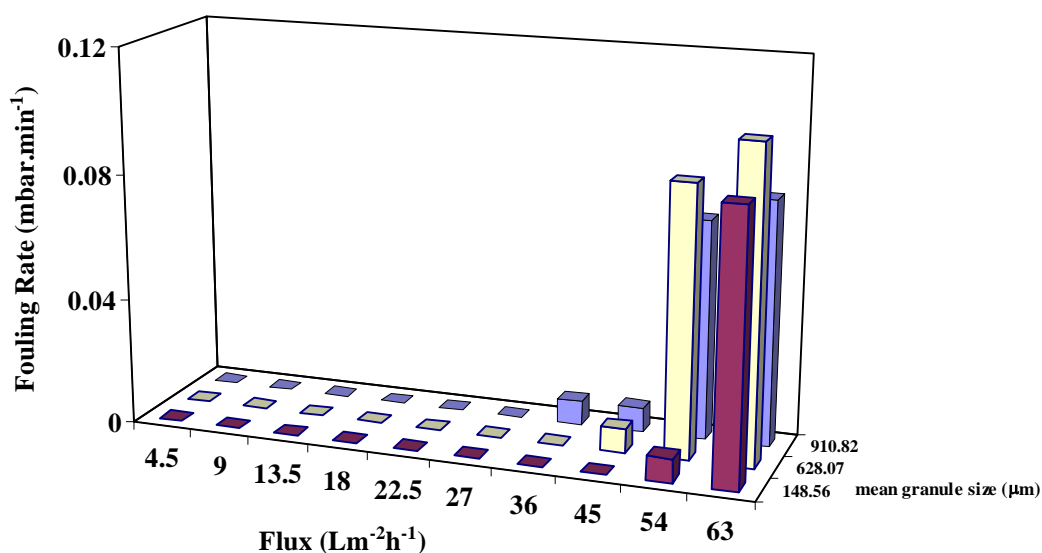


Figure 6.49: Effect of Mean Granule Size on Short-Term Fouling Rates and Critical Flux for Anaerobic Sludge

6.3 Discussion

Although both anaerobic and aerobic sludges showed some similarity with respect to the relationship of sludge properties and characteristics to membrane fouling, several differences were noted when direct comparisons were made between data obtained for both types of sludges. In general, higher critical fluxes were obtained with anaerobic sludges (4.5 to $45 \text{ Lm}^{-2}\text{h}^{-1}$) in comparison to the aerobic sludges (4.5 to $20 \text{ Lm}^{-2}\text{h}^{-1}$) inferring that membranes can be subject to much higher fluxes (before irreversible fouling occurs) in the presence of granular anaerobic biomass. Gradual minimal fouling of the membrane was noted with aerobic sludges even at sub-critical fluxes. This was in direct contrast to anaerobic sludges which showed no TMP increase and therefore no membrane fouling prior to reaching critical flux. However, post critical operation was inherently more stable with aerobic sludges despite progressive exponential increase in membrane fouling seen with these sludges. The subjection of membranes to fluxes higher than the measured critical flux for specific anaerobic sludges resulted in instantaneous high or low fluxes with no predictable trend.

Marked differences were noted when solids concentrations of both types of sludges were compared with resulting critical fluxes and short term fouling rates. A critical TS concentration was observed with anaerobic sludges beyond which further increasing the solids concentration produced no discernable increase in critical flux. Aerobic sludge on the other hand showed a negative linear relationship to critical flux with progressively higher solids concentrations producing progressively lower critical fluxes. Results from this study are in agreement with several studies including that of Maedaeni *et al.* (1999) and more recently, Le Clech *et al.* (2003). However, there are several bodies of work in publication which find no identifiable link between MLSS and critical flux. Rosenberger and Kraume (2002) showed no correlation between MLSS and filterability in their work on aerobic sludge. Work carried out by Fan *et al.* (2006) on aerobic sludge also showed no relationship between MLSS and critical flux. Authors of the latter work suggested that other sludge characteristics such as EPS and colloidal matter may be more important in determining critical flux for any specific sludge.

Results from this study contrast with these findings as a relationship is only seen in the case of EPS protein from anaerobic sludge where the compounds tend to result in lower critical fluxes. No relationship was established between EPS concentration and critical flux for any of the aerobic sludges. This is in agreement with work carried out by Rosenberger *et al.* (2002). This is in agreement with results from chapter 5 of this thesis where EPS had little or no effect on specific cake resistance of anaerobic or aerobic sludges when passed through membranes under dead end conditions.

Opposing trends were observed for each type of sludge when the six sludges were subject to increasing crossflow velocities. Critical flux fell when all three anaerobic sludges were subjected to increasing velocities between 0.6 and 1.6ms⁻¹. Aerobic sludges on the other hand showed an increase in critical flux with increased crossflow velocity. This increase was probably due to the sloughing of bacterial cells and other foulants off the membrane surface by hydrodynamic shear. The results obtained with anaerobic sludge are unexpected as Eckstein *et al.* (1977) found that hydrodynamic induced shear is proportional to the square of particle size. Consequently, it is expected that sludges with larger particle sizes (as is the case with the granular anaerobic sludges in this study) would be more easily removed from the membrane surface. However, it appears that crossflow velocities to which the membranes were subject were not high enough to remove anaerobic granules because anaerobic granules have a high settling velocity. During the experiments, progressive accumulation of anaerobic granules on the membrane surface was observed at higher crossflow velocities. It is hypothesised that crossflow velocity will need to be higher than the settling velocity of the particles or granules present in sludge to prevent biomass accumulation on the membrane surface. Linking mean particle/granule size of anaerobic sludge with critical flux once again provides evidence for this theory. Sludges containing larger sized particles had the lowest critical flux indicating that anaerobic sludges with larger particles have a higher fouling propensity when coupled with side-stream membranes. The larger the sizes of active granules/particles in the sludge, the greater the settling velocity of the said particles and therefore, the higher the crossflow velocity will need to be to prevent accumulation on the membrane surface and reduce fouling.

In general, anaerobic granular sludges appear to show a non-beneficial relationship with side-stream operation despite the fact that membrane modules in this configuration can be run at higher fluxes. It should be noted that critical flux is dependent on membrane material so results obtained in these experiments provide limited information. However, it was necessary to conduct all experiments using membranes with the same characteristics in order to ensure that results for each type of sludge were comparable.

Results obtained from the bench scale anaerobic membrane bioreactors appear to be significantly different from previous fouling work reported in literature. Although most publications do show the existence of two fouling phases, the slow fouling phase appears to occur under sub-critical conditions while the rapid fouling phase occurs while operating at fluxes higher than critical flux. Slow fouling followed by rapid fouling during post critical operation has been justified in previous studies by the existence of heterogeneous distribution of local fluxes. These local fluxes are apparently caused by gradual pore closure and surface deposition of organics leading to a loss in local permeability (Ognier *et al.*, 2001; Cho and Fane, 2002). It has already been shown that membrane fouling behaviour can differ considerably in anaerobic and aerobic systems. Le Clech *et al.* (2003), Rosenberger *et al.* (2005), Cho and Fane (2002) and Fan *et al.* (2006) are just some of the authors who have carried out extensive fouling work on membrane bioreactors. Some of these previous studies established the existence of two phase fouling in reverse to two phase fouling established in this study. Both rapid and slow fouling occurred while operating at sub-critical flux during this study. Fouling during post critical operation of the AnMBRs was unstable and unpredictable with no identifiable trend or progressive increase.

SMP content of the AnMBRs was generally higher at lower temperatures and in the presence of iron. The concentrations of iron put into the batch systems were high enough to be considered toxic to biomass and therefore cause stress to bacterial cells. Environmental stress factors such as increased heavy metal concentrations, low temperatures and general adverse operating conditions is usually accompanied by increased accumulation of SMP due to cell lysis, simulation of efflux and release of extracellular material (Aquino and Stuckey, 2004; Kuo and Parkin, 1996).

The analysis of the relationship between EPS and substrate/wastewater type as well as temperature is more complex. EPS content of the AnMBRs is generally higher where sulphate is present in high concentrations. EPS production also increased under psychrophilic conditions in the presence of sulphate but fell in its absence. The results appear to show a difference in the type of biomass or bacterial consortia present in each group of AnMBRs. It is well known that where there is an excess of sulphate as well as a carbon source, sulphate reducers will out compete methanogens resulting in a gradual decline in the numbers of the latter bacterial group (Overmeire *et al.*, 1994; Lens and Kuenen, 2001; Hulshoff Pol *et al.*, 2001). Sludges containing sulphate reducing biomass have also been shown to have larger sized granules/particles than methogenic sludges. Granules present in these sludges have higher settling velocities as well as more densely packed structures (Weijma *et al.*, 2002). Since the production of EPS has been linked to the formation of anaerobic granules and bacterial growth (Chen and Lun, 1993; Schmidt and Ahring, 1996), it would therefore be expected that sludges fed on substrates containing large amounts of sulphate would indeed have higher levels of EPS. It appears that sulphate reducers also respond to environmental stress such as reduction in operating temperature by producing more EPS.

Although higher EPS levels were noted in those AnMBRs containing sulphates, initial rapid fouling rates were lower in these AnMBRs due to the high settling velocity of the granules present in the mixed liquor. It can therefore be assumed that EPS is not a major factor in fouling during the rapid phase when particles or granules present in the mixed liquor have high enough settling velocities to prevent accumulation on the membrane surface in submerged configuration. EPS plays a role in fouling by increasing the ability of granular biomass to stick and attach to the membrane surface.

Results from this study establish a direct link between EPS, SMP and fouling with each substance affecting a different fouling phase. EPS appears to be directly linked with the rapid fouling phase under conditions where particles have low settling properties while SMP appears to be directly linked to the slow fouling phase. Evidence of this is also provided by the low membrane fouling rates seen in those AnMBRs containing sulphate where reduced concentrations of SMP were present. Several authors have linked EPS and SMP to fouling (Rosenberger *et al.*, 2006; Fan *et al.*, 2006) although little is known about the exact mechanisms behind the production of these substances. It appears that the presence of heavy metals at high concentrations in wastewaters as well as low operating temperatures (below the optima for methanogenesis) is detrimental to membrane performance as these conditions produce higher concentrations of microbial products and higher fouling rates. Inducing turbulence and hydrodynamic shear on the other hand improves membrane performance by reducing accumulation on the membrane surface. This can be achieved relatively easily by introducing gas at moderate flow velocity into MBR systems.

From results presented in this chapter, it is clear that optimisation of AnMBRs should not be confined to physical dimensions of the system and parameters such as hydraulic retention time (HRT) and solid retention time (SRT) alone

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7 RESULTS: PILOT SCALE TESTS

7.1 Scope

It has been established that the performance of membrane bioreactors is influenced by membrane fouling, operating conditions and the biology of the process (Stephenson et al., 2000). This chapter presents results obtained from the operation of a pilot scale anaerobic membrane bioreactor which was designed utilising hypothesis, results and lessons learnt from previous experiments (chapters 5 and 6).

7.2 Results

Three (start-up, acclimatising and stable) phases were identified during constant operation of the pilot scale AnMBR (Figure 7.50). During the start-up period, the system was very unstable and soluble COD levels in the mixed liquor increased from 300mgL^{-1} to 2000mgL^{-1} within 14 days. Elevated COD levels during start-up is characteristic of systems with low feed to mass (F/M) ratios as is the case in anaerobic systems treating low strength wastewaters ($<2000\text{mgL}^{-1}$). Kuo (1993) attributed this increase to the release of soluble organic matter by biomass.

The system entered into its acclimatising phase between day 15 and day 21 at which point COD removal began. Measured biomass characteristics also began to stabilise although the system was most sensitive to changes in configuration and operating conditions during this period. It is estimated that the system remained in this phase for approximately 40 days at which point the AnMBR entered into the stable phase. From this point onwards, changes to operating and process parameters produced minimum responses by the system. Biomass characteristics followed specific trends and process performance reached a stable and predictable peak.

7.2.1 Process Performance

(i) COD Removal

Soluble COD concentration of the mixed liquor measured between 300mgL^{-1} (day 0) and 2000mgL^{-1} (day 14) while the AnMBR was in start-up mode.

As the system entered into the acclimatisation phase, COD removal began and continually increased up to $80 \pm 2\%$ (Figure 7.50). COD removal during the stable phase varied between 82 and 97% depending on configuration and operating conditions. Maximum COD removal efficiency (96%) was achieved after 63 days of operation at a temperature of $35 \pm 1^\circ\text{C}$. Permeate COD concentration during this period never exceeded 90mgL^{-1} despite changes to operating temperature, membrane configuration and feed quality.

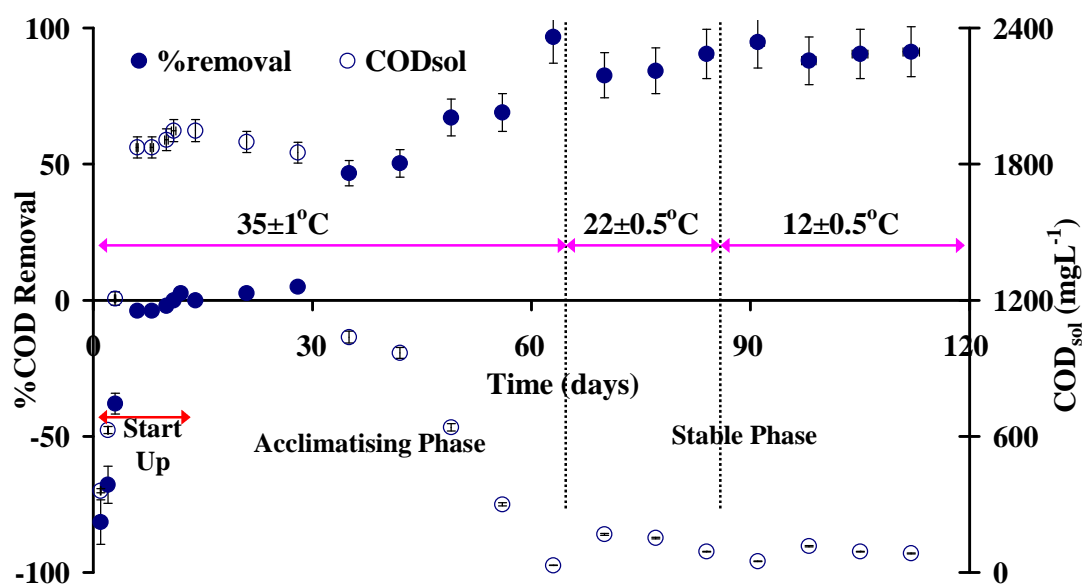


Figure 7.50: Mixed Liquor COD concentration and COD Removal over 120 Day Operation of Pilot Scale Anaerobic Membrane Bioreactor.

(ii) Biogas Production

The conversion of substrate into methane is important in the assessment of the performance an anaerobic system as it determines the energy requirements of the process.

Operation of the AnMBR over the 120days resulted in the production of biogas consisting of $75 \pm 5\%$ methane dependent on operating conditions (Figure 7.51).

However, in the first 7 to 14 days of operation (start-up phase), sulphate reduction out-competed methanogenesis resulting in the release of small amounts of hydrogen sulphide and sulphur dioxide (Figure 7.51). Total amount of hydrogen sulphide and sulphur dioxide produced measured $0.1 \pm 0.03 L_{\text{gas}} \cdot L_{\text{reactor}}^{-1} \cdot \text{d}^{-1}$. The small amounts of sulphur gasses produced can be attributed to the presence of diminutive sulphate levels in the feed to the system. During this period, there was little production of methane and the biogas produced consisted almost entirely of hydrogen sulphide.

From day 15, the rate of methanogenesis increased as sulphate reduction ceased. After system stabilisation, biogas consisted of 70 to 80% methane and 19 to 30% carbon dioxide (Figure 7.51). Methane production was at its lowest when the system was subject to a working temperature of $12 \pm 0.5^\circ\text{C}$. Specific methanogenic activity of biomass present in the system varied from $0.20 \text{ gCOD-CH}_4 \cdot \text{gMLVSS}^{-1}$ (at $12 \pm 1^\circ\text{C}$) to $0.24 \text{ gCOD-CH}_4 \cdot \text{gMLVSS}^{-1}$ (at $35 \pm 2^\circ\text{C}$). Total biogas production reached a maximum of $0.46 L_{\text{gas}} \cdot L_{\text{reactor}}^{-1} \cdot \text{d}^{-1}$.

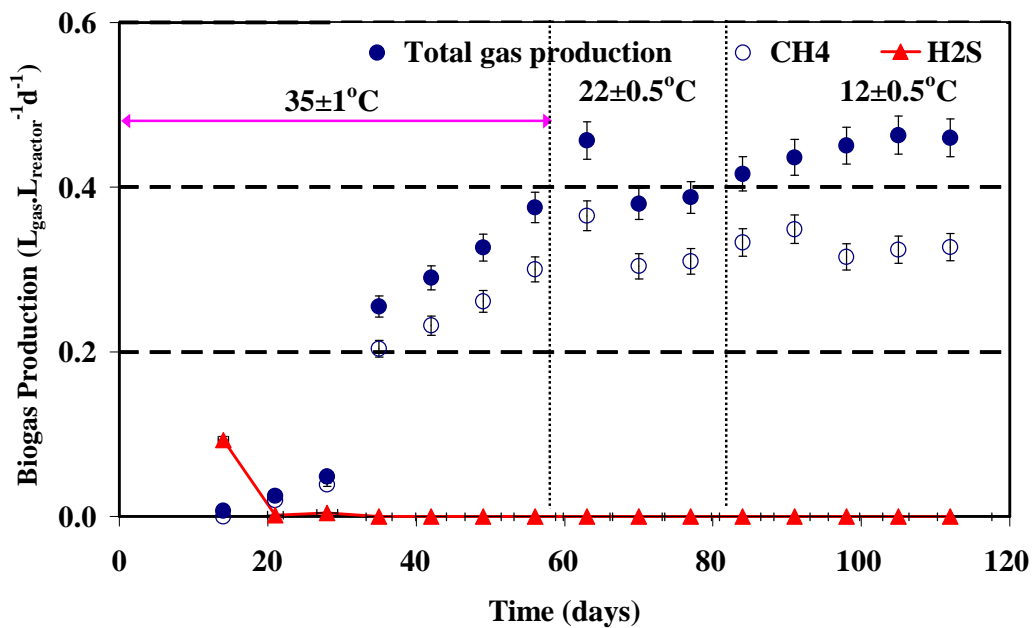


Figure 7.51: Biogas Composition during Operation of Pilot Scale Anaerobic Membrane Bio-Reactor.

(iii) Impact of Process Parameters and Operating Conditions

Operating conditions and changes in process parameters affected biogas production and composition as well as COD removal (Figure 7.50, Figure 7.51). The system was operated at three different temperatures of $12\pm0.5^{\circ}\text{C}$, $22\pm0.5^{\circ}\text{C}$ and $35\pm1^{\circ}\text{C}$ which resulted in variations in COD removal. During the stabilised phase, operation of the AnMBR at an optimal temperature of $35\pm1^{\circ}\text{C}$ with a submerged membrane resulted in maximal COD removal of approximately 97% (Figure 7.50). Dropping operating temperature to $22\pm0.5^{\circ}\text{C}$ caused an initial drop in COD removal to 82%. The system did recover so that COD removal at this temperature reached a maximum of approximately 95% within 21 days. A further drop in temperature to $12\pm0.5^{\circ}\text{C}$ caused a drop in COD removal to 88 to 91%. Initial decrease in COD removal efficiency was less severe at the latter stages of the process when the system was subject to psychrophilic conditions and operating temperature was dropped from $22\pm0.5^{\circ}\text{C}$ to $12\pm0.5^{\circ}\text{C}$.

Reducing operating temperature also affected biogas production with lower temperatures resulting in lesser amounts of methane being produced (Figure 7.51). Methane composition of biogas dropped from approximately 80% at $35\pm1^{\circ}\text{C}$ to about 70% at the lower temperature of $12\pm0.5^{\circ}\text{C}$. The proportion of carbon dioxide in the biogas remained the same at $20\pm5\%$ with higher amounts of hydrogen produced during the latter periods of operation when the system was subject to psychrophilic conditions.

The changes observed in performance of the AnMBR may be attributed to the increase in VFA production when there is a reduction in temperature. The accumulation of VFAs is usually accompanied by a drop in pH which in turn results in adverse effects on methanogenesis. Despite the installation of pH control in the system, small pH variations of ±0.25 were still observed with changes in operating temperature of 10 to 13°C (Figure 7.52, Figure 7.53). While the AnMBR was subject to a working temperature of $35\pm1^{\circ}\text{C}$, pH measured between 7.2 and 7.4. This is higher than the pH values of 6.9 to 7.1 and 6.8 to 6.9 observed when the system was subject to operating temperatures of $22\pm0.5^{\circ}\text{C}$ and $12\pm0.5^{\circ}\text{C}$ respectively (Figure 7.53).

COD removal and biogas production did not respond to changes in membrane configuration and characteristics. There was also no response by the system to changes in nitrogen gas sparging rates in terms of process performance or efficiency.

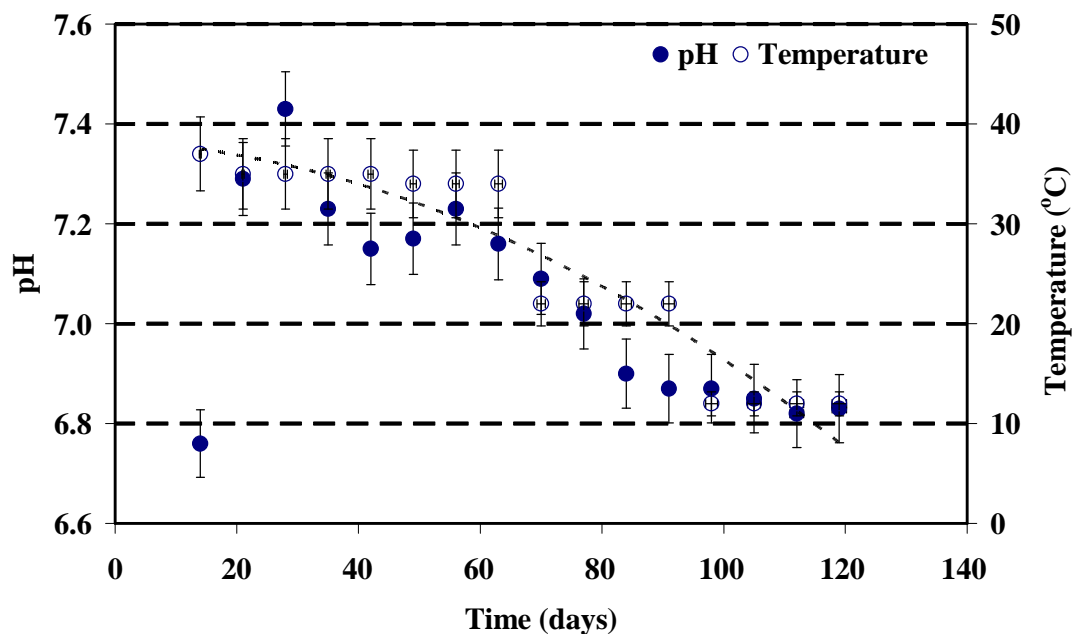


Figure 7.52: Evolution of pH and Temperature of Pilot Scale Anaerobic Membrane Bioreactor.

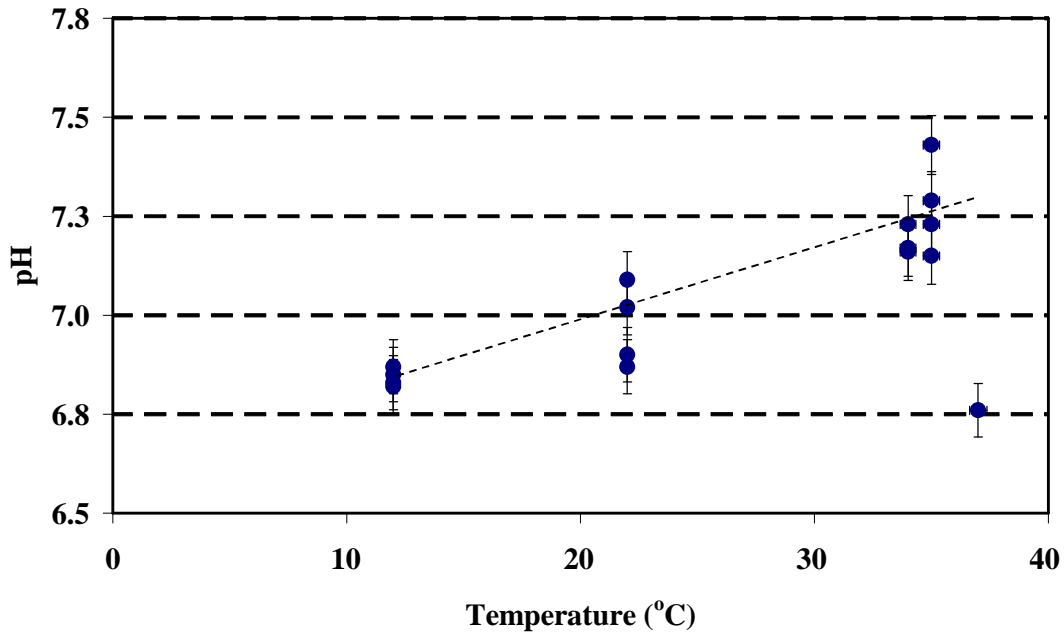


Figure 7.53: pH Variation with Changes in Operating Temperature.

7.2.2 Biomass Characteristics

(i) MLSS, MLVSS and Biomass Yield

MLSS concentration remained above 5gL^{-1} throughout AnMBR operation except during the first 14 days when the system was in start-up mode (Figure 7.54). MLSS concentration during this period measured 0.4 to 2.3gL^{-1} . The ratio of MLVSS to MLSS concentration varied from 0.52 to 0.69 after the first 14 days of operation. As soon as the system entered the stable phase, the proportion of biomass that was ascribed to MLVSS did not drop below 60% despite changes to operating temperature. MLSS concentration did show some slight variation with operating temperature during the stable phase with values dropping from 6.8 to 6.5gL^{-1} when operating temperature was reduced from $35\pm 1^\circ\text{C}$ to $22\pm 0.5^\circ\text{C}$. A further drop in MLSS concentration to 5.9gL^{-1} was also noted on day 98 after 7 days operation at $12\pm 0.5^\circ\text{C}$. In addition, the proportion of MLVSS to MLSS dropped from 0.69 to 0.64 on this day. The system did recover during the final 14 days of operation despite continual operation under psychrophilic conditions. MLSS concentration during this period remained at $6.5\pm 1\text{gL}^{-1}$ with the proportion of MLVSS remaining at 0.63 ± 0.01 .

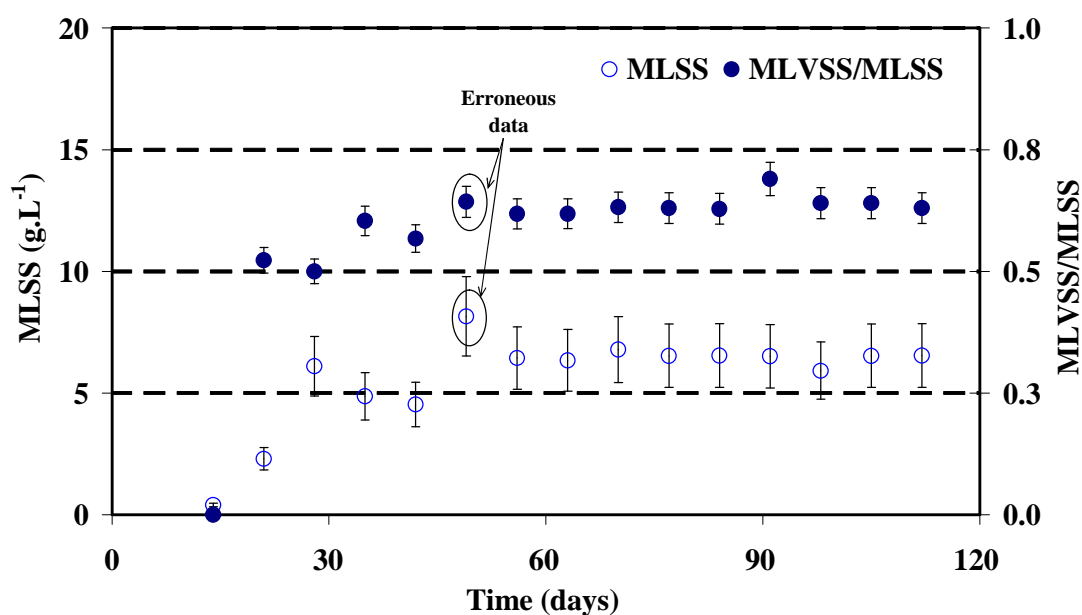


Figure 7.54: Biomass Concentration of AnMBR over Total Operational Period.

Biomass growth yield measured approximately $0.03 \text{ gMLVSS.gCOD}^{-1}\text{d}^{-1}$ after 28 days of continual operation. As the system entered into the stable phase, biomass growth yield fell to approximately $0.003\text{gMLVSS.gCOD}^{-1}\text{d}^{-1}$ (Figure 7.6). Change in temperature produced no further change in growth yield so that final values remained at $0.003\pm 1\text{gMLVSS.gCOD}^{-1}\text{d}^{-1}$. The F/M ratio in the AnMBR gradually fell from $1.9\pm 0.04 \text{ d}^{-1}$ on day 14 to $0.17\pm 0.01 \text{ d}^{-1}$ on day 56. After day 56, F/M ratio remained between $0.03\pm 0.004 \text{ d}^{-1}$ to $0.14\pm 0.01 \text{ d}^{-1}$ despite changes to operational temperature and configuration.

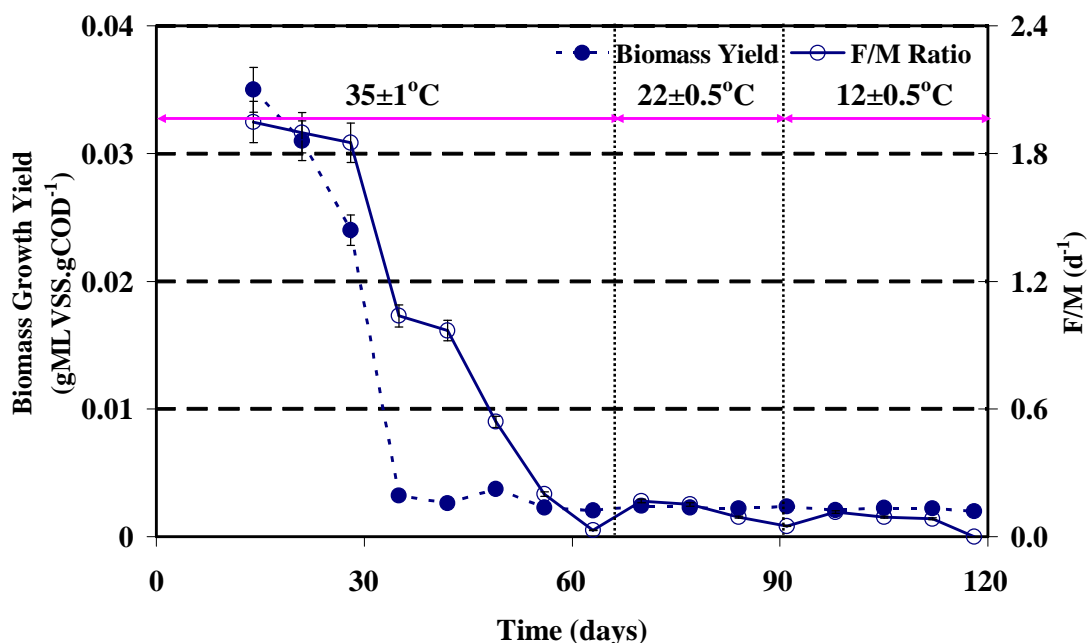


Figure 7.55: Biomass Growth Yield and F/M Ratio over AnMBR Operational Period.

(ii) Particle Size

Particle size distribution in the AnMBR changed significantly as the AnMBR entered into different operational phases (Figure 7.56). As the stability of the system increased, particle size became more evenly distributed. During the first 14 days of operation when the system was in start-up mode, approximately 55% of particles had diameters of approximately 230 to 2100 μm . By day 105 in the stable phase, the system had near equal percentage volumes of larger particle sizes above 300 μm . Analysis also showed that percentage volumes of smaller particles (<200 μm) progressively increased as the system became more stable so that by day 105 during the stable phase 80% of particles present in the mixed liquor fell between 1 and 200 μm (Figure 7.56, Figure 7.57).

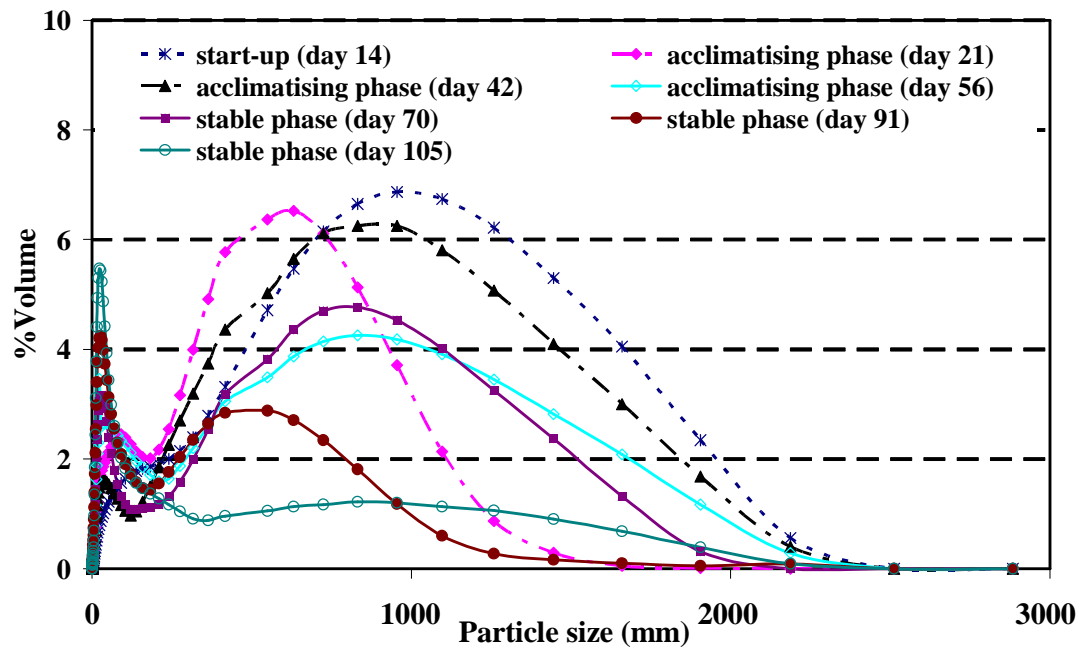


Figure 7.56: Particle Size Distributions during Different Operational Phases of the AnMBR.

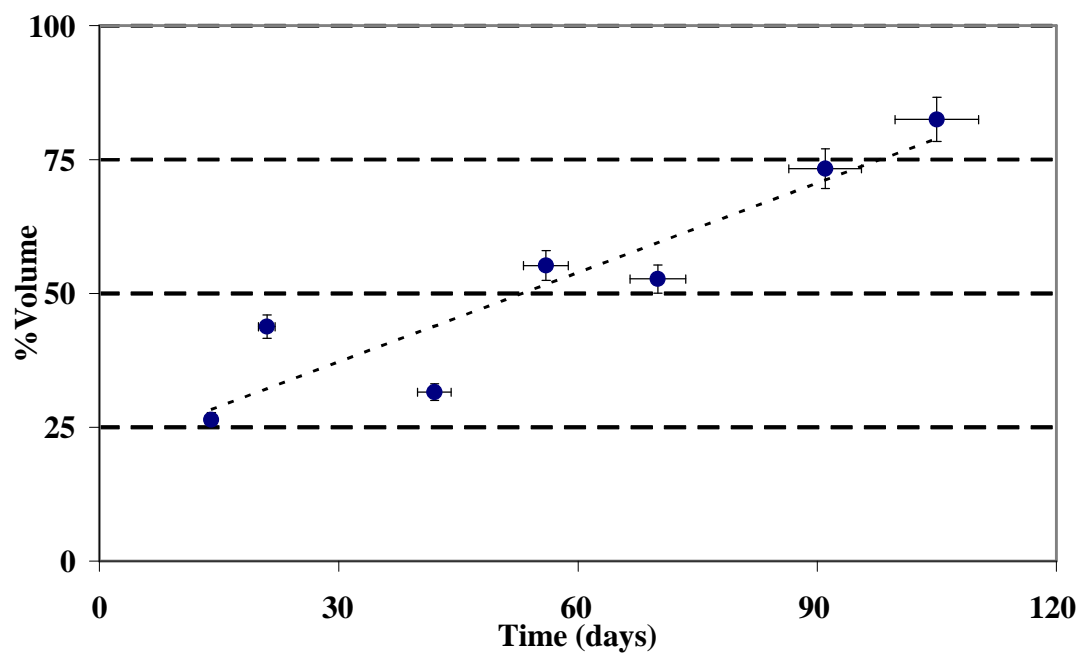


Figure 7.57: Percentage Volume of Particles Attributed to Small Particles (<200 μm) during Operation of the Pilot Scale AnMBR.

Further investigation into particle size showed that mean particle size during the start-up period measured between 550 and 630 μm (Figure 7.58). Minimum, mean and maximum particle/granule size present in the mixed liquor did drop as the system entered into the acclimatising phase. Granule size did increase after this initial drop although a return to original sizing of granules at inoculation never occurred despite stabilisation of the process.

Subjecting the system to psychrophilic conditions resulted in reduced particle sizing with the largest drop seen as the system shifted from mesophilic to psychrophilic conditions. A smaller drop in particle size was observed when the same 10 $^{\circ}\text{C}$ change in temperature was applied to the system while it remained psychrophilic. Maximum particle size fell from approximately 1417 μm to 1088 μm when operating temperature was dropped from 35 \pm 1 $^{\circ}\text{C}$ to 22 \pm 0.5 $^{\circ}\text{C}$. A further drop in maximum particle size to approximately 800 μm was also observed on day 98 when the system was subject to a lower operating temperature of 12 \pm 0.5 $^{\circ}\text{C}$. Minimum and mean particle/granule size present in the mixed liquor also dropped progressively with lower temperatures. Minimum particle size dropped from 51 μm to 9 μm over 120 days of continuous operation. Mean particle size also followed the same trend with a drop from 627 μm to 30 μm . Despite changes in particle size distribution, biomass remained distinctly granular over the entire operational period of 120 days.

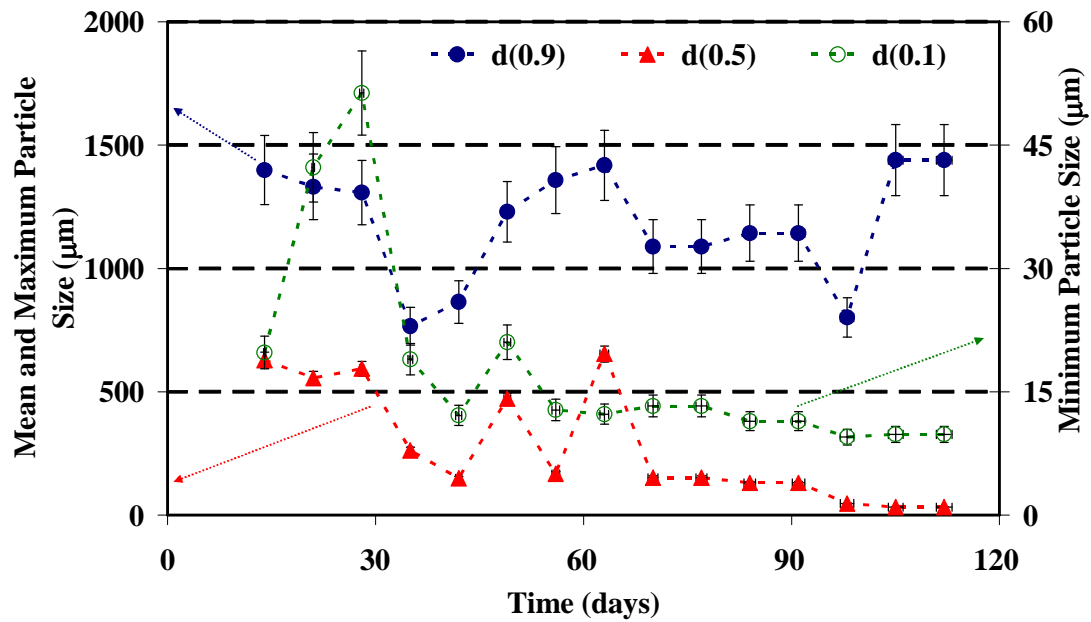


Figure 7.58: Evolution of Granule/Particle Size during Start-up, Acclimatising and Stable Phases.

(iii) CST and Viscosity

CST of the sludge from the AnMBR initially measured above 120s.gMLSS^{-1} . However, within 28 days of continuous operation, values fell between 53 and 105s.gMLSS^{-1} indicating that the sludge was more dewaterable (Figure 7.59). Viscosity followed an opposite trend to that of CST with initial values during the first twenty eight days of operation falling between 30 and 32mPa.s and latter values measuring between 27.5 and 50mPa.s at a shear rate of 12.2s^{-1} .

Changes to operating temperature from 35°C to 20°C caused a small increase in CST indicating that sludges become less easy to dewater at lower temperatures. The same drop in temperature causes the mixed liquor in the system to become more viscous. The same trend is observed in both properties when operating temperature is dropped even further to 12°C . Lesser variation was observed with both CST and viscosity as the system increased in stability and entered into progressive operational phases (start-up, acclimatising and stable). Changes to membrane configuration produced no noticeable change in the two properties.

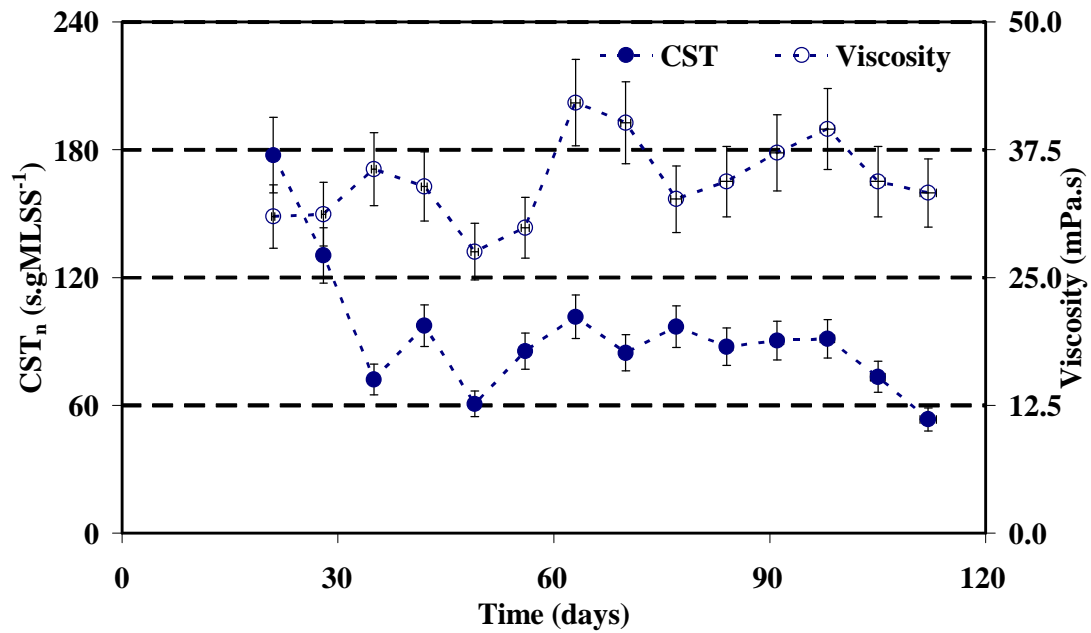


Figure 7.59: Evolution of CST and Viscosity of Sludge from Pilot Scale AnMBR.

(iv) EPS and SMP

EPS concentration generally decreased over the entire operational period of the AnMBR (Figure 7.60). EPS_{COD} measured approximately 245mg.gMLSS^{-1} at start-up but dropped off to 40mg.gMLSS^{-1} by day 77 when the system was subject to psychrophilic conditions. As the system was subject to even lower temperatures, EPS_{COD} began to increase progressively until levels peaked at 140mg.gMLSS^{-1} on day 112. Final concentrations were almost equivalent to concentrations determined during the acclimatising stage.

Levels of EPS_p varied between 16 and 107mg.gMLSS^{-1} with maximal levels present at system start-up. During latter periods, when the system was subject to an operating temperature of $12\pm 0.5^\circ\text{C}$, EPS_p remained between 16 and 50mg.gMLSS^{-1} . Final levels of EPS_p present in the mixed liquor were roughly 6 times less than levels present at start-up of the system. EPS_c followed the same trend with levels decreasing progressively as the system became more psychrophilic. Initial levels of EPS_c ($16.5\pm 0.5\text{mg.gMLSS}^{-1}$) present in the AnMBR at a temperature of $35\pm 1^\circ\text{C}$ were approximately 9 times the levels present at $12\pm 0.5^\circ\text{C}$ ($1.5\pm 0.5\text{mg.gMLSS}^{-1}$).

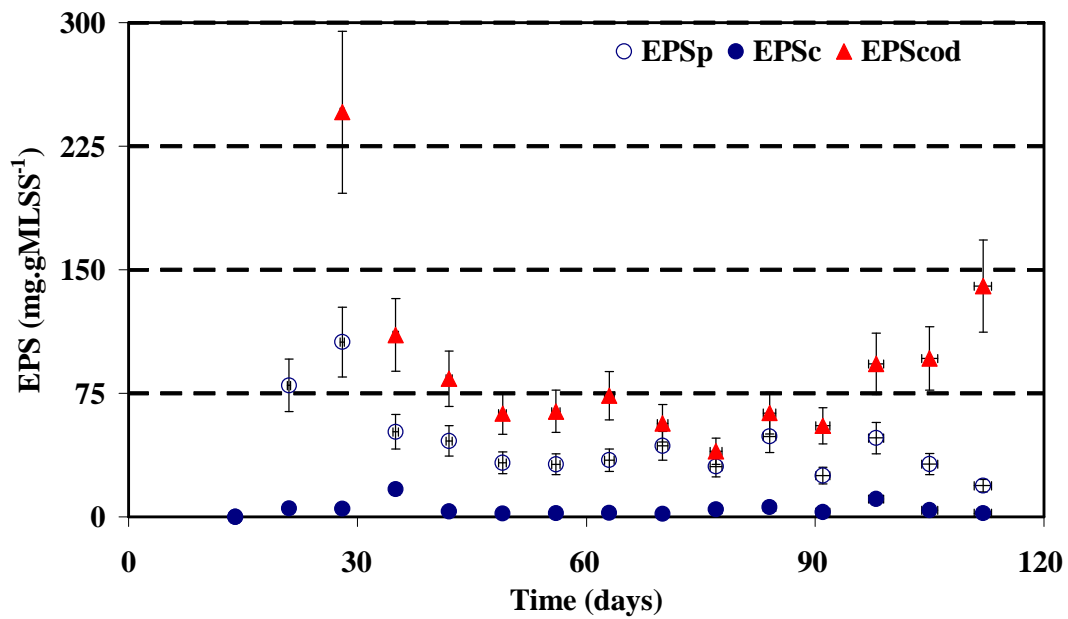


Figure 7.60: EPS Levels present in AnMBR over Total Operational Period.

Levels of SMP in the mixed liquor generally dropped off with time (Figure 7.61). Initial levels of SMP_{COD} measured 778mgL^{-1} while SMP_p and SMP_c measured approximately 320 and 80mgL^{-1} respectively at start-up. By the end of the operational period (at which point the AnMBR had been subject to psychrophilic conditions for a total of 60 days), SMP_{COD} had fallen to 180mgL^{-1} . SMP_p and SMP_c had also fallen to 59mgL^{-1} and 8mgL^{-1} respectively. The decline in SMP concentration of the mixed liquor was generally progressive throughout the operational period although small increases in concentration were noted immediately after dropping operating temperature. Membrane configuration had no effect on SMP levels.

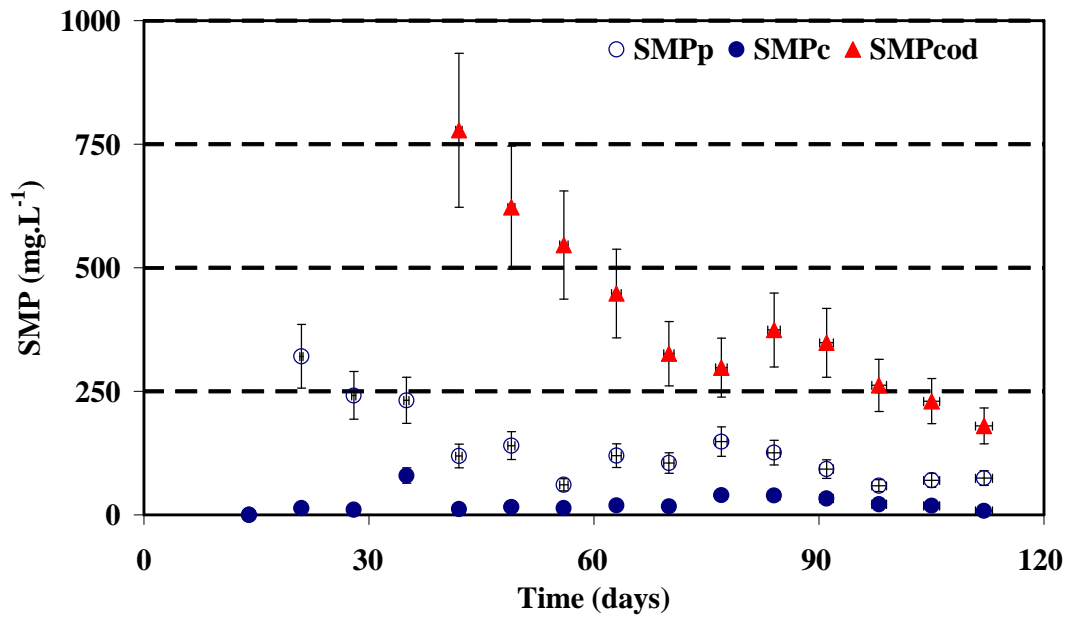


Figure 7.61: SMP Levels present in AnMBR over Total Operational Period.

Further analysis of protein and carbohydrate levels present in EPS and SMP show that ratios of both EPS_p/EPS_c and SMP_p/SMP_c decrease progressively with time (Figure 7.62). EPS_p is approximately 21 times EPS_c at start-up of the AnMBR at $35 \pm 1^\circ\text{C}$. By day 70 when the system shifts from mesophilic to psychrophilic conditions, EPS_p is just 4.5 to 8.5 times EPS_c . SMP_p at start-up measures roughly 24 times SMP_c during the same period but drops progressively over time so that between day 56 and day 120, SMP_p/SMP_c remains between 3.5 and 8.5.

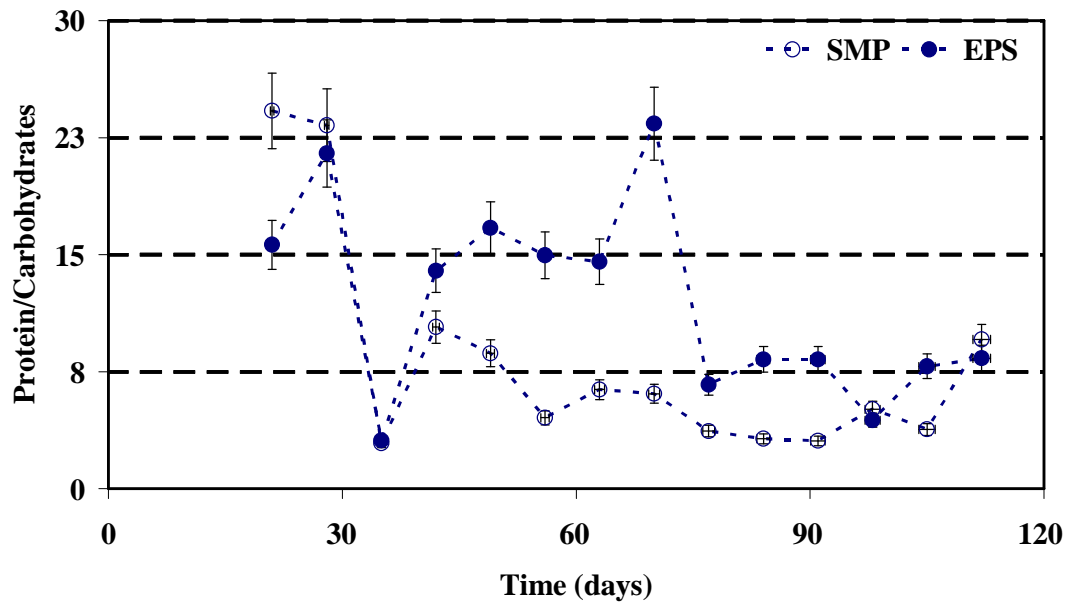


Figure 7.62: Proportions of Protein and Carbohydrate in EPS and SMP over Total Operational Period.

(v) Interactions between Normalised Biomass Characteristics

The response of any biological system to a change in operating conditions is also dependent on complex interactions between biomass characteristics and how changes to individual biomass properties may affect others. Table 7.23 is a matrix that gives an indication of the interactions between each characteristic by assigning numerical values between -1 and +1. The stronger the positive or negative correlation between the individual biomass characteristics, the closer the assigned numerical value to +1 or -1 respectively. Characteristics that show correlations between -0.1 to 0.1 are assumed to have no significant correlation.

The strongest positive correlation was observed between MLSS and MLVSS with a value of 0.9695. SMP_p and CST, EPS_p and CST, SMP_p/SMP_c and CST, EPS_p and SMP_p , EPS_{COD} and SMP_{COD} as well as EPS_c and SMP_c all showed high positive correlations with values that fell between 0.7 and 0.8. It can therefore be inferred from these results that EPS and SMP are inextricably linked.

It should be expected that if EPS_p , EPS_c and EPS_{COD} increase, a corresponding increase should be observed in SMP_p , SMP_c and SMP_{COD} . EPS and SMP are also important in determining the dewaterability of sludge from an AnMBR. The higher the proportion of protein present in these substances, the longer it takes to dewater the sludge. The sludge therefore becomes more difficult to dewater as EPS_p and SMP_p increase in concentration.

Correlation values between 0.5 and 0.7 were assigned to $d_{0.5}$ and EPS_p , EPS_p/EPS_c , SMP_p and SMP_p/SMP_c . EPS levels therefore have some effect on granule/particle size. The positive correlation values assigned to SMP_p could be explained by the fact that EPS levels tend to increase with SMP levels. SMP_{COD} and MLSS as well as EPS_{COD} and MLSS all showed correlations between 0.1 and 0.45 suggesting the existence of weak relationships between these properties.

The strongest negative correlations (-0.6 to -0.8) were assigned to CST and MLSS, SMP_p and MLSS, MLVSS and CST, SMP_p and MLVSS, SMP_p/SMP_c and MLVSS as well as EPS_p and MLVSS. MLVSS depicts the proportion of MLSS that can be attributed to active bacteria/biomass. The higher the amount of MLVSS, the lower the levels of SMP_p and EPS_p present in the mixed liquor or locked in the biomass. Higher MLVSS concentration also results in a decrease in the amount of time required to dewater a sludge (sludge dewaterability is increased). The same trend is seen with MLSS and CST as well as MLSS and SMP_p (The higher the MLSS concentration of the sludge or mixed liquor, the lower the amounts of SMP_p present).

SMP_p/SMP_c and EPS_p both showed negative correlations of -0.5 ± 0.05 to MLSS concentration. All other biomass characteristics showed no correlation or less significant negative correlations between -0.1 and -0.4.

Table 7.23: Correlation Matrix showing Interactions between Normalised Biomass Characteristics in the Pilot Scale AnMBR

| | MLSS | MLVSS | CST _n | Viscosity | d(0.5) | SMP _p | SMP _c | SMP _{COD} | SMP _p /SMP _c | EPS _p | EPS _c | EPS _{COD} | EPS _p /EPS _c |
|------------------------------------|----------------|----------------|------------------|----------------|----------------|------------------|------------------|--------------------|------------------------------------|------------------|------------------|--------------------|------------------------------------|
| MLSS | 1.0000 | | | | | | | | | | | | |
| MLVSS | 0.9695 | 1.0000 | | | | | | | | | | | |
| CST _n | -0.7403 | -0.7805 | 1.0000 | | | | | | | | | | |
| Viscosity | 0.0228 | 0.0944 | -0.0860 | 1.0000 | | | | | | | | | |
| d(0.5) | -0.2208 | -0.3301 | 0.5664 | -0.1402 | 1.0000 | | | | | | | | |
| SMP _p | -0.6530 | -0.7217 | 0.7174 | -0.3136 | 0.6706 | 1.0000 | | | | | | | |
| SMP _c | -0.0741 | -0.0097 | -0.2079 | 0.1777 | -0.1397 | 0.2293 | 1.0000 | | | | | | |
| SMP _{COD} | 0.1835 | -0.0337 | 0.2234 | -0.2681 | 0.4190 | 0.1818 | -0.3613 | 1.0000 | | | | | |
| SMP _p /SMP _c | -0.5284 | -0.6564 | 0.7427 | -0.4180 | 0.6447 | 0.7291 | -0.4666 | 0.5082 | 1.0000 | | | | |
| EPS _p | -0.5037 | -0.6595 | 0.7396 | -0.1929 | 0.5796 | 0.7629 | -0.0606 | 0.6063 | 0.7735 | 1.0000 | | | |
| EPS _c | -0.3532 | -0.3376 | 0.0113 | 0.1729 | -0.0727 | 0.3396 | 0.7724 | -0.2068 | -0.1679 | 0.2896 | 1.0000 | | |
| EPS _{COD} | 0.1931 | -0.0014 | -0.1228 | -0.0729 | 0.1402 | 0.0628 | -0.1028 | 0.7519 | 0.3038 | 0.4294 | 0.1554 | 1.0000 | |
| EPS _p /EPS _c | 0.0518 | -0.0778 | 0.3466 | -0.1545 | 0.5346 | 0.2260 | -0.6046 | 0.5529 | 0.5789 | 0.4228 | -0.5772 | 0.1456 | 1.0000 |

MLSS, MLVSS in g.L⁻¹; SMP in mg.L⁻¹; EPS in mg.gMLSS⁻¹; CST_n in s.gMLSS⁻¹; Viscosity in mPa.s at 12.24 s⁻¹ shear rate; d_{0.5} in µm.. Note that all significant correlations are marked in bold.

7.2.3 Membrane Fouling

Fouling amelioration is critical in maintaining adequate process efficiency in a membrane bioreactor. The optimal flux to which any membrane can be subject is highly dependent on its fouling characteristics.

During the 120day operational period of the anaerobic membrane bioreactor, fouling was determined by analysing transmembrane pressure and its response to process parameters, membrane configuration and biomass characteristics. TMP is a good indicator of fouling after initial biomass and cake deposition as it tends to increase with deposition of foulants onto the membrane surface. All experiments were conducted with the AnMBR operating in submerged mode at sub-critical conditions ($<40\text{Lm}^{-2}\text{h}^{-1}$) except where membrane configuration comparison tests were being carried out.

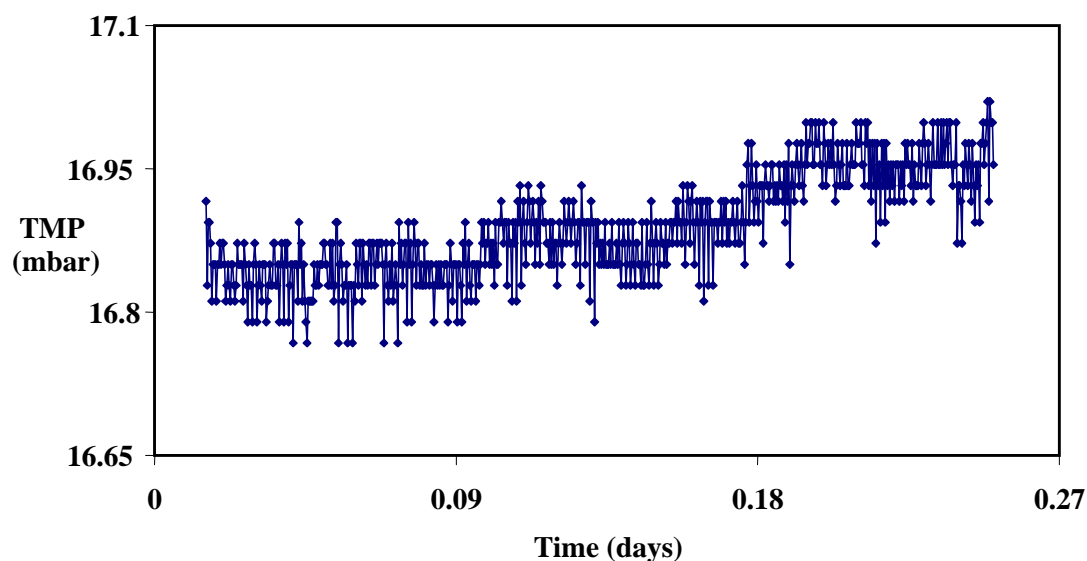


Figure 7.63: TMP Evolution over a 4 Hour Period during Operation of the Pilot Scale AnMBR.

Long term membrane fouling rate was highly dependent on operational and process parameters and followed specific trends over the entire operational period. The highest membrane fouling rates were observed during start up as well as acclimatising operational phases (Figure 7.64). During the first two weeks of membrane installation in the AnMBR, fouling rates averaged approximately $28\text{mbar}\cdot\text{d}^{-1}$ which made it necessary to clean the membranes twice weekly. However, fouling rates had dropped to $6\text{mbar}\cdot\text{d}^{-1}$ by the start of the stable phase. As soon as the system was subject to an operating temperature of $22\pm0.5^\circ\text{C}$, fouling rates began to increase again reaching a maximum of approximately $90\text{mbar}\cdot\text{d}^{-1}$. A further increase in average fouling rate to $10\text{mbar}\cdot\text{d}^{-1}$ was noted on subjection of the system to an even lower temperature of $12\pm0.5^\circ\text{C}$.

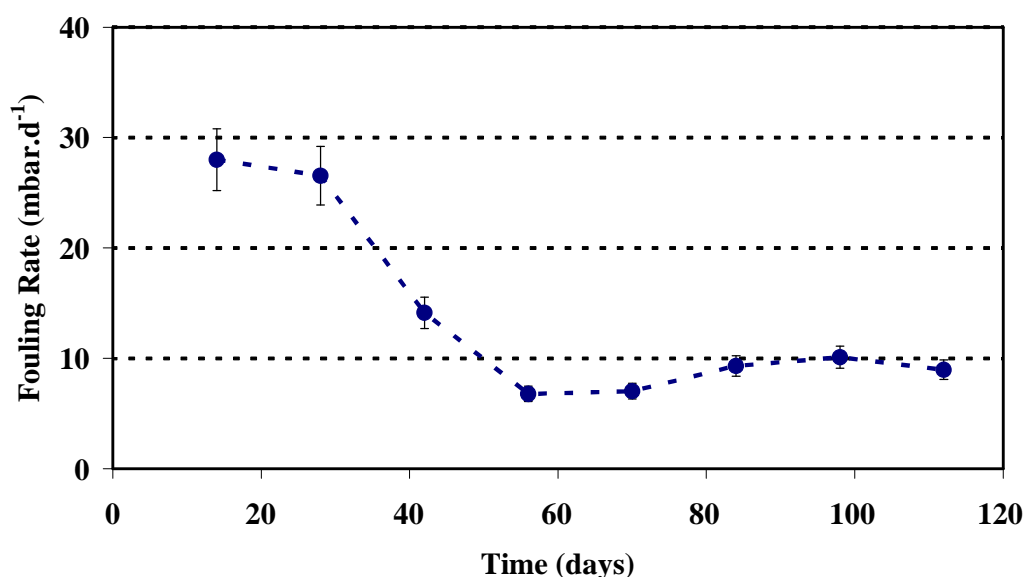


Figure 7.64: Average Membrane Fouling Rates during AnMBR Operation.

(i) Membrane Type, Configuration, Pore Size and Fouling Rate

Fouling rate showed a different relationship to flux for each of the membranes utilised in experiments. Operational profiles were developed based on membrane type. In side-stream configuration, fouling rate appeared to have an exponential relationship with flux despite differences in make, pore size and total filtration area (Figure 7.65).

For the Milleniumpore polyethylene membrane with a filtration area of 0.502m^2 and pore size of $0.1\mu\text{m}$, fouling rate at a minimal flux of $9\text{Lm}^{-2}\text{h}^{-1}$ was only 1.06mbard^{-1} as opposed to 100mbard^{-1} seen with the submerged system. However, fouling rate increased substantially to 2.71mbard^{-1} at a flux of $20\text{Lm}^{-2}\text{h}^{-1}$. Despite having a smaller filtration area of 0.175m^2 and pore size of $0.03\mu\text{m}$, the Zenon polyethersulphonic membrane exhibited the lowest initial fouling rates than the other two membrane modules. However, the same exponential relationship observed with the Milleniumpore polyethylene membrane was exhibited with the application of higher fluxes. Fluxes above $20\text{Lm}^{-2}\text{h}^{-1}$ produced higher fouling rates than observed with the submerged membrane module. Fouling of the Mitsubishi Rayon submerged membrane module (with the largest filtration area of 0.9m^2 and pore size of $0.1\mu\text{m}$) showed a linear relationship to flux with increasing flux producing proportional increases in fouling rate. During operation of the system in submerged mode during fouling experiments, fouling rates did not measure above 4.5mbard^{-1} despite being subject to similar fluxes of 9 to $24\text{Lm}^{-2}\text{h}^{-1}$ for similar amounts of time (4 hours for each flux step).

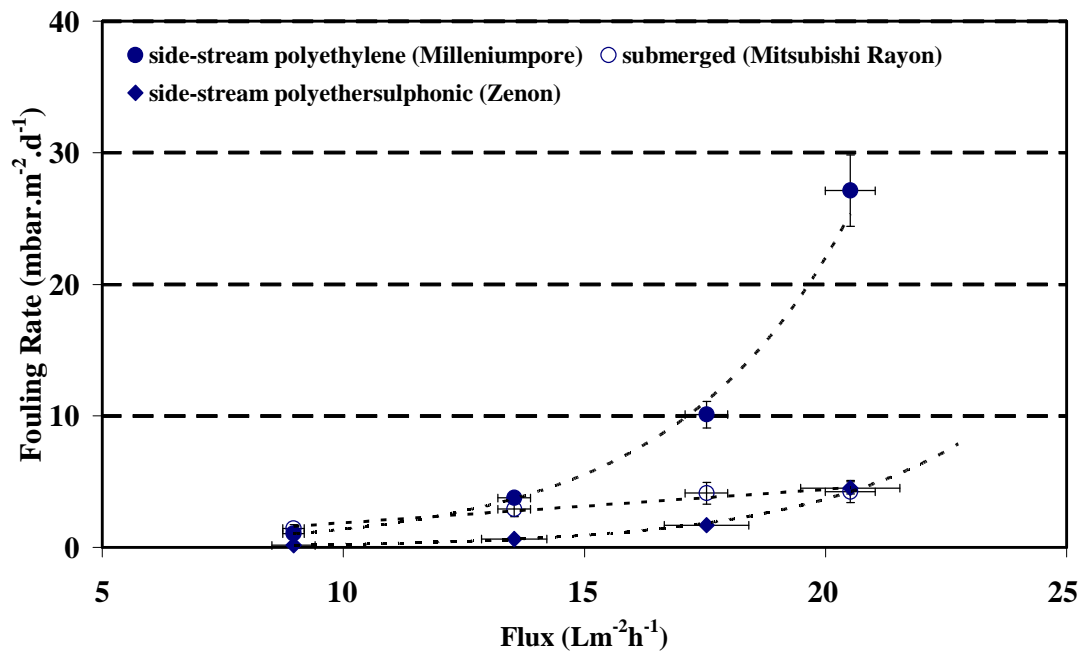


Figure 7.65: Operational Profiles for Submerged and Side-stream Membrane Configurations.

(ii) **Impact of Biomass Characteristics on Membrane Fouling****Table 7.24: Correlation Matrix showing Relationships between Average Fouling Rate (at a Flux of $14\text{Lm}^{-2}\text{h}^{-1}$) and Normalised Biomass Characteristics.**

| | <i>Fouling Rate</i> | | |
|-------------------------------|---|---|-----------------------------------|
| | <i>Zenon Side-Stream Polyethersulphonic</i> | <i>Milleniumpore Side-Stream Polyethylene</i> | <i>Mitsubishi Rayon Submerged</i> |
| Fouling Rate | 1 | 1 | 1 |
| Viscosity | -0.3187 | -0.3612 | -0.3905 |
| MLSS | -0.8150 | -0.7945 | -0.7869 |
| MLVSS/MLSS | -0.7296 | -0.7440 | -0.7336 |
| $d(0.5)$ | 0.5575 | 0.5975 | 0.5975 |
| CST_n | 0.5218 | 0.5347 | 0.5273 |
| $\text{SMP}_p + \text{SMP}_c$ | 0.9675 | 0.9731 | 0.9729 |
| $\text{EPS}_p + \text{EPS}_c$ | 0.3014 | 0.3190 | 0.3198 |

MLSS, MLVSS in g.L^{-1} ; SMP in mg.L^{-1} ; EPS in mg.gMLSS^{-1} ; CST_n in s.gMLSS^{-1} ; Viscosity in mPa.s at 12.24 s^{-1} shear rate; $d_{0.5}$ in μm .

Table 7.24 summarises correlations between biomass characteristics and fouling rates at a flux of $14\text{Lm}^{-2}\text{h}^{-1}$. All biomass characteristics analysed had some effect on membrane fouling rates. Characteristics such as EPS concentration, viscosity, CST and mean particle size were assigned correlation values between 0.3 and 0.6 for their impact on membrane fouling rate. EPS concentration and viscosity showed the lowest correlation to membrane fouling rates (0.3 to 0.4). It can be inferred from these results that EPS has little effect on long term fouling rates as stated previously in chapter 6 of this thesis. The slight correlation between membrane fouling rate and EPS as well as viscosity may be indirect and a result of the correlation of these characteristics with other biomass characteristics such as SMP and MLSS (which both show very high correlations with membrane fouling).

The highest correlations were noted for fouling rate and SMP, MLSS and MLVSS/MLSS with assigned values over 0.7. SMP concentration showed the highest correlation (>0.9) with membrane fouling rates for all membrane types and configurations utilised. Further investigation into the effect of SMP concentration on average membrane fouling rates shows up a parabolic relationship between the two parameters (Figure 7.66) for all membrane types and configurations tested. This is also in agreement with results previously presented in chapter 6 of this thesis.

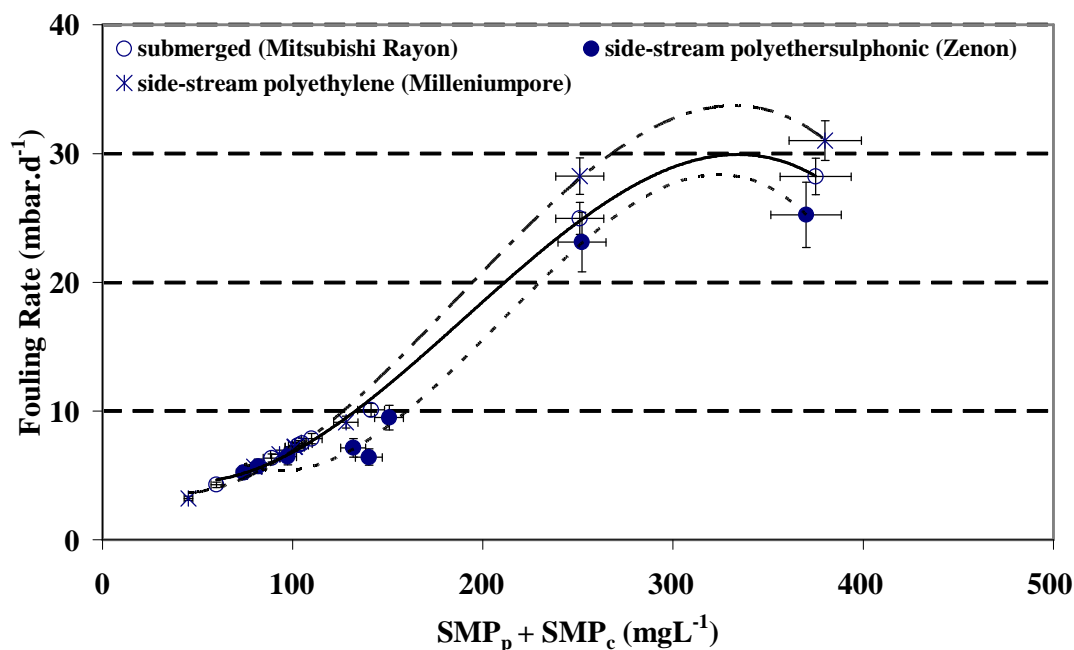


Figure 7.66: SMP Concentration and its Relationship to Membrane Fouling Rate at a Flux of $14\text{Lm}^{-2}\text{h}^{-1}$ for MLSS concentrations of 2 to 6.5gL^{-1} .

Comparison of SMP concentrations in the AnMBR mixed liquor and permeate (after passing through the membrane) further shows the retention of significant amounts of SMP by membranes. Throughout the entire operational period, the effluent produced by the system had SMP concentrations lower than that present in the mixed liquor (Figure 7.67, Figure 7.68). On day 14 (at the end of the start up period), mixed liquor SMP_p concentration measured approximately 350mgL^{-1} while SMP_c measured 27mgL^{-1} . Permeate concentrations of both SMP fractions measured about 185mgL^{-1} and 22mgL^{-1} respectively. By the end of the operational period, SMP_p measured approximately 80mgL^{-1} and 42mgL^{-1} in the mixed liquor and permeate respectively. Reduced permeate concentrations of SMP_c (2 to 15mgL^{-1}) were also noted compared with 5 to 20mgL^{-1} present in the mixed liquor.

Approximately 47 to 51% of SMP protein was retained by the membrane despite changes to membrane configuration and type as well as operating temperature. Approximately 20% of SMP carbohydrate was also retained by both the side-stream polyethersulphonic and the submerged hollow fibre membrane despite changes to operating conditions.

The side-stream polyethylene membrane retained approximately equal amounts of SMP carbohydrates and protein (47 to 48%). Table 7.25 is a summary of SMP rejection factors specific to each membrane type utilised in operation of the AnMBR when it was subject to long term operation. SMP rejection did not change with operating conditions.

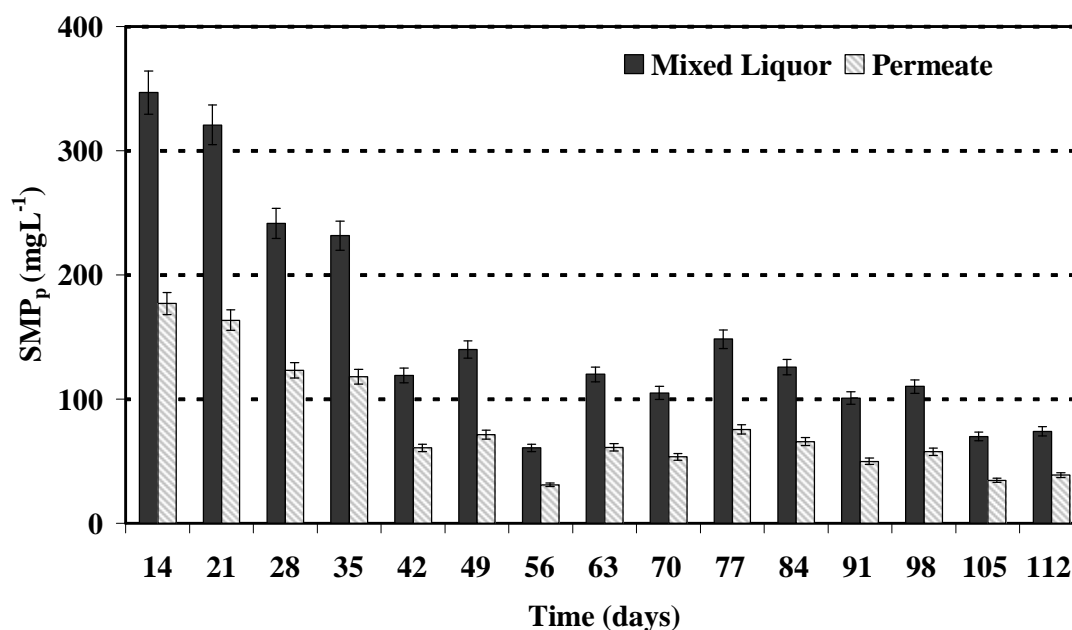


Figure 7.67: Concentration of SMP_p in Mixed Liquor and Permeate over AnMBR Operational Period.

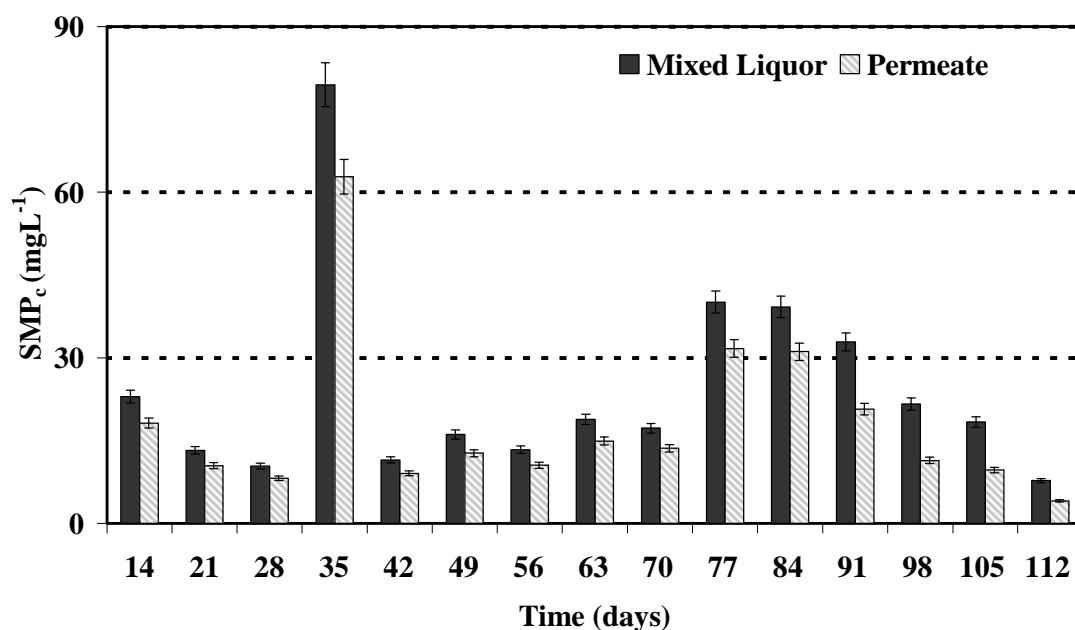


Figure 7.68: Concentration of SMP_c in Mixed Liquor and Permeate over AnMBR Operational Period.

Table 7.25: Summary of Rejection Factors for Each Membrane Type and SMP Fraction.

| Membrane Type | Configuration | Pore size | Rejection factors | |
|------------------------------------|---------------|-----------|-------------------|-----------------|
| | | | SMP_p | SMP_c |
| Mitsubishi Rayon Hollow Fibre | Submerged | 0.1 | 0.51 ± 0.01 | 0.20 ± 0.01 |
| Zenon X-flow Polyethersulphonic | Side-stream | 0.03 | 0.49 ± 0.01 | 0.20 ± 0.01 |
| Milleniumpore Tubular Polyethylene | Side-stream | 0.1 | 0.47 ± 0.01 | 0.47 ± 0.01 |

As the proportion of SMP retained by the membrane did not vary, it follows that the higher the amounts of SMP present in the mixed liquor, the higher the amount of foulant to be deposited on the membrane surface (Figure 7.69).

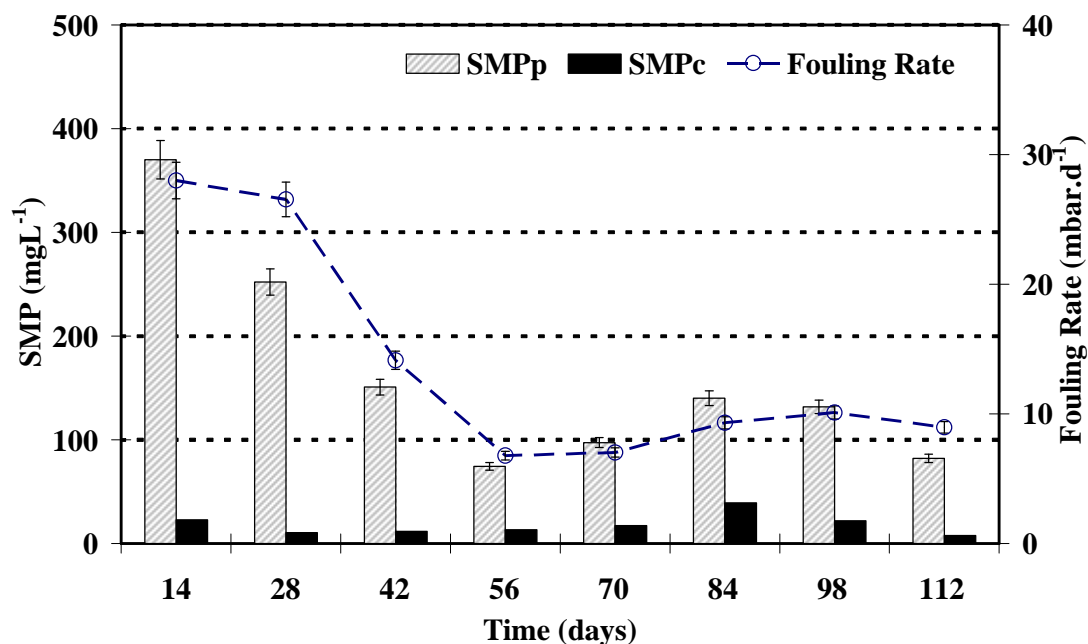


Figure 7.69: Direct Comparison of Average Membrane Fouling Rates with Mixed Liquor SMP Concentrations.

(iii) Membrane Fouling Rates and Gas Sparging

The lowest membrane fouling rates observed during operation of the AnMBR occurred on introduction of nitrogen gas into the AnMBR. Specific experiments into the effect of gas sparging on membrane fouling produced results which showed a reverse linear relationship between the two parameters (Figure 7.70). Gas sparging appeared to reduce membrane fouling for all configurations tested. At a sparging rate of $0.45 \pm 0.02 L_{\text{gas}} \cdot L_{\text{reactor}} \cdot d^{-1}$, fouling rates measured approximately 3.5, 4.2 and 4.5 mbar.d⁻¹ for the Mitsubishi Rayon submerged, Milleniumpore side-stream polyethylene and Zenon side-stream polyethersulphonic membranes respectively. The sharpest decrease in fouling rate was observed with the Zenon side-stream polyethersulphonic membrane. Fouling rate decreased four fold when gas sparging was increased to $1.13 \pm 0.02 L_{\text{gas}} \cdot L_{\text{reactor}} \cdot d^{-1}$. The same trend was seen with the other two membranes with the Milleniumpore side-stream polyethylene and Mitsubishi Rayon submerged membranes dropping three fold with the same increase in gas sparging rate.

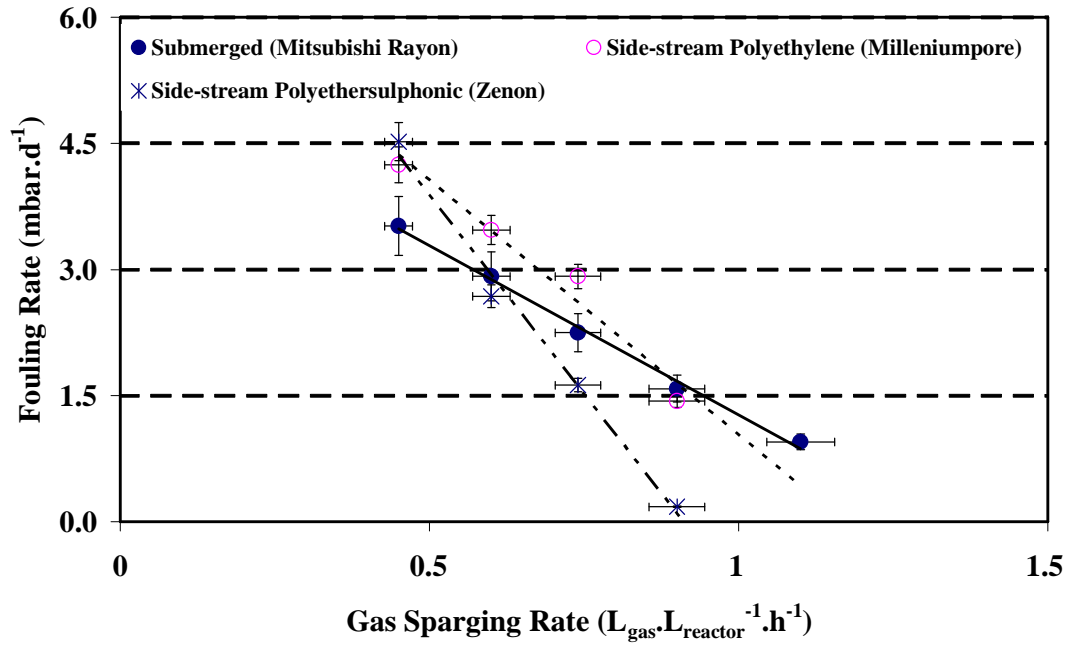


Figure 7.70: Gas Sparging and its Effect on Membrane Fouling Rates.

7.3 Discussion

Anaerobic systems have historically proven to be inadequate for the treatment of municipal and domestic wastewaters due to their low organic content (Mergaert *et al.*, 1992). However, the AnMBR used in this study was able to achieve COD removals of up to 97%. The performance of this system is comparable to aerobic systems (including MBRs) which have achieved treatment efficiencies (while treating domestic and municipal wastewaters) exceeding 90% with some reported cases as high as 98% at MLSS concentrations of 2.5 to 50 gL⁻¹ (Germaine, 2004; Alvarez, 2005; Stephenson *et al.*, 2000). The use of conventional anaerobic systems for the treatment of domestic wastewater has however produced less impressive results with reported COD removals averaging between 40 and 70%. Comparisons between results obtained in this study and other work which focused on the use of conventional anaerobic treatment systems are given in Table 7.26.

Table 7.26: Comparison of Anaerobic Systems Treating Municipal and Domestic Wastewaters.

| Reactor/Treatment Type | HRT (hours) | COD _{inf} (mgL ⁻¹) | Operating Temperature (°C) | COD removal (%) | Reference |
|------------------------------------|----------------|--|-------------------------------|--------------------|-------------------------------------|
| Anaerobic Membrane Bioreactor | 5.6-6.4 | 200-700 | 12-35 | 82-97 | This study |
| Anaerobic Baffled Reactor | 1.3-6 | 500 | 35 | 40-80 | Lagenhoff <i>et al.</i> , 2000 |
| Anaerobic Baffled Reactor | 20 | 350-1200 | 30-35 | 70-90 | Dama <i>et al.</i> , 2002 |
| UASB | 24 | 688 | 12-16 | 55-75 | Lettinga <i>et al.</i> , 1983 |
| UASB | 2-9 | 152.6 | 22 | 70-80 | Seghezzi <i>et al.</i> , 2002 |
| EGSB | 1-3.5 | 391 | 13-19 | 16-34 | Van der Last and Lettinga, 1992. |
| Modified Anaerobic Baffled Reactor | 4-10 | 920-2430 | 18-20 | 50-83 | Yu and Anderson, 1996 |
| Fluidized Bed Reactor | 6.4 | 267 | 17-25 | 67 | Switzenbaum <i>et al.</i> , 1984 |
| Anaerobic Filter | 24 | 288 | 20-35 | 73 | Kobayashi <i>et al.</i> , 1983. |

Table 7.26 shows the relatively high treatment efficiencies achieved with the AnMBR even though the system was subject to low operating temperatures and a short HRT. The incorporation of the membrane into the anaerobic bioreactor therefore extended its application window by allowing sufficient time for the acclimatisation and growth of specialised (such as *Methanothrix* microbes) and psychrotolerant anaerobic biomass which are more effective in treating dilute wastewaters at low temperatures (Mergaert *et al.*, 1992; McHugh *et al.*, 2005). Other anaerobic MBR systems have been successfully used in the treatment of domestic and municipal wastewaters although most of these systems have been at bench scale level. Chu *et al.* (2005) achieved 76 to 96% COD removal while treating a synthetic wastewater prepared to simulate domestic sewage using a bench scale EGSB reactor coupled with a hollow fibre membrane module. Wen *et al.* (1999) achieved similar COD removal rates while treating raw domestic sewage in an AnMBR with a total volume of 17.7L. Both systems were subject to operating temperatures of 11 to 15°C and HRTs of 3.5 to 6 hours.

The AnMBR has one major advantage over aerobic MBRs in that it produces methane which can be converted to re-usable energy. As a result, it is less energy intensive. Biogas production from the AnMBR in this study was comparable to published literature on the subject with methane forming about 70 to 80% of total biogas produced (Seghezzo *et al.*, 2002; Lagenhoff *et al.*, 2000).

Specific methanogenic activity of biomass in this study varied from 0.20gCOD-CH₄.gMLVSS⁻¹ to 0.24gCOD-CH₄.gMLVSS⁻¹. Seghezzo *et al.* (2002) also treated a settled sewage at temperatures of 18 to 20°C with a pilot scale UASB reactor and found mean specific methanogenic activity to be approximately 0.09 to 0.13gCOD-CH₄.gMLVSS⁻¹ (significantly lower than values reported in this study). The same authors also found SMA to be inversely proportional to MLVSS concentration. The latter observation is not consistent with results in this study as changes to operating temperature were found to affect both MLVSS and SMA profiles of the AnMBR. MLVSS concentration dropped with falling temperature and so did specific methanogenic activity. It is worth noting that the response of SMA to a drop in MLVSS depends on the reason for the change in the first instance.

If reactor HRT is increased for instance, sludge concentrations increase and so does the uptake of inert solids as suspended solids removal increases. MLVSS will decrease in this situation causing reactor volume increase, larger sludge mass and decreased specific methanogenic activity (Zakkour *et al.*, 2001).

Changes to operating temperature of the AnMBR system resulted in slightly lower steady state pH values. According to Borja and Banks (1995), this is typical of anaerobic wastewater treatment systems. Shock temperature changes are usually characterised by an immediate pH drop in the reactor, which then stabilises at a value slightly below the previous steady state pH value. The authors attributed this phenomenon to the increase in VFA concentration of the mixed liquor which stabilises at new levels during operation at reduced temperatures. The increase in VFA concentration also affects COD removal rates negatively although this will not automatically lead to system failure if pH is adequately controlled (and remains within optimum operational window of 6.5 to 7.5). Therefore, critical to the successful treatment of dilute wastewaters at psychrophilic temperatures with anaerobic systems is pH control. pH must be kept neutral or near neutral to avoid system failure.

The identification of start-up, acclimatising and stable phases in this study is supported by previous studies on aerobic MBRs. Boubahila *et al.* (2001) defines the stable or steady state phase as the period when the COD concentration of influent was constant and the biomass concentration was stable. Smith *et al.* (2002) imposed an acclimatisation period equal to twice the SRT prior to verifying steady state operation by the measurement of MLVSS and effluent COD concentration over successive days. As anaerobic systems usually have long SRTs (typically between 28 to 600 days depending on process conditions), this author defines the stable or steady state phase in AnMBRs as that point when biomass concentration is either constant or growth and decay continues at a specific rate while COD reduction remains relatively constant if there are no substantial operational and process changes. Where operational and configuration changes are made to the process, then the response of the system is the minimum or near minimum that it can possibly be for the said process change. This definition is supported by results from this study.

Biomass characteristics and COD removal showed comparatively minimal responses to changes in operating temperature and membrane configuration.

Biomass characteristics showed the same complex interrelationship previously shown in chapter 5 of this thesis. However, concentrations of microbial substances were generally lower than previously noted when sludges were not actively treating substrates. Latter MLSS concentrations achieved in the AnMBR were lower than optimal MLSS concentrations reported for aerobic MBR systems but significantly higher than values reported for conventional anaerobic as well as anaerobic MBR systems due to the increased use of granular biomass in the former systems.

Aerobic MBRs usually operate at MLSS concentrations of 5 to 20gL⁻¹ (Germaine, 2004; Judd *et al.*, 2004; Brookes *et al.*, 2003; Brindle and Stephenson, 1996). Vallero *et al.* (2005) achieved a maximal MLSS and MLVSS concentration of 1.75±0.1gL⁻¹ and 0.85±0.02gL⁻¹ respectively while using the SAMBAR system to treat a synthetic wastewater with high salinity. The proportion of MLSS ascribed to MLVSS was also significantly lower than results in this study at 0.4±0.09. This value is also somewhat lower than values determined for conventional anaerobic systems used in treating domestic sewage. Singh and Viraraghavan (1998) for instance found that MLVSS formed approximately 50% of total suspended solids while treating a municipal wastewater at an ambient temperature of 20°C in a UASB reactor. MLSS concentration in the said system remained between 0.28 to 0.3gL⁻¹. The differences between the AnMBR used in this study and other anaerobic systems in terms of solids concentration can be ascribed to greater mixing present in this system. Although the system was inoculated with granular biomass, it was also subject to gas sparging which improved mixing and recirculation and therefore resulted in higher amounts of suspended solids in the mixed liquor. However, this does not explain the increased organic matter content present in the system. MLVSS is an adequate indicator of active biomass or bacteria present in a biological reactor (Metcalf and Eddy, 2003). It therefore follows that a larger amount of active biomass remains in the AnMBR in comparison to conventional anaerobic systems when both types of systems are subject to similar process conditions while treating domestic and municipal wastewaters.

The presence of higher MLVSS concentrations in the AnMBR is further evidence that the incorporation of membranes into biological systems promotes biomass acclimatisation and reduces biomass washout.

MLVSS and MLSS concentration were also found to have a significant impact on dewaterability and viscosity suggesting that these two parameters affect flux decline in AnMBRs. Increased MLSS and MLVSS levels in the AnMBR resulted in a mixed liquor that was more dewaterable. The increase in MLSS in the AnMBR is accompanied by a slight decrease in granular material and smaller particle sizes. The correlation between the three properties (CST, MLSS and MLVSS) can be attributed to this factor.

MLSS and MLVSS concentrations remained relatively constant during latter periods of AnMBR operation suggesting that biomass in the AnMBR favoured maintenance conditions rather than cell division and growth. Where a biological reactor is subject to starvation conditions and low F/M ratios (as was the case in this study), biosynthesis is inhibited although bacterial cells are still able to take part in active substrate degradation for the satisfaction of maintenance energy requirements (Lobos *et al.*, 2004). The low growth yield during latter operation of the AnMBR provides further evidence of this theory. Biomass growth yield was relatively high during the first 35 days of AnMBR operation at 0.03 when F/M ratio measured between 0.8 and 1.9d^{-1} . As F/M ratios fell further and then remained at $0.1 \pm 0.05\text{d}^{-1}$, biomass growth yield followed the same trend and dropped by a factor of 10. MLVSS concentration did increase at start-up of the AnMBR up to a maximum of approximately 4gL^{-1} on day 56. This point corresponds to the saturation point of the biomass beyond which no further storage of cellular and lipid polymers can occur. Chudoba *et al.* (1992) states that storage of these lipid polymers is responsible for initial increase in solids concentrations in biological reactors subject to starvation conditions. Initial biomass yield ($0.03\text{ gMLVSS.gCOD}^{-1}$) were in agreement with theoretical values as stated in work carried out by Rebac (1998) on the psychrophilic anaerobic treatment of low strength wastewaters. Liu *et al.* (2005) on the other hand established a growth yield of approximately 0.11 to $0.29\text{gMLVSS.gCOD}^{-1}$ while examining aerobic microbial behaviour in an MBR with complete sludge retention.

The biomass yield and F/M profiles obtained from the latter study were similar to observed trends in this study. F/M ratios were initially high and then fell as sludge growth increased. This accounts for the low biomass yields during the latter stages of AnMBR operation. Biomass yield is also known as sludge yield and may be used as an indicator of the amounts of surplus sludge produced by a biological treatment plant or reactor. Low biomass yields reduce the frequency of sludge wasting and therefore result in the production of less surplus sludge. A reduction in the volumes of surplus sludge produced is beneficial as it represents a cost saving in terms of its treatment and disposal.

Particle sizes were generally smaller than would be expected in an anaerobic system with granular biomass but larger than would be found in aerobic systems. Mean size in the AnMBR varied between 150 μ m during latter stages of operation and 500 μ m during initial periods. These values are comparable to work done by Vallero *et al.*, 2005 who obtained a mixed liquor with an average particle size of 370.2 and 463.2 μ m while treating a high salinity wastewater using the novel anaerobic SAMBAR system. Aerobic systems on the other hand will rarely contain biomass with mean particle size exceeding 100 μ m as biomass present in these systems is usually flocculent (Snidaro *et al.*, 1997; Germaine, 2004). In fact, aerobic MBRs have been known to operate with particles of less than 50 μ m in size (Yi and Harper, 2005; Wisniewski *et al.*, 2000; Henriques *et al.*, 2005). This is detrimental to withdrawal of effluent by membranes because these smaller particles give a high specific surface area which in turn increases filtration resistance. Karr and Keinath (1978) showed that the presence of particle sizes from 1 to 100 μ m is detrimental to dewaterability. This observation is corroborated by Nellenschulte and Kayser (1997) who found that an increase in fine suspended solids (or smaller particles) will reduce sludge and mixed liquor dewaterability as well as surface charge. Conventional anaerobic systems however have much larger granules present with most particles measuring between 800 and 1500 μ m as measured in chapter 5. Jin and Lant (2004) showed that larger particles contained more bound water and are therefore more difficult to dewater although their work was based on flocculent sludge. Results from all of these bodies of work suggest that there is an optimum particle size which ensures good dewaterability.

The particle sizes achieved in this study were not large enough or small enough to be detrimental to dewaterability as the range achieved was midway between those seen in conventional anaerobic systems and aerobic systems. Changes to particle size and therefore surface charge can potentially influence membrane fouling and performance in membrane bioreactors. Permeate flux decline strongly depends on the charge conditions of the membrane surface and the charge of the particles, molecules or ions in the feed solution since electrostatic repulsion (created by similar charges on membrane surface and feed solution) inhibits the formation of a flux reducing fouling layer on the membrane surface (Moritz *et al.*, 2001). Also, particles should be large enough to prevent intrinsic pore blocking but not large enough to cause too much of an increase in the resistance of the cake layer.

Viscosity and dewaterability of the mixed liquor affect membrane permeability as more viscous fluids and increased dewaterability will reduce permeate fluxes and are detrimental to membrane performance. The mixed liquor from the AnMBR in this study became less dewaterable and more viscous as mean particle size fell progressively with time. Subjecting the system to psychrophilic conditions appeared to increase CST and viscosity of the mixed liquor in the AnMBR.

A possible link between EPS, SMP and membrane fouling was established from results in previous chapters. However, the systems studied were only minimally representative of real life situations due to their small size and the use of synthetic substrates or no substrate at all in the said systems. On continuous operation of the large scale AnMBR, differences were noted in the amounts of EPS and SMP present in the mixed liquor compared with previous results from chapters 5 and 6 of this thesis. Concentrations were much lower than previously determined and concentrations of both types of microbial products (EPS and SMP) generally fell with time. 9 to 20 mgL⁻¹ of SMP was produced per unit mass of biomass, slightly lower than reported for aerobic systems (15 to 25mgL⁻¹ per g of biomass) but comparable to anaerobic systems which will usually produce an average of 15.7mgL⁻¹ per g of biomass (Chudoba, 1985b). These results are in agreement with those of Kuo *et al.* (1996) and Germirli *et al.* (1993) who also agree that anaerobic systems produce lesser amounts of SMP than aerobic systems.

Average concentrations of EPS varied from 20 to 110mg per g of biomass, once again less than average aerobic concentrations of 50 to 125 mg per g of biomass (Sponza, 2002).

Both EPS and SMP showed small increases in concentration when operating temperature was dropped to make the system more psychrophilic. Analysis of results from previous chapters suggests that microbes produce SMP in response to environmental stress. It would therefore be expected that levels of this substance will increase when operating temperature is dropped below the optima of methanogenesis. The same trend was not observed in previous experiments on EPS. No direct relationship was found to exist between EPS and surrounding temperature. However, there is a strong correlation as seen in Table 7.23 (correlation matrix) between EPS and SMP. Both SMP_p and SMP_c show strong correlations greater than 0.7 to EPS_p and EPS_c respectively. Protein and carbohydrate fractions in both EPS and SMP are inextricably linked. Therefore, if environmental stress was to cause increased levels of SMP while the system is actively degrading substrate, then it follows that increased levels of EPS will be seen in the system. Many authors refer to SMP as soluble EPS as there is much difficulty in providing absolute definitions for each of these microbial substances. It may be said that some crossover exists between the two substances with some SMP contributing to EPS and vice versa. This statement is supported by Laspidou and Rittman (2002) who developed a unified theory stating that SMP (equivalent to soluble EPS where hydrolysis of particulate organics is unimportant) polymerises into EPS and EPS can be hydrolysed to SMP.

Further analysis of results show that as the AnMBR system entered into the stable phase, the ratio of Protein to carbohydrate present in both EPS and SMP generally decreased. However, slight increases were noted in the concentration of the protein fractions of these substances when the system was subject to lower operating temperature indicating that the protein fraction will increase in response to temperature as conditions become more psychrophilic. In contradiction to results from chapter 6, gas sparging appeared to have no effect on EPS and SMP concentrations despite the system being subject to increased gas sparging rates during fouling tests.

These results while unexpected can be attributed to the relatively short amounts of time in which the system was subject to increased gas sparging rates. In addition, the system was subject to a base gas sparging rate throughout the entire period of operation except for the first two weeks of start-up. As a result, increase in shear stress which is responsible for the break up of biomass and increased EPS concentration (Zhou *et al.*, 2005), was minimal.

Results appear to highlight the strong dependency of membrane fouling on biomass characteristics. The highest correlation (>0.9) was assigned to the relationship between the organic fraction of SMP and membrane fouling indicating that the strongest membrane foulant is colloidal matter. SMP is a suitable indicator of colloidal matter as the latter has previously been linked to this microbial substance (Park *et al.*, 2005; Rosenberger *et al.*, 2006)). Membrane fouling rates in the AnMBR system were directly dependent on SMP levels present in the system. The parabolic relationship observed between SMP and membrane fouling in bench scale tests was repeated during operation of the pilot scale system whether in side-stream or submerged configuration. Results obtained in chapter 5 of this thesis also established total organic carbon (of which protein and carbohydrates are predominant components) as the fouling fraction of SMP. Rosenberger *et al.* (2006) attributes the retention of SMP by membranes to the formation of a secondary membrane with a relatively smaller pore size by bacteria and EPS. This is in agreement with all of the fouling results obtained during previous experiments. This author suggests that this secondary membrane is formed during the initial rapid fouling phase where there is deposition of biomass on the membrane surface. In contrast to previously published literature (Lee *et al.*, 2003; Police *et al.*, 2004; Rosenberger *et al.*, 2005), EPS barely affected fouling during AnMBR operation although the substance appeared to impact on fouling rates indirectly by its direct relationship with more important foulants such as SMP and MLSS.

Membranes used were also specific in the way SMP and colloidal matter fouled the membrane. Higher levels of carbohydrate were retained by the tubular side-stream membrane than the other two types of membranes utilised suggesting that the interaction of membranes with colloidal matter is dependent on membrane characteristics as well as amounts of colloidal matter present in the system. As previously stated, rejection factors for each of the organic fractions of SMP with respect to membrane type did not change so that higher fouling occurs in the presence of higher amounts of SMP.

For each of the membranes tested, fouling rates decreased with progressive increases in gas sparging rates providing further evidence that gas sparging is an effective fouling inhibitor in an anaerobic membrane bio-reactor. It has long been established that effective aeration reduces fouling in aerobic membrane bio-reactors. Ji and Zhou (2005) attribute this phenomenon to the resulting increased volatile suspended solids concentration produced on subjecting systems to increased aeration rates. However, in the case of the AnMBR studied during this project, there was no resulting effect on MLVSS or MLSS concentration. It is therefore hypothesised that decreased fouling rates observed are due to the sloughing of foulants of the membrane surface. As previously stated in chapter 6, crossflow velocity (in the case of side-stream membrane configuration) must be greater than particle settling velocity to increase foulant sloughing and prevent deposition and accumulation on the membrane surface. Extending this thinking to all membrane configurations and including gas flow velocity in the AnMBR, it can be said that the greater the gas flow velocity near the membrane surface, the less likely for foulants such as colloidal and bacterial matter to remain or stick to the membrane surface. Hence, the reduction in fouling rates observed in the system. Increased gas sparging rates also injects energy into the system transferring kinetic energy to particles in all microbial fractions, thereby reducing the energy barrier that would need to be exceeded to remove foulants and clean the membrane. It should be noted that although the anaerobic MBR appeared to be in the stable phase prior to the end of the experiments, it was run for a relatively short amount of time. It is possible that the observations noted may change the longer the system is run for.

For example, particle size distribution within the system may decrease even further due to the absence of hydraulic selection pressure within the system (Hulshoff Pol *et al.*, 1983; Lettinga *et al.*, 1980; Lettinga, 1995; Alphenaar *et al.*, 1995), organic matter and microbial substance concentrations may vary and fouling properties of anaerobic mixed liquors may then invariably be affected.

GENERAL DISCUSSION

8 GENERAL DISCUSSION

8.1 The Anaerobic Membrane Bioreactor vs. Conventional Anaerobic Treatment Technologies

Conventional anaerobic treatments such as the UASB and EGSB reactors have been widely used in the treatment of wastewaters. In general, these established anaerobic technologies have mainly been utilised in tropical climates for the treatment of municipal and domestic wastewaters. In temperate climates, where temperatures are below the optima for methanogenesis for most of the year, anaerobic treatment has been limited to high strength wastewaters such as industrial effluents and leachates.

Results from this thesis highlight the sensitivity of the anaerobic process to temperature and pH variation. Chapter 7 showed that a drop in temperature below the optima for methanogenesis (30 to 35°C) will result in a drop in pH. However, where there is adequate pH control, this drop is less severe with pH remaining within an acceptable range for methanogenesis to continue to occur. Without pH control, pH continues to fall so that the system eventually fails. Anaerobic systems are still unable to compete with their aerobic counterparts in terms of performance and flexibility at psychrophilic temperatures. COD removal in conventional anaerobic systems treating municipal or domestic wastewaters at low temperatures have typically averaged between 40 and 90% (Lagenhoff *et al.*, 2000; Dama *et al.*, 2002; Seghezzo *et al.*, 2002; Van der Last and Lettinga, 1992; Yu and Anderson, 1996) with most systems to date confined to lab and pilot scale. In contrast, conventional aerobic systems will typically achieve >95% removal in the treatment of dilute wastewaters with the added bonus that operating conditions are not constrained to such a narrow range.

The anaerobic membrane bioreactor utilised in this study was able to overcome many of the limitations typically experienced with conventional anaerobic systems. The incorporation of a membrane into the anaerobic bioreactor allowed sufficient time for biomass acclimatisation and so reduced biomass washout.

Evidence of this is shown by the consistent performance data obtained with the pilot scale system (80% to 97% COD removal) as well as the increased proportion of suspended solids attributed to volatile matter. Specific methanogenic activity was also higher in the case of the anaerobic MBR in this study when compared with conventional anaerobic systems. The pilot scale system was able to achieve SMAs of $0.20\text{gCOD-CH}_4\text{.gMLVSS}^{-1}$ to $0.24\text{gCOD-CH}_4\text{.gMLVSS}^{-1}$ in contrast to SMAs of 0.09 to $0.13\text{gCOD-CH}_4\text{.gMLVSS}^{-1}$ achieved by Seghezzo *et al.* (2002) while treating settled domestic sewage.

The main advantage that other anaerobic systems have had to date over the anaerobic membrane bioreactor is in the area of membrane fouling due to the absence of membranes in these systems. In all three results chapters, it was established that fouling of a membrane exposed to anaerobic biomass and mixed liquors can be attributed to colloidal matter as well as bacterial cells and other solid matter. While it is not yet possible to eradicate membrane fouling altogether, it is possible to attenuate fouling with the use of gas sparging (as shown in chapters 6 and 7). Gas sparging was able to reduce fouling in all systems utilised during this study irrespective of operating conditions. In addition, operating conditions such as pressure, temperature and pH were found to affect biomass and mixed liquor characteristics which in turn had an effect on membrane fouling. Results from all three chapters indicate that limiting SMP concentrations in the mixed liquor may improve fouling considerably.

8.2 Anaerobic Membrane Bioreactor vs. Aerobic Membrane Bioreactors

This study established significant differences between the anaerobic and aerobic MBR systems. While both incorporate membranes, the method in which these membranes became fouled is very different.

During this study, anaerobic biomass remained distinctly granular in all experiments in comparison to aerobic systems where biomass is flocculent (Germaine, 2004; Alvarez, 2005). Chapter 5 established that the increased compressibility and smaller particle size of aerobic mixed liquors in comparison to anaerobic mixed liquors was detrimental to maintenance of flux during continuous operation.

Aerobic systems generally had lesser amounts of SMP than the anaerobic system when both systems were not actively degrading substrates. However, this trend was reversed with continuous operation. SMP concentrations in the pilot scale anaerobic MBR were generally lower than SMP concentrations of aerobic systems in published literature. 9 to 20 mgL⁻¹ of SMP was produced per unit mass of biomass. Chudoba (1985b) reports that aerobic systems will usually produce 15 to 25mgL⁻¹ per g of biomass. In addition, biomass concentrations were lower in comparison to aerobic systems despite the consistent performance of the latter system. This is a significant advantage in the treatment of municipal and domestic wastewaters as the amounts of sludge for disposal is reduced. Results from chapter 5 highlighted the importance of the initial cake formed by anaerobic mixed liquors in attenuating fouling in these systems. Results from chapters 6 and 7 also established the existence of a rapid and slow fouling phase with the rapid fouling phase characterised by the formation of a cake layer and the slow fouling phase characterised by the travel of colloidal matter towards the membrane surface. All results appear to indicate that colloidal matter causes intrinsic pore blockage and therefore irreversible fouling (Cho and Fane, 2002). Chapter 6 appears to indicate that cake and solid deposition characterises sub-critical operation in anaerobic systems. This explains the high TMP values that were seen with the anaerobic system in comparison to aerobic systems. However, this type of fouling is reversible in contrast to aerobic systems where it has been established that solid deposition on the membrane surface usually characterises post-critical operation (Ognier *et al.*, 2004). The initial cake formed during the rapid fouling phase in anaerobic MBR systems is advantageous in trapping smaller organics in the mixed liquor which may cause intrinsic pore blockage. This advantage is lost with the aerobic system.

Several authors have investigated fouling attenuation with the use of gas sparging although much of the research has focused on the use of air in aerobic MBR systems (Germaine, 2004). Generally, fouling was reduced significantly in all systems studied during these experiments by the introduction of gas into the systems. In addition to reducing membrane fouling, gas sparging also increased turbulence and mixing efficiency within the membrane bioreactors whether at pilot scale or bench scale.

The main advantage the aerobic MBR has historically had over the anaerobic system is the versatility and flexibility of the process in that it can be used to treat a variety of wastewaters under a wide range of operating conditions. The anaerobic MBR system in this study however suffered a lesser degree of irreversible fouling in comparison to published work on aerobic MBRs. In addition, a relatively high performance was obtained while using the process to treat settled domestic sewage, a dilute wastewater. Performance of the system was indeed comparable to aerobic systems despite changes to operating conditions. Although a drop in temperature initially reduced COD removal by approximately 10%, the system recovered and stabilised so that even at temperatures as low as 12°C, final treatment efficiencies were >90%.

Fouling of the membranes when in submerged configuration appears to be lower than in side-stream configuration as seen in chapters 6 and 7. The same trend is seen with aerobic systems (Judd, 2004). Ghosh and Cui (1999) attribute this difference (in the presence of gas sparging) to improved mass transfer and higher permeabilities as a result of shear at the membrane surface.

Table 8.27: Anaerobic MBRs vs. Aerobic MBRs and Conventional Anaerobic Systems.

| Reactor/Treatment Type | HRT (hours) | COD _{inf} (mgL ⁻¹) | Operating Temperature (°C) | COD removal (%) | Reference |
|--------------------------------|-------------|---|----------------------------|-----------------|----------------------------------|
| Anaerobic Membrane Bioreactor | 5.6-6.4 | 200-700 | 12-35 | 82-97 | This study |
| | 2.2-6.48 | 350-490 | 30-35 | 83-90 | Kataoka <i>et al.</i> , 1992 |
| | 7.2 | 400 | 25-28 | 73 | Kiriyama <i>et al.</i> , 1992 |
| Conventional Anaerobic Systems | | | | | |
| Anaerobic Baffled Reactor | 20 | 350-1200 | 30-35 | 70-90 | Dama <i>et al.</i> , 2002 |
| UASB | 2-9 | 152.6 | 22 | 70-80 | Seghezze <i>et al.</i> , 2002 |
| EGSB | 1-3.5 | 391 | 13-19 | 16-34 | Van der Last and Lettinga, 1992. |
| Aerobic MBR | 11.5-17 | 105-532 | - | 89-97.2 | Germaine, 2004 |
| | 8 | 100-420 | - | 54-83 | Alvarez, 2005 |

8.3 The Anaerobic Membrane Bioreactor: A Credible Alternative for the Treatment of Municipal and Domestic Wastewaters at Low Temperatures?

Results from chapters 6 and 7 indicate the possibility of using anaerobic MBR technology for the treatment of domestic or other dilute wastewaters under psychrophilic conditions. The anaerobic membrane bioreactor allows a wider window of application for anaerobic treatment. For example, problems which have historically limited the use of anaerobic technology such as failure of the system at low temperatures and slow responses where there has been toxic shock, can be overcome by the incorporation of a membrane into the anaerobic bioreactor.

While fouling has consistently been a problem with all membrane bioreactors, this phenomenon is successfully inhibited by gas sparging, and adequate mixing in the system.

The anaerobic MBR has one major advantage over the aerobic MBR in that it produces methane which can be converted into recoverable energy. There is potential for electricity consumption by membranes to be offset by this reusable energy. As a result, the process is less energy intensive and may reduce the relatively high costs which have historically been associated with the installation and operation of MBR systems. However, the reduction in typical capital and operating costs should be weighed against the cost of technology required for the conversion of produced biogas into energy.

CONCLUSIONS

9 CONCLUSIONS

- Anaerobic biomass is significantly different from aerobic biomass. Aerobic sludge and mixed liquors are usually flocculent in contrast to the granules which are normally found in anaerobic wastewater treatment systems. Particle sizes are generally higher in anaerobic mbr systems. As a result, anaerobic mixed liquors are more dewaterable than mixed liquors in aerobic mbrs under continuous operation. In addition EPS and SMP levels differed between the two types of MBR systems. SMP levels were relatively lower in anaerobic mbrs in comparison to aerobic mbrs under continuous operation. Temperature, pH, wastewater/substrate type were also found to affect mixed liquor properties and microbial substance concentrations. A drop in temperature, pH or a change to substrate type appears to cause the release of microbial substances as a response to environmental stress.
- A high COD removal of >90% was achieved even at temperatures as low as 12°C despite the use of anaerobic biomass initially acclimatised to temperatures of 30 to 35°C as inoculum. Results were consistent irrespective of membrane configuration suggesting that the system was successful in forcing the acclimatisation of anaerobes to psychrophilic temperatures.
- Membrane fouling is affected by biomass characteristics. The assessment of fouling in anaerobic and aerobic systems indicates that membranes in the two types of systems foul differently. Both systems are fouled by a combination of microbial substances and bacterial cells. It appears that membranes exposed to anaerobic mixed liquors are fouled initially by bacterial cells before fouling with colloidal matter. In contrast, membranes in aerobic systems appear to be fouled firstly by colloidal matter before being fouled with bacterial cells. Colloidal matter is a major foulant in both the anaerobic and aerobic mbr system. Fouling within the anaerobic membrane bioreactor showed a parabolic relationship to colloidal matter present in the mixed liquor. EPS appeared to have little or no effect on membranes in anaerobic systems except as far as its correlation with SMP levels within the system.

- Fouling rates were found to decrease at all times when gas was introduced into the anaerobic system whether in side-stream or submerged configuration. The same effect is seen in aerobic mbr systems. Indications are that a reduction in fouling is brought about by higher shear rates and sloughing of foulants from the membrane surface. In addition, inducing turbulence increases kinetic energy of particles thereby reducing the energy barrier required to remove cells from the membrane surface.
- Operating conditions influence process efficiency and performance in AnMBRs with drops in temperature and pH resulting in reduced COD removal and methanogenic activity. However, the anaerobic MBR is able to operate at lower temperatures provided that there is adequate pH control, all other operating conditions (such as MLSS and MLVSS concentrations) are favourable and the system is given enough time to stabilise.

FUTURE WORK

10 FUTURE WORK

- The system was run for a relatively short period. It is possible that imposing longer acclimatisation periods such as twice the SRT may change the system characteristics and properties. The system should be run with a longer acclimatisation phase to determine whether this is the case.
- Fouling was found to take place in two consecutive phases-rapid and slow. The exact reasons for the existence of these two phases were not investigated during this study. Experiments should be carried out in order to determine the reasons for the existence of these two phases as further knowledge of these phases may be helpful in trying to identify novel methods for fouling amelioration.
- The difference in fouling mechanisms between the aerobic and anaerobic membrane bioreactor were established with initial fouling in the former taking place via the pore blocking model and the latter via the cake filtration model. However, results were based on short term experiments. It will be useful to know if these models and mechanisms hold true in the long term.
- It has been established that colloidal matter and microbial substances are major foulants in the anaerobic membrane bioreactor. In addition, it was established that SMP is released in reaction to environmental stress. However, there is still much unknown about the exact mechanisms behind the formation of these compounds. Methods by which concentrations of these substances may be kept at minimum levels (in spite of system stress) should be identified.
- The pilot scale AnMBR used in this study consistently achieved high treatment efficiencies. However, the system may be scaled up in order to determine if these results are replicable at full scale in the long term.

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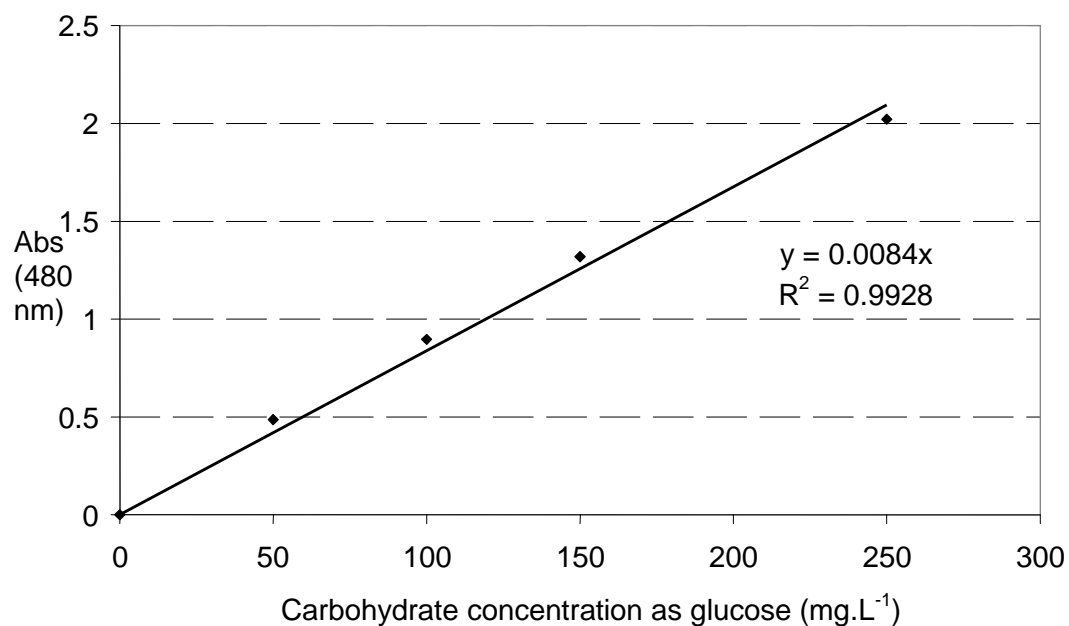
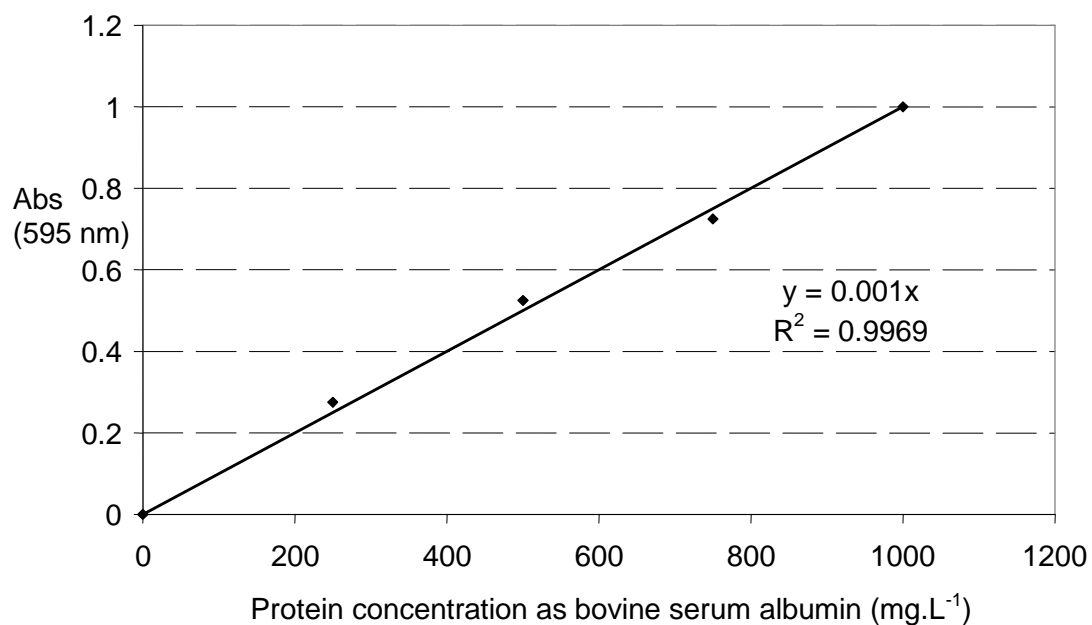
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APPENDICES

Appendix A CALIBRATION CURVES FOR EPS ANALYSIS**Figure A.1: Carbohydrate Calibration Curve****Figure A.2: Protein Calibration Curve**

Appendix B CLASSIC FILTRATION LAWS

Two classic filtration laws were originally developed by Hermia (1982) to describe dead end filtration (Table 1). These models can be further applied to continuous filtration at constant pressure.

Table B.1: Classic filtration laws

| Law | Equation | Description |
|-----------------|------------------------|---|
| Cake Filtration | $t/V = aV + b$ | Deposition of particles larger than membrane pore size onto the membrane surface resulting in cake formation. |
| Pore Blocking | $\frac{t}{V} = at + b$ | Reduction of membrane pore size by deposition of particles smaller than membrane pore size onto pore walls with particle overlay. |