EVALUATION OF FLUIDISED-BED REACTORS FOR THE BIOLOGICAL TREATMENT OF SYNTHOL REACTION WATER, A HIGH-STRENGTH COD PETROCHEMICAL EFFLUENT

by

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This work is dedicated to my parents.
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"Imagination is more important than knowledge"

- Albert Einstein

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The study represents original work undertaken by the author and has not been previously submitted for degree purposes to any other university. Appropriate acknowledgments in the text have been made where the use of work conducted by other researchers has been included.

Katharine Gaenor Aske Swabey

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Language and style used in this dissertation are in accordance with the requirements of the Journal of Water Science and Technology.

This dissertation represents a compilation of manuscripts, where each chapter is an individual entity and some repetition between the chapters has been unavoidable.

Abbreviations Used in this Dissertation

AOPs	Advanced Oxidation Processes
API	Oily Sewer Water
BAF	Biological Aerated Filters
BFBRs	Biological Fluidised-Bed Reactors
BOD	Biological Oxygen Demand
CMA	Catchment Management Agencies
C:N	Carbon and Nitrogen Ratio
C:N:P	Carbon, Nitrogen and Phosphate Ratio
COD	Chemical Oxygen Demand (mg/L)
D_{eq}	Equivalent Diameter
DGGE	Denaturing Gradient Gel Electrophoresis
dO_2	Dissolved Oxygen (mg/L)
DO	Dissolved Oxygen Concentration (mg/L)
DWAF	Department of Water Affairs and Forestry
EPS	Extracellular Polysaccharides
Ft	Feet
GAC	Granular Activated Carbon
$\Delta G^{0'}$	Change in Gibb's Free Energy
HRCR	High-rate compact reactor
HRTs	Hydraulic Retention Times
ICT	Intercatchment Transfer
IW	Industrial Waters
NEMA	National Environmental Management Act
NF	Nitrification
NWA	National Water Act
OD	Diameter
OLR	Organic Loading Rate
OSBG	Optimised Support of Biological Growth

PAC	Powdered Activated Carbon
PVC	Polyvinyl Chloride
RBC	Rotating Biological Contactor
SBR	Sequencing Batch Reactor
SEM	Scanning Electron Microscope
SGL	Stripped Gas Liquor
SOCs	Synthetic Organic Chemicals
SSF	SASOL Synthetic Fuels, Secunda, South Africa
STP	Standard Temperature and Pressure
SVI	Sludge Volume Index
TF	Trickling Filters
TS	Total Solids (mg/g)
TSS	Total Suspended Solids (mg/L)
TT	Tertiary Treatment
UASB	Up-flow Anaerobic Sludge Blanket
UCT	University of Cape Town
UFC	Uniformity Coefficient
USBR	Up-flow Sludge Blanket Reactor
UV	Ultraviolet
UW	Urban Waters
VFA	Volatile Fatty Acids (mg/L)
VOC	Volatile Organic Carbon
VS	Volatile Solids (mg/g)
VSS	Volatile Suspended Solids (mg/L)

Summary

Reaction water, a high-strength COD (chemical oxygen demand) petrochemical effluent, is generated during the Fischer-Tropsch reaction in the SASOL Synthol process at SASOL SynFuels, Secunda, South Africa. Distillation of the reaction water to remove non- and oxygenated hydrocarbons yields approximately 25 - 30 ML/d of an organic (carboxylic) acid-enriched stream (average COD of 16 000 mg/L) containing primarily C_2 - C_5 organic acids, light oils, aldehydes, ketones, cresols and phenols. Together with the Oily sewer water (API) and Stripped Gas Liquor (SGL) process streams, this process effluent is currently treated in ten dedicated activated sludge basins. However, the successful operation of these activated sludge systems has proven to be difficult with low organic loading rates (3.5 kg COD/m^3.d), low COD removal efficiencies (< 80 %) and high specific air requirements (60 – 75 m^3 air/kg COD_{rem}). It is hypothesised that these operational difficulties can be attributed to organic shock loadings, variation in volumetric and hydraulic loadings, as well as variations in the composition of the various process streams being treated. Due to the fact that the Fischer-Tropsch (Synthol) reaction water constitutes 70 % of the COD load on the activated sludge systems, alternative processes to improve the treatment cost and efficiency of the Fischer-Tropsch acid stream are being investigated. Various studies evaluating the aerobic and anaerobic treatment of Fischer-Tropsch reaction water alone in suspended growth wastewater treatment systems have proven unsuccessful. High rate fixed-film processes or biofilm reactors, of which the fluidised-bed reactors are considered to be one of the most effective and promising processes for the treatment of high-strength industrial wastewaters, could be a suitable alternative. The primary aim of this study was to evaluate the suitability of biological fluidised-bed reactors (BFBRs) for the treatment of Fischer-Tropsch reaction water.

During this study, the use of aerobic and anaerobic biological fluidised-bed reactors (BFBR), using sand and granular activated carbon (GAC) as support matrices, were evaluated for the treatment of a synthetic effluent analogous to the Fischer-Tropsch reaction water stream. After inoculation, the reactors were operated in batch mode for 10 days at a bed height expansion of 30 % and a temperature of 30 °C to facilitate biofilm

formation on the various support matrices. This was followed by continuous operation of the reactors at hydraulic retention times (HRTs) of 2 days. While the COD of the influent and subsequent organic loading rate (OLR) was incrementally increased from 1 600 mg/L to a maximum of 20 000 mg/L and 18 000 mg/L for the aerobic and anaerobic reactors, respectively. Once the maximum influent COD concentration had been achieved the OLR was further increased by decreasing the HRTs of the aerobic and anaerobic reactors to 24 h and 8 h, and 36 h, 24 h and 19 h, respectively. The dissolved O_2 concentration in the main reactor columns of the aerobic reactors was constantly maintained at 0.50 mg/L.

Chemical Oxygen Demand (COD) removal efficiencies in excess of 80 % at OLR of up to 30 kg COD/m^3.d were achieved in the aerobic BFBRs using both sand and GAC as support matrices. Specific air requirements were calculated to be approximately 35 and 41 m^3 air/kg COD_{rem} for the BFBRs using sand and GAC as support matrices, respectively. The oxygen transfer efficiency was calculated to be approximately 5.4 %. At high OLR (> 15 kg COD/m^3.d) significant problems were experienced with plugging and subsequent channeling in the BFBR using GAC as support matrix and the reactor had to be backwashed frequently in order to remove excess biomass. Despite these backwash procedures, COD removal efficiencies recovered to previous levels within 24 hours. In contrast, no significant problems were encountered with plug formation and channeling in the BFBR using sand as support matrix. In general the overall reactor performance and COD removal efficiency of the aerobic BFBR using sand as support matrix was more stable and consistent than the BFBR using GAC as support matrix. This BFBR was also more resilient to variations in operational conditions, such as the lowering of the hydraulic retention times and changes in the influent pH. Both aerobic reactors displayed high resilience and COD removal efficiencies in excess of 80 % were achieved during shock loadings. However, both reactors were highly sensitive to changes in pH and any decrease in pH below the pKa values of the volatile fatty acids in the influent (pKa of acetic acid = 4.76) resulted in significant reductions in COD removal efficiencies. Maintenance of reactor pH above 5.0 was thus an essential facet of reactor operation.

It has been reported that the VFA/alkalinity ratio can be used to assess the stability of biological reactors. The VFA/alkalinity ratios of the aerobic BFBRs containing sand and GAC as support matrices were stable (VFA/alkalinity ratios of < 0.3 - 0.4) until the OLR increased above 10 kg/m^3.d. At OLRs higher than 10 kg/m^3.d the VFA/alkalinity ratios in the BFBR using sand support matrix increased to 4, above the failure limit value of 0.3 - 0.4. In contrast the VFA/alkalinity ratios of the BFBR using GAC support matrix remained stable until an OLR of 15 kg/m^3.d was obtained, where the VFA/alkalinity ratios then increased to > 3. Towards the end of the study when an OLR of approximately 25 kg/m^3.d was obtained the VFA/alkalinity ratios of both the BFBRs using sand and GAC as support matrices increased to 9 and 6 respectively, indicating the decrease in reactor stability and acidification of the process. Total solid (TS) and volatile solid (VS) concentrations in the aerobic BFBRs were initially high and decreased over time. While the total suspended solids (TSS) and volatile suspended solids (VSS) concentrations were initially low and increased over time as the OLR was increased, this is thought to be as a result of decreased HRT leading to biomass washout.

The anaerobic BFBR using sand as support matrix never stabilised and COD removal efficiency remained very low (< 30 %), possibly due to the high levels of shear forces. Further studies concerning the use of sand as support matrix were subsequently terminated. An average COD removal efficiency of approximately 60 % was achieved in the anaerobic BFBR using GAC as a support matrix at organic loading rates lower than 10 kg COD/m^3.d. The removal efficiency gradually decreased to 50 % as organic loading rates were increased to 20 kg COD/m^3.d. At OLRs of 20 kg COD/m^3.d, the biogas and methane yields of the anaerobic BFBR using GAC as support matrix were determined to be approximately 0.38 m^3 biogas/kg COD_{rem} (0.3 m^3 biogas/$m^3_{reactor\ vol}$.d), and 0.20 m^3 CH_4/kg COD_{rem} (0.23 m^3 CH_4/$m^3_{reactor\ vol}$.d), respectively. This value is 57 % of the theoretical maximum methane yield attainable (3.5 m^3 CH_4/kg COD_{rem}). The methane yield increased as the OLR increased, however, when the OLR reached 8 kg/m^3.d the methane yield leveled off and remained constant at approximately 2 m^3 CH_4/$m^3_{reactor\ vol}$.d. Although the methane content of the biogas was initially very low (< 30 %), the methane content gradually increased to 60 % at OLRs of 20 kg COD/m^3.d. The anaerobic BFBR

using GAC as support matrix determined that as the OLR increased (> 12 $kg/m^3.d$), the VFA/alkalinity ratio increased to approximately 5, this is indicative of the decrease in stability and acidification of the process. The anaerobic BFBR using GAC as support matrix experienced no problems with plug formation and channeling. This is due to the lower biomass production by anaerobic microorganisms than in the aerobic reactors. The TS and VS concentrations were lower than the aerobic concentrations but followed the same trend of decreasing over time, while the TSS and VSS concentrations increased due to decreased HRTs. The anaerobic BFBR was sensitive to dramatic variations in organic loading rates, pH and COD removal efficiencies decreased significantly after any shock loadings.

Compared to the activated sludge systems currently being used for the biological treatment of Fischer-Tropsch reaction water at SASOL SynFuels, Secunda, South Africa, a seven-fold increase in OLR and a 55 % reduction in the specific air requirement was achieved using the aerobic BFBRs. The methane produced could also be used as an alternative source of energy. It is, however, evident that the support matrix has a significant influence on reactor performance. Excellent results were achieved using sand and GAC as support matrices in the aerobic and anaerobic BFBRs, respectively. It is thus recommended that future research be conducted on the optimisation of the use of aerobic and anaerobic BFBRs using these support matrices.

Based on the results obtained from this study, it can be concluded that both aerobic and anaerobic treatment of a synthetic effluent analogous to the Fischer-Tropsch reaction water as generated by SASOL in the Fischer-Tropsch Synthol process were successful and that the application of fluidised-bed reactors (attached growth systems) could serve as a feasible alternative technology when compared to the current activated sludge treatment systems (suspended growth) currently used.

Keywords: aerobic treatment, anaerobic treatment, biological fluidised-bed reactors, petrochemical effluent, Fischer-Tropsch reaction water, industrial wastewater.

Opsomming

Reaksiewater, 'n hoë-sterkte CSB (Chemiese suurstofbehoefte) petrochemiese afvalwater, word tydens die Fischer-Tropsch reaksie in die SASOL Synthol proses, gegenereer. Distillasie van die reaksiewater om nie-koolwaterstowwe en geoksigeneerde koolwaterstowwe te verwyder, lewer 'n afvalwaterstroom van ongeveer 25 - 30 ML/d wat verryk is met C_2 - C_5 organiese sure, aldehiede, ketone, kresols en fenole (met 'n gemiddelde CSB van 16 000 mg/L). Hierdie afvalwaterstroom word tesame met olierige afvalwater (API) en gestroopte-gasvloeistof (SGL) behandel in tien groot geaktiveerde slykdamme. Die suksesvolle bedryf van die geaktiveerde slykstelstel is egter baie problematies as gevolg van lae organiese lading tempo's (3.5 kg CSB/m^3.d), lae CSB verwyderingseffektiwiteit (< 80 %) en hoë spesifieke lug behoefte (60 - 75 m^3 lug/kg $CSB_{verwyder}$). Die hipotese is dat hierdie operasionele probleme primêr te wyte is aan die organiese skok ladings, variasies in volumetriese en hidroliese ladings asook variasies in die samestelling van die verskeie prosesstrome van behandel word. Weens die feit dat die SASOL Fischer-Tropsch reaksiewater 70 % van die CSB lading tot die geaktiveerde slykstelsels bydra, word alternatiewe prosesse om die behandelingskoste en –effektiwiteit te verbeter, ondersoek. Verskeie studies voortydens die aërobe en anaërobe behandeling van SASOL Fischer-Tropsch reaksiewater alleen in gesuspendeerdegroei afvalwaterbehandelingstelsels bestudeer is, was onsuksesvol. Hoë-tempo vaste-film prosesse of biofilmreaktors, waarvan opvloei-bed-reaktors as die mees effektiewe en belowende prosesse beskou word, kan 'n moontlike alternatiewe tegnologie wees om die afvalwater te behandel. Die primêre doel van hierdie projek is om die geskiktheid van biologiese opvloei-bed-reaktors (BOBRs) vir die behandeling van Fischer-Tropsch reaksiewater te evalueer.

Tydens hierdie projek is die gebruik van aërobe en anaërobe biologiese opvloei-bed-reaktors (BOBRs) met sand en geaktiveerde koolstof as ondersteuningsmatrikse, vir die behandeling van 'n sintetiese afvalwater analoog aan die Fischer-Tropsch reaksiewaterstroom, geëvalueer. Na inokulasie, is die reaktors in 'n lot-toestand vir 10 dae bedryf om biofilmvorming op die verskeie ondersteuningsmatrikse te bewerkstellig.

Dit is opgevolg deur kontinue bedryf van die reaktors met 'n hidroliese retensie tyd (HRT) van 2 dae, 'n bed-hoogte van 30 % en 'n temperatuur van 30 °C, terwyl die CSB van die toevoer en gepaardgaande organiese ladingstempo stapsgewys verhoog is vanaf 1 600 mg/L tot 'n maksimum van 20 000 mg/L vir die aërobe reaktors en 18 000 mg/L vir die anaërobe reaktors. Met die daarstel van die maksimum CSB konsentrasie is die organiese ladingstempo (OLT) verder verhoog deur die hidroliese retensie tyd te verlaag van 24 h tot 8 h by die aërobe BOBRs, en by die anaërobe BOBRs vanaf 36 h na 24 h tot 19 h. Die lugtoevoer in die aërobe reaktors is voortdurend by 'n opgeloste O_2 konsentrasie van 0.50 mg/L in die hoof reaktorkolomme gehandhaaf.

Met die verloop van die projek is CSB verwyderingstempo's van meer as 80 % verkry met organiese ladingstempo's van tot 30 kg CSB/m^3.d in die BOBRs vir beide die sand en geaktiveerde koolstof as ondersteuningsmatrikse. Spesifieke lugbehoeftes is bereken as ongeveer 35 en 41 m^3 lug/kg $CSB_{verwyder}$ vir die BOBRs met sand en granulêre geaktiveerde koolstof ondersteuningsmatrikse, onderskeidelik. Die suurstofoordrag effektiwiteit is bereken as ongeveer 5.4 %. Aansienlike probleme is ondervind met geaktiveerde koolstof as 'n ondersteuningsmatriks in die reaktor by hoë organiese ladingstempo's (> 15 kg CSB/m^3.d). Prop- en kanaalvorming, as gevolg van 'n oormaat biomassa, het gereeld plaasgevind wat die teruwas ven die matrikse veries het om die oortollige biomassa t verwyder. Die CSB verwyderingstempo's het telkens binne 24 uur na 'n wasstap herstel, na vlakke soos voor die wasstap. Hierteenoor is geen probleme in terme van prop- en kanaalvorming met sand as ondersteuningsmatriks in die aërobe reaktors ondervind nie. In die geheel beskou was reaktor-werksverrigting en CSB verwydering meer stabiel en eweredig in die aërobe reaktor met sand in vergelyking met geaktiveerde koolstof. Verder was die aërobe BOBR meer tolerant vir variasies in operasionele toestande soos verlaging van die hidroliese retensie tyd en veranderinge in die pH van die toevoer. Beide reaktors het goeie verdraagsaamheid vir skokladings getoon en CSB verwyderingstempo's van meer as 80 % is deurentyd gehandhaaf. Die reaktors was albei egter baie gevoelig vir veranderinge in die pH. Enige veranderinge onder die pKa waardes van die vlugtige organiese sure in die toevoer (pKa van asynsuur = 4.76), het 'n drastiese verlaging veroorsaak in die verwyderingseffektiwiteit van die

reaktors. Die handhawing van reaktor pH bo 5.0 is dus 'n uiters belangrike deel van die reaktor se bedryf.

Literatuur vermeld dat die VVS/alkaliniteit verhouding (vlugtige vetsure:alkaliniteit) gebruik kan word om die stabiliteit van biologiese reaktors te evalueer. Die VVS/alkaliniteit verhoudings vir die aërobe BOBR met sand en granulêre geaktiveerde koolstof was stabiel (VVS/alkaliniteit verhouding < 0.3 – 0.4) tot dit verhoog is tot vlakke bo 10 kg/m^3.d. By organiese ladings tempo's hoër as 10 kg/m^3.d het die VVS/alkaliniteit verhouding van die BOBR met sand toegeneem tot 4, aansienlik hoër as die algemene limiet van 0.3 – 0.4. In kontras hiermee was die VVS/alkaliniteit van die BOBR met granulêre geaktiveerde koolstof, stabiel tot 'n organiese ladings tempo van 15 kg/m^3.d oorskry is, waarna die VVS/alkaliniteit verhouding gestyg het tot > 3. Teen die einde van die ondersoek was 'n organiese ladings tempo van ongeveer 25 kg/m^3.d bereik, vir beide die BOBRs met sand en granulêre geaktiveerde koolstof, en het die VVS/alkaliniteit verhouding toegeneem tot 9 en 6, onderskeidelik, wat aanduidend is van versuring van die proses en 'n verlaging in reaktor stabiliteit.

Totale soliedes (TS) en vlugtige soliedes (VS) konsentrasies in die aërobe BOBRs was aansienlik hoog en het gedaal teenoor tyd. Hierteenoor was totale gesuspenderde soliedes (TSS) en vlugtige gesuspenderde soliedes (VSS) konsentrasies aansienlik laag en het toegeneem teenoor tyd soos die organiese ladings tempo toegeneem het. Dit kan moontlik toegeskryf word aan verlaging in die hidroliese retensie tyd wat lei tot uitwas van biomassa.

Die anaërobe BOBR met sand het nooit gestabiliseer en die CSB verwyderingseffektiwiteit het baie laag gebly (< 30 %), moontlik as gevolg van hoë vlakke van wrywingskragte. Verdere ondersoeke op hierdie BOBR is gevolglik gestop vir die anaërobe reaktor is gevolglik gestop. 'n Gemiddelde CSB verwyderingseffektiwiteit van ongeveer 60 % was behaal in die anaërobe BOBR met granulêre geaktiveerde koolstof met organiese lading tempo's laer as 10 kg CSB/m^3.d. Die verwyderingseffektiwiteit het geleidelik gedaal tot 50 % namate die organiese lading

tempo's tot 20 kg CSB/m^3.d verhoog is. By organiese lading tempo's van 20 kg CSB/m^3.d was die biogas- en metaanopbrengs van die anaërobe BOBR met granulêre geaktiveerde koolstof bereken as ongeveer 0.38 m^3 biogas/kg $CSB_{verwyder}$ (0.3 m^3 biogas/$m^3_{reaktor\ vol}$.d), en 0.20 m^3 CH_4/kg $CSB_{verwyder}$ (0.23 m^3 $CH_4/m^3_{reaktor\ vol}$.d), onderskeidelik. Laasgenoemde waarde is 57 % van die teoretiese maksimum metaanopbrengs haalbaar (0.35 m^3/g $CSB_{verwyder}$). Die metaanopbrengs het toegeneem soos die organiese lading tempo toegeneem het, maar wanneer 'n organiese lading tempo van 8 kg/m^3.d oorskry was, het die metaanopbrengs afgeplat tot ongeveer 2 m^3 $CH_4/m^3_{reaktor\ vol}$.d. Alhoewel die metaan inhoud van die biogas aanvanklik baie laag was (< 30 %), het die metaan inhoud geleidelik toegeneem tot 60 % by organiese lading tempo's van 20 kg CSB/m^3.d. Die anaërobe BOBR met granulêre geaktiveerde koolstof het getoon dat indien die organiese lading tempo verhoog (> 12 kg/m^3.d), die VVS/alkaliniteit verhouding verhoog na 5, wat 'n aanduiding is van 'n verlaging in stabiliteit en versuring van die proses. Die anaerobe BOBR met granulêre geaktiveerde koolstof het geen probleme getoon met prop- en kanaalvorming. Dit is te wyte aan laer biomassa produksie deur anaerobe mikro-organismes in vergelyking met mikro-organismes in die aerobe reaktors. Die TS en VS konsentrasies was laer as in die aërobe reaktors, maar het dieselfde tendens oor tyd gevolg, terwyl VSS en TSS konsentrasies voortdurend toegeneem het soos die hidroliese retensie tyd verminder is. Die anaërobe reaktor was egter uiters gevoelig vir drastiese variasies in die organiese ladingstempo's en pH. Aansienlike verlaging in die verwyderingeffektiwiteit is waargeneem met skok-ladings.

In vergelyking met geaktiveerde slykstelsels wat tans gebruik word vir die biologiese behandeling van Fischer-Tropsch reaksiewater by SASOL SynFuels, Secunda, Suid Afrika, is 'n sewevoudige toename in organiese ladingstempo's en 'n 55 % verlaging in die spesifieke lugbehoefte bereik met die aërobe BOBR. Die metaan kan ook as 'n alternatiewe bron van energie gebruik word. Dit is egter duidelik en opvallend dat die keuse van ondersteuningsmatriks 'n beduidende invloed op reaktor werksverrigting het. Uitstekende resultate is verkry met sand en granulêre geaktiveerde koolstof in die aerobe en anaerobe BOBRs, onderskeidelik. Dit word dus aanbeveel dat toekomstige navorsing

nodig is vir die optimalisering van die gebruik van aërobe en anaërobe BOBR met hierdie ondersteuningsmatrikse.

Gebaseer op die resultate verkry tydens hierdie projek, kan die gevolgtrekking gemaak word dat beide aerobe en anaerobe behandeling van 'n sintetiese afvalwater analoog aan die Fischer-Tropsch reaksiewater wat deur SASOL gegenereer word tydens die Fischer-Tropsch Synthol proses, met opvloei-bedreaktors suksesvol was en dat opvloei-bed-reaktors (gehegte groei) kan dien as 'n vatbare alternatiewe tegnologie in vergelyking met die geaktiveerde slykstelsel (gesuspendeerde groei) wat tans gebruik word.

Sleutelwoorde: aërobe behandeling, anaërobe behandeling, biologiese opvloei-bed-reaktors, petrochemiese afvalwater, Fischer-Tropsch reaksiewater, industriële afvalwater.

Chapter 1

Introduction

1. Introduction

Water is the most basic requirement for all living ecosystems and habitats. It affects everything and everyone and is affected by everything (Hoffman, 2000). However, water is not as abundant as originally thought (Bouler, 1999). In 1999 the United Nations published high, medium and low population projections for all countries. The low and medium projections are considered the more realistic values. The medium projections estimate that the world population will reach an estimated 7.8 billion people by the year 2025 and will continue to increase in the future. The low projection of the world population is estimated at 7.3 billion people in the year 2025 but will cease increasing around the year 2040 at approximately 7.5 billion people (Seckler and Amarasinghe, 1999). Statistics indicate that at this time the majority of the world's population will be living in urban areas. This will result in significant competition for fresh water resources for urban and industrial development. Currently the flow of fresh water is decreasing rapidly, while the amount of pollution is increasing (Seckler and Amarasinghe, 1999).

In the Southern African region the water distribution is currently uneven, some areas have abundant water supplies, while others have serious water scarcities (Global Water Partnership, 2000). In South Africa the water demand is projected to increase by 3 % annually and it is anticipated that by the year 2020 South Africa will suffer severe water stress (Sherman, 2001). Due to water pollution occurring through increased industrialisation and urbanisation the lack of fresh water resources of suitable quality is becoming more pronounced. In South Africa legislation has been designed to control the amount of pollution being released into the natural receiving water bodies (Whalmsley, 2000). With due consideration of the assimilative capacity of the respective water body this legislation demands strict discharge standards in order to achieve the target water

quality objectives as set by the Department of Water Affairs and Forestry (DWAF) and the respective Catchment Management Agencies (CMAs). In the pursuit of these objectives the need for developing industrial wastewater treatment processes has emerged (Ochieng *et al.*, 2003). Industries consume a large amount of water and as a result water shortages have become a limiting factor for the establishment of new industries or the expansion of already existing industries. In order to conserve water, industries have recently begun reusing this natural resource by recycling the water internally in their plants and using it as process cooling water (Mohsen and Jaber, 2002). Depending on the required water quality, the water may be treated before re-use. Biological and chemical treatment processes are frequently used to treat industrial waste effluents. The choice of either biological or chemical treatment methods for industrial wastewaters is based on the composition of the water as well as the required water quality (Ochieng *et al.*, 2003).

Chemical processes have been developed to remove heavy metals from wastewater and are used for the advanced treatment of wastewater (Tchobanoglous *et al.*, 2003). Chemical treatment methods involve chemical reactions in order to bring about a change in the quality of the wastewater. Typically chemicals are added to the wastewater being treated to bring about this change (Tchobanoglous and Schroeder, 1987). However, the use of chemicals in treating wastewater generally results in an increase in the salt concentration of the effluent, which if released into river systems will result in increased levels of salinisation (Mohsen and Jaber, 2002). Chemical treatment is also expensive, prohibiting the general application of this treatment process (Hosten, 1989). An alternative to chemical treatment is the application of biological treatment methods. There are three main types of biological treatments used for wastewater treatment, these include aerobic processes in which the microorganisms have access to oxygen, the anoxic process which operates on limited oxygen and anaerobic processes in the which the microorganisms do not have access to oxygen. Previously aerobic systems were extensively used in wastewater treatment, as anaerobic systems were considered unreliable. However, more recently anaerobic systems are increasingly being used, primarily due to an improved understanding of these biological systems (Fitzgerald, 1996). Biological treatment processes are generally less expensive than chemical

processes and generally do not produce any effluents harmful to the environment. However, biological systems are extremely sensitive to environmental parameters, such as pH, temperature, etc., which may affect their treatment efficiencies (Chong *et al.*, 1997).

Various biological technologies are used in wastewater treatment. The biological processes for the wastewater treatment are divided into two major categories according to the nature of the bacterial growth (Lazarova and Manem, 1994). These categories include suspended culture systems, in which flocculated bacteria are grown in suspension and attached or fixed-film culture systems in which the growth of bacteria in biofilm occurs on the surfaces of solid media (Cooper, 1981; Cooper and Williams, 1990).

A typical example of the suspended culture system is the activated sludge process. The conventional activated sludge system consists of three main zones; the primary clarifier, the aeration tank and the settling tank (EPA, 1993). The activated sludge process requires organic carbon, nitrogen and phosphorous, as well as recycled activated sludge to maintain a healthy bacterial population to aid the removal of COD from the wastewater. The activated sludge system has been extensively tested for the treatment of domestic and industrial wastewater (Lazarova and Manem, 1994). The advantages of suspended growth systems include low maintenance and ease of operation. While the disadvantages include low COD removal efficiencies due to variations in composition of the influent stream, frequent cell washout, the need for high retention times (days) and the addition of oxygen which increases operational costs (Sokol, 2003). Further disadvantages associated with conventional activated sludge processes include the need to operate at low specific organic loading rates and the requirement for a large footprint (Csikor *et al.*, 1996). As a result of these associated disadvantages the conventional process has been extensively changed and modified. Modifications to the activated sludge process were based mainly on the physical configuration to enhance nutrient removal, oxygen distribution and the organic loading rates. These modifications resulted in the development of processes such as the Bardenpho process, sequencing batch reactors (SBRs) and the University of Cape Town (UCT) process as well as the

development of attached growth systems (Rittman and McCarty, 2001; Marais and Ekama, 1984).

Attached growth systems consist of inert biocarriers on which microorganisms can attach and form a biofilm (Edwards *et al.*, 1994). These biological reactors with fixed biomass have been used in the treatment of wastewater in removing organic matter (Boller *et al.*, 1994). Immobilisation of microorganisms onto inert support matrices is a promising alternative to suspended culture systems, solving the problems related to that type of wastewater treatment (van Loosdrechdt *et al.*, 2000). The major advantages of attached growth systems include the ability to be operated at lower hydraulic retention times, allowing greater biomass retention, with subsequent higher volumetric loads, the treatment of wastewaters with high or low organic loading rates and improved mass transfer efficiencies. The disadvantages of the attached growth systems include long start-up periods, greater amount of biomass accumulation resulting in the need for frequent backwash, which requires high maintenance, as well as speed limitation in aerated filters (Huang and Lo, 1995). Different types of attached growth systems include trickling filters (TF), rotating biological contactors (RBC) and fluidised-bed reactors (van Loosdrechdt *et al.*, 2000; Boller *et al.*, 1994).

The use of attached growth biological systems, such as the fluidised-bed reactor, has generated a significant amount of interest (Ochieng *et al.*, 2003). Fluidised-bed reactors consist of a bed packed with small particles contained in a vertical column. These particles are expanded upwards via the hydraulic force introduced at the base of the vertical column (Bull, *et al.*, 1983). The flow rate is adjusted to maintain the particles in constant motion but is kept low enough to avoid particle carry-over in the effluent. The particles (support matrix) provide a large surface area (Bull, *et al.*, 1983), in the region of 3 000 – 4 000 m^2/m^3 particle bed (Cooper, 1981), for microbial growth as a thin biofilm layer around the support matrix (Bull, *et al.*, 1983). This process allows the retention of a greater amount of biomass in the reactor resulting in increased productivity (Garcia-Calderon, *et al.*, 1998). The advantage of using fluidised-bed reactors over other biological systems is its ability to obtain a higher biomass concentration, as well as, a

higher mass transfer and a drastic decrease in hydraulic retention times resulting in the higher biodegradation rates. The use of fluidised-bed reactors enables phase homogeneity and provides a larger solid-liquid contact area. These characteristics make it possible to operate the reactors at high volumetric loading rates (Hosaka *et al.*, 1991; Ochieng *et al.*, 2003). Although fluidised-bed reactors have been applied extensively in the nitrification and denitrification of wastewater as well as organic carbon removal in anaerobic reactors (Bull *et al.*, 1982), they have also been designed for biological treatment of wastewater with a high rate of organic removal (Bull *et al.*, 1983). They have been successfully used to treat a wide variety of wastewaters including high and low strength wastes. This has resulted in the increased application of fluidised-bed reactors to industrial applications (Edwards *et al.*, 1994; Sutton and Mishra, 1994; Sen and Demirer, 2003). Fluidised-bed and fixed film reactors have been used extensively in recirculating aquaculture systems, where greater ammonia removal efficiencies have been observed than in suspended growth systems. Due to an increase in biofilm surface area and increased mass transfer efficiencies, plus the ability to produce less excess sludge in comparison to the activated sludge process, the fluidised-bed reactors have already been successfully applied in the treatment of several kinds of industrial wastewaters (Summerfelt and Cleasby, 1996; Hirata *et al.*, 2000).

The modern choice between aerobic and anaerobic wastewater treatment processes has historically favoured the aerobic process, as the anaerobic systems were considered less reliable and very little was known about these systems (Fitzgerald, 1996). However, aerobic reactors need to be aerated and usually enriched oxygen is used to satisfy the high oxygen utilisation rate required so the reactors can be operated at a high rate of liquid recycle (Bull *et al.*, 1983; Edwards *et al.*, 1994). Broader application of these processes is, however, hampered by the costs of this aeration using oxygen and the associated sophisticated construction requirements (Frijters *et al.*, 1997; Nicolella *et al.*, 2000). As a result interest in anaerobic systems has increased primarily due to a better understanding of these systems. New high-rate treatment processes are now being applied in the treatment of industrial wastewater (Chen *et al.*, 1988; Fitzgerald, 1996). Anaerobic systems have few economic limitations and produce less sludge than aerobic systems

which prevents plugging and subsequent channelling (Fitzgerald, 1996; Opoku-Gyamfi *et al.*, 2000). A further motivation for the application of anaerobic biological fluidised-bed reactor (BFBR) technology is due to the potential to recover usable energy in the form of biogas (containing methane) with good process efficiency and stability (Chen *et al.*, 1988). The methane can be used to heat the reactor or supply power to the plant (Fitzgerald, 1996; Opoku-Gyamfi *et al.*, 2000).

2. Problem Statement

During the Fischer-Tropsch reaction in the Synthol process (SASOL SynFuels, Secunda, South Africa), a mixture of CO and H_2 (syngas) is converted to a range of hydrocarbons. The reaction can be represented as $CO + 2H_2 \rightarrow CH_2 + H_2O$ (Dry, 1999). During this process, an aqueous stream, referred to as Fischer-Tropsch (Synthol) reaction water, is generated. Approximately 25 - 30 ML of Fischer-Tropsch reaction water is produced daily at SASOL SynFuels, Secunda, South Africa. Distillation of the reaction water to remove non- and oxygenated hydrocarbons yields on organic acid-enriched stream. This effluent contains 1 to 1.5 % v/v $C_2 - C_4$ organic acids (> 85 % acetic acid), as well as $C_5 - C_{18}$ organic acids, including light oils, aldehydes, ketones, cresols and phenols.

Together with Fischer-Tropsch reaction water, two other aqueous process effluents are generated by SASOL SynFuels, Secunda, South Africa. These include Stripped Gas Liquor (SGL) and Oily sewer waters (API). Biological treatment of these combined process effluents currently includes the use of ten dedicated activated sludge systems. After treatment the effluent is used as process cooling water within the SASOL SynFuels (SSF) system. The Fischer-Tropsch reaction water, which constitutes 70 % of the COD load treated by the activated sludge systems, contains an average COD of 16 000 mg/L, but this can vary between 12 000 mg/L and 22 000 mg/L. Such a high degree of variation usually results in shock loadings to the biological system with a negative impact on the microbial populations in the system. These factors result in instability of the activated sludge system, making them prone to bulking and failure. Due to these shock loadings, variation in volumetric and hydraulic loadings, as well as constant variations in

the composition of the aqueous process effluent, COD removal efficiencies of these activated sludge systems never exceed 80 %. This may also be attributed to the presence of toxic or recalcitrant compounds in the various process effluents (primarily SGL and API) which may have a negative impact on the activated sludge treatment process. Low organic loading rates (3.5 kg COD/m^3.d) and high specific air requirements (60 - 75 m^3 air/kg COD_{rem}) currently make the existing activated sludge systems inefficient to operate and economically non-viable. Currently the aeration process using the activated sludge systems at SASOL is the major cost factor amounting to approximately to R20 million per annum (pers comm: Phillips, T).

Due to these major limitations, possible changes to the existing water recovery systems of SASOL SynFuels, Secunda, South Africa are being assessed. The fact that Fischer-Tropsch reaction water constitutes a major fraction of the COD load to the activated sludge systems, alternative biological treatment processes for the treatment of this Fischer-Tropsch reaction water effluent are being investigated in order to optimise operational costs and effluent treatment efficiencies. However, various studies evaluating the aerobic and anaerobic treatment of SASOL Fischer-Tropsch reaction water alone in suspended growth wastewater treatment systems have proven unsuccessful. This is thought to be as a result of the disintegration of existing granules due to shear forces and the lack of formation of new granules. It is generally accepted that the formation of granules is connected with the production of extracellular polysaccharides (EPS), which surround the bacteria to form granules or floc (Schmidt *et al.*, 1992). It is not yet known whether specific species produce EPS or whether several or all species are able to do so. However, the population balance within the granules appears to be influenced primarily by the EPS production by acidogenic populations (Forster and Quarmby, 1994). Due to the absence of complex organic matter in the effluent, growth of acidogenic bacteria is restricted resulting in very little EPS being produced. This in turn reduces the granule formation in the reactor. EPS is also believed to be responsible for the strength of the granules formed (Quarmby and Forster, 1995), therefore if only a few acidogens are present in the reactor to produce EPS the granules become more susceptible to disintegration due to the shear forces occurring within the reactors. In contrast, Joubert

and Britz, (1987) reported a 90 % reduction in COD at an organic loading rate of 15 $kg/m^3.d$ using a hybrid anaerobic digester treating a synthetic effluent analogous to Fischer-Tropsch reaction water. These results suggested that fixed-film or biofilm reactors could possibly be used for the biological treatment of Fischer-Tropsch reaction water alone.

Limited research has, however, been undertaken to evaluate the suitability of using fluidised-bed reactor technology in the treatment of high strength industrial effluents, and no research has been undertaken concerning the aerobic and anaerobic treatment of the Fischer-Tropsch reaction water as generated in the Fischer-Tropsch process by SASOL SynFuels, Secunda, South Africa. Due to the various advantages frequently associated with the application of BFBRs it is hypothesised that the aerobic and anaerobic treatment of Fischer-Tropsch reaction water in BFBRs may prove to be a suitable alternative to the activated sludge systems currently used.

The primary aim of this study was thus to assess the suitability of two-phase biological fluidised-bed reactors (BFBRs) for the aerobic and anaerobic treatment of a synthetic high-strength COD petrochemical effluent analogous to the Fischer-Tropsch reaction water, while comparing sand and granular activated carbon (GAC) as support matrices.

3. Objectives

The specific objectives of this study included the following:

- The characterisation of two-phase BFBRs in terms of bed expansion of the various support matrices versus up-flow velocities;
- The characterisation and comparative evaluation of the two-phase BFBRs in terms of two different support matrices (sand and granular activated carbon);

- Optimisation and comparative evaluation of COD removal efficiencies in two-phase BFBRs while treating a synthetic effluent analogous to the Fischer-Tropsch reaction water; During this study the following was evaluated:
  - The effect of increased COD loading rates on COD removal efficiencies; and
  - The effect of increased COD loading rates on the removal efficiencies of specific volatile fatty acids.
- The evaluation and optimisation of aerobic and anaerobic treatment of a synthetic effluent analogous to Fischer-Tropsch reaction water effluent using biological fluidised-bed reactors:
  - Determination of the specific air requirements and oxygen transfer efficiencies of aerobic fluidised-bed reactors using sand and GAC as support matrices; and
  - Determination of biogas and methane yields of the anaerobic BFBR using sand and GAC as support matrices.
- Comparative evaluation of aerobic and anaerobic BFBRs to the conventional activated sludge systems currently being utilised by SASOL SynFuels, Secunda, South Africa.

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Chapter 2

Literature Review

1. Availability and Use of Fresh Water in South Africa

Fresh water resources in South Africa are limited (Bouler, 1999) and, in global terms, scarce. The demand for water is, however, growing continuously due to an increase in population and a developing economy. The sustainability of water resources within South Africa is therefore threatened both in terms of quality and quantity. Unless the current manner in which water is used and managed is changed, future water demand for both rural and industrial development, will significantly exceed existing available fresh water resources. Evidence of inefficient water use can be found throughout the country and the value of water seems largely unrecognised by the majority of water users. Water management is essential in promoting the national goals of the South African National Water Act (36 of 1998) in supplying the basic water needs for all South Africans, the natural reserve and sustaining the use of water resources (Singh and Constantinides, 2000).

1.1. Availability of Fresh Water

South Africa's water supply is vital for economic growth of the country, as well as the health and prosperity of the people (Basson, 1997). The South African climate varies between arid and semi-arid in the western regions to humid along the eastern coastal areas. The average rainfall (497 mm/annum) in South Africa is just over half that of the world average (860 mm/annum) (Basson, 1997; DWAF, 1986). The seasonal rainfall pattern differs dramatically in different regions, ranging from 4 000 mm per annum to less than 50 mm per annum (Global Water Partnership, 2000). The area with the highest demand for water, namely the Gauteng Province, receives the lowest rainfall in the country (Fuggle and Rabie, 1992). Twenty one percent of the country receives less than

200 mm per annum, while sixty five percent receives less than 500 mm annual rainfall. This value (500 mm/a) is regarded as the minimum for successful dry-land farming (DWAF, 1986). Deteriorating water quality and water scarcity in South Africa will result in an increased competition for water resources between industrial and rural development (Mayell, 1999).

1.2. Water Demand

The water demand in South Africa is projected to rise by almost 3 % annually and it is anticipated that by 2020 South Africa will experience severe water stress. Furthermore, it is anticipated that the country will have moved to a situation of insolvable water scarcity by 2025 (Shermon, 2001). Growth in water demand is foreseen in the domestic, urban and industrial sectors primarily due to population growth, increased urbanisation, and increased standards of living and services (Basson, 1997). However, the lower than predicted economic growth, industrialisation rate (Basson, 1997) and the population growth rate being lower than anticipated primarily due to the current AIDS pandemic may have a significant impact on the projected values. Although this advent of insolvable water scarcity in South Africa may be postponed, it is an inevitable situation. Furthermore, the possible impacts of global warming and changes in weather patterns on the water supply in South Africa have not yet been determined.

1.3. Water Use

The main use of water in South Africa is irrigation. This activity accounts for approximately 54 % of the total amount of water used in South Africa (Basson, 1997), while 1.5 % of water is used for watering of livestock (Fuggle and Rabie, 1992). Domestic or urban use constitutes approximately 11 % of total usage, while mining and some of the larger industries outside the municipal areas use 8 % of the water in the country (Basson, 1997). Deteriorating water quality may be attributed to both point source and non-point source pollution of water bodies. Although the control of non-point source pollution is very difficult to achieve the discharge of wastewater not meeting

permit discharge conditions from point sources are a major source of both organic and inorganic pollution in South Africa. The deteriorating water quality affects both the industrial and agricultural sectors of South Africa and recent attempts to improve water quality by the setting of effluent discharge targets (receiving water quality objectives) focuses on the required water quality of the most sensitive water users within a catchment.

1.4. Water Legislation

South Africa has undertaken comprehensive and participative reviews of its national water resource and environmental management policies. These reviews resulted in the drafting of the National Environmental Management Act (NEMA 107 of 1998) and the National Water Act (NWA 36 of 1998). Both Acts have brought new perspectives to the manner in which wastes and the natural environment should be managed in South Africa (Whalmsley, 2000). These acts have a significant impact on the industrial sector of South Africa and require that industries must apply for effluent discharge permits of a prescribed limit before discharge of treated effluents is allowed back into the waterbody from which the water was originally abstracted.

The National Water Act (NWA 36 of 1998) promotes sustainability and equity as the central guiding principle in the protection, use, development, conservation, management and control of water resources. The NWA deals with pollution prevention, particularly where pollution of water resources occurs or might occur as a result of activities on land. Within this act it is stated that the person who owns, controls, occupies or uses the land is responsible for taking measures to prevent pollution of the water resources (Whalmsley, 2000).

Due to the continuing deterioration of quality and declining quantity of water, several changes to the water legislation have recently occurred and the emphasis has shifted from the implementation and enforcement of pollution prevention by the application of general and special standards, to the management of catchments and the establishment of

receiving water quality objectives, which are established by respective Catchment Management Agencies (CMA). These objectives must be achieved by the reduction of the total pollution load to a catchment and is to be achieved through the granting of discharge permits. Although the Department of Water Affairs and Forestry (DWAF) is the custodian of all water resources in South Africa, and ultimately responsible for the management of the water to meet the country's requirements and maintain the quality for all water users, the Catchment Management Strategy and the establishment of catchment management agencies has become a priority in the management of the water resources in South Africa (Pema *et al.*, 2000).

Some key elements of the National Water Act (NWA 36 of 1998) include; all effluent must be re-used, wastewater effluents must be treated before disposal, economic development should not destroy the water resources and no water may be privately owned (NWA 36 of 1998).

2. Current and Future Solutions to the Water Problems in South Africa

Water conservation has become increasingly important throughout the world (Basson, 1997) and it has long been recognised that water is one of the prime limiting natural resources in South Africa (DWAF, 1986; Huntley *et al*, 1987). This has resulted in the necessity to find solutions to solve the water shortage problems.

2.1. Current solutions

Water conservation should play a significant role in the extension of the life of South Africa's water resources. Areas where water can be saved include urban areas in which up to 10 – 15 % water saving can be achieved, the agricultural sector can save up to an additional 30 % with improved irrigation efficiencies. Other savings are effected through better catchment management, such as the removal of alien vegetation in the catchment area and along watercourses (Basson, 1997). This is currently being achieved with the implementation of the 'Working for Water' program. Large scale engineering has been

used to store water behind dam walls and to distribute water from regions of plenty to regions of need. This is called the intercatchment transfer (ICT) scheme, which involves the transfer of water from catchments with good supply and low demand to those where demand is high but supply is poor. There are a number of ICT schemes already in operation in South Africa and more under construction. An example of a major scheme is the Orange-Fish River Scheme, where water gravitates from the Orange River at the Gariep Dam and is piped through tunnels and canals to the Sundays and the Fish Rivers of the Eastern Cape. Another example is the Lesotho Highlands Water Project which transports water from the Orange River in Lesotho to the Vaal River for use in Gauteng (Paxton, 2000). Physical, chemical and biological treatment methods can be applied to treat industrial wastewaters in order to prevent the organic and inorganic pollution of the country's rivers, enabling the reuse of water in different areas, thereby lowering the demand on the fresh water systems.

2.2. Future Solutions

Should the water demand exceed the supply, future solutions to the impending water crisis need to be considered before extreme shortages are experienced. Basson (1997) suggested that possible solutions could include the following:

1. Efficient storage of water;
2. Application of protective layers to water surfaces, the construction of larger and deeper reservoirs, the siting of dams in regions of low evaporation and the storage of water underground to prevent water losses due to evaporation;
3. Better hydrological planning of catchment development;
4. Desalination of sea water;
5. Reuse of water after treatment and purification;
6. Prevention of water pollution to maintain the water resources that are being used;
7. Improvement of irrigation techniques;
8. Extraction of water from atmospheric moisture;

9. Adoption of suitable price policies to prevent the over exploitation of current water resources;
10. Buying water from neighbouring states, e.g. from the Okavango River in Botswana and Zambezi River in Zimbabwe; and
11. Supplementation of water from adjacent river systems that have surpluses.

Recently the concept of "virtual water" has become more important. This concept states that it may be economically beneficial to import fresh produce from neighbouring countries rather than attempting to produce the products in South Africa, where conditions are unfavourable to agriculture. This concept may release more fresh water for sectors, which contribute substantially to the South African economy such as industries. Although these aspects could potentially be solutions, the current emphasis should be on more efficient use, treatment and reuse of existing water resources.

3. Treatment options

Rapid industrialisation and urbanisation in many countries has resulted in the deterioration of existing water quality primarily due to high levels of pollution (both organic and inorganic). Due to increasing environmental concerns associated with industrial waste, companies are being forced to incorporate waste management and prevention strategies into their industrial processes (Abou-Elela and Zaher, 1998). These strategies including the open circuit and closed circuit water plants should be addressed in the companies Environmental Management plan. Due to the impending water crisis facing South Africa, legislation has been designed to enforce strict discharge standards on industrial wastewater in order to prevent further pollution and deterioration of the existing water quality. Where possible, attempts are being made via the Catchment Management Strategy to improve existing water quality (NWA 36 of 1998). As a result different treatment processes are being employed by different industries, depending on their type of waste effluent, to treat their wastewater. These processes include chemical, physical and biological methods. Wastewater treatment systems are important in controlling the contamination of water in the environment. Through wastewater

treatment the water quality is improved, and both the ecology of receiving waterbodies, as well as the public health are protected, and potential reuse applications become more favourable (Jimenez *et al.*, 2001). In order to prevent eutrophication and possible salinisation of receiving water bodies, biological treatment processes are used to remove organic loads, as they are less expensive than chemical processes. However, in some cases, due to the high organic load, toxicity or presence of biorecalcitrant compounds, biological wastewater treatment processes cannot be used. In these cases chemical treatment processes are used to reduce COD levels and/or toxicity (Martinez *et al.*, 2003). Waste treatment goals and objectives have resulted in extensive research to develop and evaluate new chemical, physical and biological wastewater treatment technologies (Edwards *et al.*, 1994).

3.1. Physical Wastewater Treatment

Physical treatment methods are used to alter or remove particulate matter present in wastewater (Tchobanoglous and Schroeder, 1987). Wastewaters often have suspended or floating debris of various sizes. These solid particles can damage or clog pumps or prevent flow in open channels and pipes. Generally screening is the first step in treating these wastewaters (Viessman and Hammer, 1998; Tchobanoglous and Schroeder, 1987).

Sedimentation is another method frequently used in the physical treatment of wastewater. It is also referred to as clarification and involves the removal of solid particles from a liquid phase using gravity (Tchobanoglous and Schroeder, 1987). Sedimentation of a flocculent suspension results from the combined effects of gravity settling and flocculation (Viessman and Hammer, 1998). Flocculation forces the particles to collide causing them to aggregate, resulting in larger particles (Tchobanoglous and Schroeder, 1987). These larger particles are heavier in weight and have greater settling velocities surpass and bine with smaller lighter solids to form larger flocs with increasing rates of settling. The opportunity for contact among settling solids increases with depth. As a result, removal of suspended solids depends on water depth, as well as overflow rate and retention time. In the treatment of wastewater, sedimentation is used to reduce the

suspended solids in the influent wastewater and to remove settleable solids after biological treatment (Viessman and Hammer, 1998).

Membrane filtration is a relatively new technology that is rapidly expanding in wastewater and industrial wastewater treatment. During the last decade the treatment of wastewater effluents, especially through ultrafiltration, has grown in interest. However, due to excessive fouling tendencies, the application of membrane filtration technology for the treatment of many industrial effluents is extremely complicated. This may be due to the great variations in quality of the effluent. Furthermore, the normal parameters such as COD, BOD, suspended solids, turbidity and nutrients give insufficient information on the expected or occurring membrane fouling rates (Roorda and van der Graaf, 2001). Dissolved solids can be removed from water and wastewater though the use of semipermeable membranes (Tchobanoglous and Schroeder, 1987). However, very few of these physical methods are available to treat industrial wastewaters, as a result chemical and biological treatment processes are more in demand.

3.2. Chemical Wastewater Treatment

With chemical treatment methods, chemical reactions are used to bring about a change in water quality. Chemical treatment processes are used to treat industrial wastewater to aid in water reclamation and recycling (Jarusutthirak and Amy, 2001). Typically, chemicals have to be added to the wastewater being treated to effect a change (Tchobanoglous and Schroeder, 1987). The major disadvantage commonly associated with the use of chemical treatment processes is the increase in the salt concentrations (total dissolved solids) of the effluent. In South Africa this aspect could be especially problematic since the majority of the river systems are already experiencing increased levels of salinisation, primarily due to the large discharge of industrial effluents with high salt loads into these systems (Mohsen and Jaber, 2002). This is especially relevant to the Vaal River system, which is situated in the industrial hub of the country. Chemical treatment has high operational and maintenance costs, prohibiting the general use of this treatment process (Hosten, 1989; Kaksonen *et al.*, 2003).

In chemical wastewater treatment, hardness can be reduced by lime-soda ash softening and iron and manganese can be removed by chemical oxidation (Viessman and Hammer, 1998). Both temporary and permanent hardness of water affects all equipment through which the water is pumped or treated. Chemical oxidation is also frequently used to reduce organic matter content in wastewater during wastewater reclamation, recycling and reuse. Advanced oxidation processes (AOPs) are particularly promising methods for this purpose. Advanced oxidation processes are defined as those reactions, which involve the generation of hydroxyl radicals in sufficient quantity to affect water purification. Advanced oxidation processes use different combinations of oxidation agents, irradiation and catalysts in order to generate hydroxyl radicals (Huang *et al.*, 1993; Tanaka *et al*, 2001). Different chemical oxidation methods have recently been investigated and compared for reducing specific organic compounds and organic matter in certain industrial wastewaters. These include ozone (O_3), ultraviolet radiation (UV) and titanium-dioxide catalysts (TiO_2) (Tanaka *et al.*, 2001). Other chemical treatment methods used to treat industrial wastewater include ozone/hydrogen peroxide, ozone/UV, electron beam with and without oxygen and hydrogen peroxide, potassium permanganate, wet air oxidation and natural sunlight (Pulgarin *et al.*, 1999).

Another method of chemical treatment of wastewater includes coagulation. Coagulation is used in floc formation in the reactors and subsequent settling in order to remove solid particles from suspension. The most commonly used coagulants for wastewater treatments are aluminium and iron salts. Aluminium sulphate is a good coagulant for water containing organic matter. Iron coagulants are effective over a wider pH range and are more effective in removing colour from water but are more costly. Cationic polymers are used in some waters as primary coagulants but polymers are more commonly used as coagulant aids. The choice of chemical aids and coagulants are based on the ability to achieve the removal of the contaminants and low turbidity desired in the filtered water at the lowest cost (Viessman and Hammer, 1998).

3.3. Biological Wastewater Treatment

Biological wastewater treatment systems are 'living' systems that rely on mixed biological cultures to degrade organic compounds and remove the organic matter from solution (Viessman and Hammer, 1998). Microorganisms are used to remove organic material and inorganic ions that are available in wastewater to support growth (Tchobanoglous and Schroeder, 1987).

Both aerobic and anaerobic methods have been used in the biological degradation of complex organic carbon in industrial effluents (Sreekrishnan and Ali, 2003). The current choices between the aerobic and anaerobic processes has tended to favour the aerobic, as the anaerobic systems were considered less reliable and the biochemical mechanisms were not well investigated (Fitzgerald, 1996). This has, however, recently started to change and the anaerobic treatment of industrial wastewater is becoming more apparent.

Many industrial wastewaters are resistance to treatment using biological processes frequently used in treating municipal and domestic wastes. It is hypothesised that microorganisms are able to degrade oxidisable material as long as suitable environmental conditions are provided. However, due to the development of new industrial processes synthetic compounds unfamiliar to the microorganisms and therefore resistant to biodegradation using these microorganisms, are continuously being released in wastewaters. A possible solution to this problem is the use of mixed cultures, such as those found in biological treatment methods or by using a designed microbial consortium, which has a wide range of metabolic pathways. Mixed cultures are becoming increasingly more important in the degradation of organic toxins to carbon dioxide and often enhance the microbial metabolism by degrading toxins produced by metabolism and allowing cometabolism to occur (Burgess *et al.*, 1999).

Biological processes can be classified into four major categories. These categories depend on the presence or absence of aeration and the location of the microorganisms involved in the treatment process (Hamoda and Al-Sharekh, 2000; Tchobanoglous and

Schroeder, 1987). These categories include suspended growth and attached growth as well as aerobic and anaerobic systems, respectively. Commonly used aerobic biological treatment processes include activated sludge, waste stabilisation ponds, oxidation ditches, trickling filters, rotating biological contactors, and contact aeration. The first three processes are referred to as suspended growth systems, while the last three are attached growth or biofilm systems (Huang and Lo, 1995).

The advantage of the suspended growth systems is its low maintenance. Suspended growth processes also frequently obtain better effluent qualities due to the oxygen transfer limitations experienced in the attached growth process (Al-Sharekh and Hamoda, 2001). The disadvantages of using suspended growth systems include low COD removal efficiencies due to variations in composition of the influent stream, cell washout is frequently experienced, the need for high retention times (days), the reactors require a large surface area and the addition of aeration to provide oxygen increases operational costs (Sokol, 2003). However, the performance of the suspended growth processes is variable and operation is often more complex than attached growth systems. Attached growth systems are relatively simple to operate and are usually more stable than suspended growth systems (Tchobanoglous and Schroeder, 1987). The attached growth systems have proven to be successfully operated at lower hydraulic retention times, retain greater amounts of biomass, enabling higher volumetric loads, treat wastewater with high or low organic loading rates and have a greater mass transfer efficiency than suspended growth systems. The disadvantages of the attached growth systems include long start-up periods, greater amount of biomass accumulation resulting in the need for backwashing which results in high maintenance (Huang and Lo, 1995). For many decades reactors with a fixed biomass have been used in wastewater treatment for the removal of organic matter, nitrification and denitrification. The different reactor types and the possible process schemes offer a great variety of operating conditions which may lead to a difference in performance (Boller *et al.*, 1994).

Significant differences exist in the pathways of aerobic and anaerobic degradation. During the aerobic process the microbial consortium utilises the organic compounds

present in the effluent as their carbon energy source (Sreekrishnan and Ali, 2003). Aerobic degradation can be conducted in conventional activated sludge reactors, packed bed biofilm reactors or fluidised-bed reactors. Fluidised-bed reactors have a higher biomass concentration, limited cell washout, small external mass transfer resistance and are significantly easier to operate continuously compared to the first two reactor types (Yu *et al.*, 1999). During this process, complex organic compounds are converted to microbial biomass and carbon dioxide. In contrast, during the anaerobic process, the complex organic compounds are broken down to a mixture of volatile fatty acids, mostly acetic, propionic and butyric acids. This is achieved by acidogens, a consortium of hydrolytic and acidogenic bacteria. The volatile fatty acids are then converted to carbon dioxide and methane by acetogens and methanogens, respectively. While both the aerobic and anaerobic degradation routes remove the complex organic compounds from the industrial effluents, the anaerobic process also produces methane, which can be used as an energy source (Sreekrishnan and Ali, 2003).

3.3.1. Suspended Growth Technology

Suspended growth wastewater treatment processes are biological processes that have been designed to encourage growth of specific microorganisms that are able to purify effluent wastewater (Horan, 2003). During the suspended growth process mixes active biological solids are mixed with the wastewater, and the solids are held in suspension by agitation as the organic matter is removed from solution by the metabolic activity of the microbial flocs (Viessman and Hammer, 1998). Typical examples of suspended growth processes include activated sludge, waste stabilisation ponds and oxidation ditches.

3.3.1.1. Activated Sludge

Activated sludge processes are the most commonly applied suspended growth treatment methods and are used extensively for the treatment of a wide range of industrial and domestic wastewaters (Burgess *et al.*, 1999). Activated sludge is an aerobic biological treatment system (Ambaram, 2001) consisting mainly of microorganisms, which are able

to metabolise the principal compounds of the wastewater (Kasan, 1986). The microbial populations grow and function within a neutral pH range between 6.5 - 8.0. Treatments using activated sludge processes are influenced by temperature, pH and the concentration of the pollutant compounds including heavy metals. When one or more of these conditions are affected, biological treatment of the wastewater becomes difficult and pretreatment of the wastewaters may be necessary to protect the system against failure (Chong *et al.*, 1997).

Due to these disadvantages, the conventional activated sludge process has been changed and modified extensively. Modifications of the activated sludge process are based on physical configurations, oxygen distribution and the organic loading rate. These modifications have resulted in the development of processes such as the Bardenpho process, sequencing batch reactors (SBR) and the University of Cape Town (UCT) processes (Rittmann and McCarty, 2001). The Bardenpho process is used to remove nitrogen and phosphorous (EPA, 1993) and consists of different reaction zones which are the anoxic denitrification zone, the aerobic combined oxidation nitrification zone, the anoxic zone, the aerobic zone and the settling tank (Marais and Ekama, 1984; Tchobanoglous, 1991). An advantage of this process is its ability to remove 90 % of the total nitrogen, however, the main disadvantage of the process is the need for many reaction tanks and long hydraulic retention times (Rittmann and McCarty, 2001). The SBR systems are also known as the draw-and-fill reactors (Tchobanoglous, 1991). During nitrogen removal the following reaction sequences are used: the aerobic stage and the settling stage (Rittmann and McCarty, 2001). An advantage of the SBR system is the lack of requirement for return sludge, as in some plants the processes are carried out in a single tank (Tchobanoglous, 1991). The main disadvantage of the SBR is the requirement for long hydraulic retention times. However, numerous modified SBR systems and continuous flow SBR systems are currently in use worldwide (Rittmann and McCarty, 2001). The UCT process was developed to minimise the effect of nitrate in weaker wastewaters in entering the anaerobic contact zone. The amount of nitrate in the anaerobic zone is critical to the biological phosphorus-removal efficiency. The return activated sludge is recycled to the anoxic stage, this eliminates the introduction of the

nitrate to the anaerobic improving the uptake of phosphorus. The internal reduction is from the anoxic stage to the anaerobic stage, this provides for increased organic utilisation in the anaerobic stage. The recycle of the anoxic mixed liquor provides for optimal conditions for fermentation uptake in the anaerobic stage (Tchobanoglous *et al.*, 2003).

Activated sludge is an aerobic treatment process, as the biological flocs are suspended in a liquid medium containing dissolved oxygen. Aerobic conditions must be maintained in the aeration tank, however, in the final clarifier, the dissolved oxygen concentration can become extremely low. Dissolved oxygen extracted from the mixed liquor is replenished by air supplied to the aeration tank (Viessman and Hammer, 1998).

The sludge generated during activated sludge treatment of wastewater is treated and stabilised via a number of processes, which include aerobic digestion, anaerobic digestion, composting, landfill disposal or incineration. Numerous strategies to enhance the performance of the activated sludge treatment systems when treating industrial wastes have recently been proposed. These include the introduction of support media into the aeration basins, thereby combining suspended and fixed growth processes. It has been reported that the presence of biofilm (attached growth) in the activated sludge systems resulted in improved settling properties of the flocs and made nitrification efficiency independent of the solids retention time of the suspended biomass (Gebara, 1999). Typical examples of the activated sludge treatment processes with suspended packing material include Linpor® and Kaldnes®. In the Linpor® process, foam pads with a density of approximately 0.95 g/cm^3 are placed in the reactor in a free-floating manner. Mixing from the diffused aeration system circulates the foam pads in the system. However, without additional mixing methods the foam pads may accumulate at the effluent discharge end of the aeration basin and float to the surface. The Linpor® foam pads are retained in the system by a screen. The main advantage of the sponge packing system is the ability to increase the loading of an existing plant without increasing the solids load in the secondary clarifiers, as most of the biomass is retained in the aeration basin. The Kaldnes® process involves the addition of small cylindrical shaped polyethylene carrier

elements with a specific density of 0.96 g/cm^3, in the aerated or non-aerated basins to support biofilm growth. The packing is continuously circulated using air agitation or mixers (Tchobanoglous *et al.*, 2003).

Due to disadvantages such as low COD removal efficiencies caused by variations in volumetric and hydraulic loadings, variations in composition of the influent stream, bulking and cell washout are frequently experienced in activated sludge systems. This necessitates high sludge retention times (days) and frequent re-inoculation. Sludge bulking is also frequently encountered when treating industrial wastewaters. Bulking is a condition where the microbial population becomes dominated by filamentous bacteria. The presence of filamentous bacteria results in poor floc settling characteristics (high sludge volume indices) which leads to cell washout (Springer, 1993; Jobbagy *et al.*, 2000; Foot and Robinson, 2003). It has been reported that low dissolved oxygen levels and high levels of carbohydrates found in some wastewaters stimulated these filamentous growths. It is believed that the filaments prevent the floc forming bacteria from adhering, which leads to a sludge with a high sludge volume index (SVI) and a high water content (Foot and Robinson, 2003). Other disadvantages regarding the operation of activated sludge reactors include the increase in operational costs due to the requirement for aeration and the large area required (Tchobanoglous and Schroeder, 1987). Due to these disadvantages, as well as the excessive production of sludge generated during the activated sludge process, other biological treatment methods such as anaerobic digestion and attached growth systems are being investigated for the treatment of industrial wastewater.

3.3.1.2. Anaerobic Digestion

Anaerobic digestion is a commonly applied sludge treatment method and may be defined as the biological oxidation of degradable organic sludges by microbes under anaerobic conditions. This process uses microbes that survive in an environment which has no molecular oxygen and where there is a substantial amount of organic matter. The organic matter provides the nutrient source for the microorganisms, which convert it into oxidised

materials, new cells, energy for their life processes and some gaseous end products, such as methane and carbon dioxide (Kasan, 1986). Anaerobic digestion has been a recognised technology for the stabilisation of sludge and treatment of industrial and domestic wastewater for almost a century (Shroder and De Haast, 1987). However, the use of anaerobic digestion for the treatment of high-strength organic wastes has only recently become increasingly popular (Britz *et al.*, 1990). Anaerobic digesters produce very little excess biomass and offer the opportunity to produce methane, which may be used as an alternative source of energy (Shroder and De Haast, 1987). Up-flow anaerobic sludge bed (UASB) reactors are commonly applied reactors in anaerobic digestion. The UASB is a recently developed high rate system that has been used in the treatment of sludges and medium to high strength industrial wastewater because of its high biomass concentration and rich microbial diversity (Torkian *et al.*, 2003; Liu *et al.*, 2003). The high biomass concentration increases the contaminant transformation and highly concentrated or large volumes of organic waste can be treated in these compact reactors (Liu *et al.*, 2003). Advantages of the UASB reactors include the ability to exhibit less dead reactor space (Buijs *et al.*, 1982), obtain adequate treatment at low-costs (Hwu *et al.*, 1998) and have good process stability and the ability to operate effectively at low hydraulic residence times (Christensen *et al.*, 1984). Disadvantages of anaerobic digestion treatment using UASB reactors include long start-up periods and the lack of formation of granular settleable sludge while treating some industrial effluents (Joubert and Britz, 1987). This may result in biomass washout and subsequent decrease in COD removal efficiency. As a result the development of various techniques for the immobilisation of biomass within the bioreactors have been encouraged in order to prevent loss of the microorganisms through the effluent stream and hence increase the process rates (Borja *et al.*, 2001). This has resulted in the development of the hybrid UASB as well as the anaerobic fluidised-bed reactors. The hybrid UASB reactor combines two different reactor types, usually an anaerobic UASB reactor and a fixed-film reactor, in an attempt to increase the biomass retaining capacity and overall performance (Augoustinos *et al.*, 1989). The anaerobic fluidised-bed reactors use anaerobic microorganisms which have a low growth rate, this prevents loss through the effluent stream resulting in diminished process rates (Borja *et al.*, 2001).

For moderate to high-strength wastewater, anaerobic processes have shown considerable advantages over the aerobic processes. Anaerobic digestion is considered the preferred process for the treatment of high strength organic effluents especially when pretreatment down to chemical oxygen demand levels of municipal wastewater is adequate (Rajeshwari *et al.*, 2000; von Sachs *et al.*, 2003). Anaerobic processes are well established in treating certain industrial wastewaters which contain easily degradable nutrients and little variation in composition (von Sachs *et al.*, 2003). The advantages of using anaerobic processes include the low demand for energy, the ability of the anaerobic bacteria to transform most of the organic substances present in the wastewater into methane, minimal sludge formation, a low demand for nutrients and unpleasant odour formation can be avoided (Borja *et al.*, 2001; Hidalgo and Garcia-Encina, 2002). Disadvantages of using the anaerobic system is the slow growth rate of the microbes, which lead to the requirement of long start-up periods, since longer times for bacterial growth and support colonisation are required (Hidalgo and Garcia-Encina, 2002). Increasing use of anaerobic, methanogenic treatment during the past decade has resulted in the need for appropriate post-treatment of the effluent. Typical compounds in the effluent of such reactors are short chain fatty acids (mostly acetate), ammonium and hydrogen sulphide (Gommers *et al.*, 1988).

Interest in the anaerobic fluidised-bed reactors has increased in recent years. These fluidised-bed reactors have been used in the treatment of wastewater generated during the production of proteins from extracted sunflower flour (Borja *et al.*, 2001), as well as in the treatment of textile wastewater in order to remove the dye, which is one of the most difficult constituents of the textile wastewater to treat (Sen and Demirer, 2003). Anaerobic reactors containing high levels of methanogenic biomass are used in the treatment of industrial food wastewater, this includes the wastewater from slaughterhouses. Conventional digesters that have been used here achieved low removal rates of organic matter and required long hydraulic retention times, resulting in the need for large reactor volumes.

Under anaerobic conditions, complex organic material is converted by the acidogens into volatile fatty acids (VFA) (Lau and Fang, 1997). The volatile fatty acids produced consist of a number of different acids, with acetic acid, propionic acid, butyric acid and valeric acid being the most common (Buchauer, 1998). These are then converted by the acetogens into acetate and hydrogen, following reactions (1) and (2). After which the acetate is converted by acetotrophic methanogens, into methane, following reaction (3), and H_2/CO_2 is converted by hydrogenotrophic methanogens, following reaction (4) (Lau and Fang, 1997).

Butyrate-utilising acetogenesis

$$CH_3CH_2CH_2COO^- + 2H_2O \rightarrow 2CH_3COO^- + 2H_2 + H^+ \qquad \Delta G^{0'} = +48.1 \text{ kJ} \quad (1)$$

Propionate-utilising acetogenesis

$$CH_3CH_2COO^- + 3H_2O \rightarrow CH_3COO^- + HCO_3^- + H^- \qquad \Delta G^{0'} = +76.1 \text{ kJ} \quad (2)$$

Acetotrophic methanogenesis

$$CH_3COO^- + H_2O \rightarrow CH_4 + HCO_3^- \qquad \Delta G^{0'} = -31.0 \text{ kJ} \quad (3)$$

Hydrogenotrophic methanogenesis

$$4H_2 + HCO_3^- + H^+ \rightarrow CH_4 + 3H_2 \qquad \Delta G^{0'} = -133.4 \text{ kJ} \quad (4)$$

where $\Delta G^{0'}$ represents the change of standard Gibbs free energy at pH 7. Based on the positive $\Delta G^{0'}$ values, reactions (1) and (2) are non-feasible under normal conditions. Neither reaction will take place unless the products are kept at low concentrations. If the concentrations of hydrogen or acetate are not lowered, reactions (1) and (2) would be inhibited. This would result in an accumulation of butyrate and propionate. The build-up of these fatty acids would result in a decrease in the pH of the system resulting in the suppression of the methanogenic reaction, ultimately causing the system to fail primarily due to acidification (Kasan, 1986). An example of this occurs when a sudden excess of organic matter is fed into the reactor, acid formers process this organic matter rapidly, developing excess organic acids. The methanogens are unable to metabolise the organic acids quickly enough to prevent a drop in the pH. When the pH drops, the methanogenic bacteria are affected first, further reducing their ability to break down the acids. Under severe or prolonged overloading, bacterial activity is inhibited. The digestion process can

also be upset by a sudden increase in temperature, a significant shift in the type of substrate or additions of toxic or inhibiting substances from industrial wastes (Viessman and Hammer, 1998).

Anaerobic digestion is accomplished by four trophic groups of microorganisms, acidogens, acetogens, homoacetogens and methanogens. The acidogens catabolise polysaccarides, proteins, lipids and other minor chemical constituents of biomass. The acetogens use complex organic substrates such as carbohydrates, proteins, oils or their degradation products and produce organic fatty acids, mainly acetate and propionic acid with some butyric and valeric acids (Kasan, 1986; Shroder and De Haast, 1988; Aguilar *et al.*, 1995). Evidence has been found that butyrate-degrading and propionate-degrading acetogens syntrophically associated with hydrogenotrophic and acetotrophic methanogens inside UASB biogranules are formed so that the hydrogen and acetate produced by the acetogens is readily consumed by the methanogens (Lau and Fang, 1997). The homoacetogens use compounds such as H_2/CO_2 or HCOOH to produce acetic acid. The methanogens then catabolise acetate and mono-carbon compounds to methane using a complex consortium of microorganisms working together (Kasan, 1986; Shroder and De Haast, 1988; Aguilar *et al.*, 1995). Degradation of propionate is more sensitive to the build-up of hydrogen than that of butyrate. Propionate accumulates easily in mesophilic anaerobic digesters during overloading and it is difficult to remove during recovery (Lau and Fang, 1997). Riedel and Britz (1993) reported the isolation of propionic acid producing bacteria in UASB reactors during conditions of organic overloading such as the start-up period. Acetate has shown to be the precursor of more than 75 % of the methane produced in anaerobic digesters and is seen as the rate-limiting step in the decomposition of more complex substrate organic molecules (Aguilar *et al.*, 1995). A schematic diagram of the carbon flow to methane in anaerobic digestion is shown in Figure 1 (Anderson *et al.*, 2003).

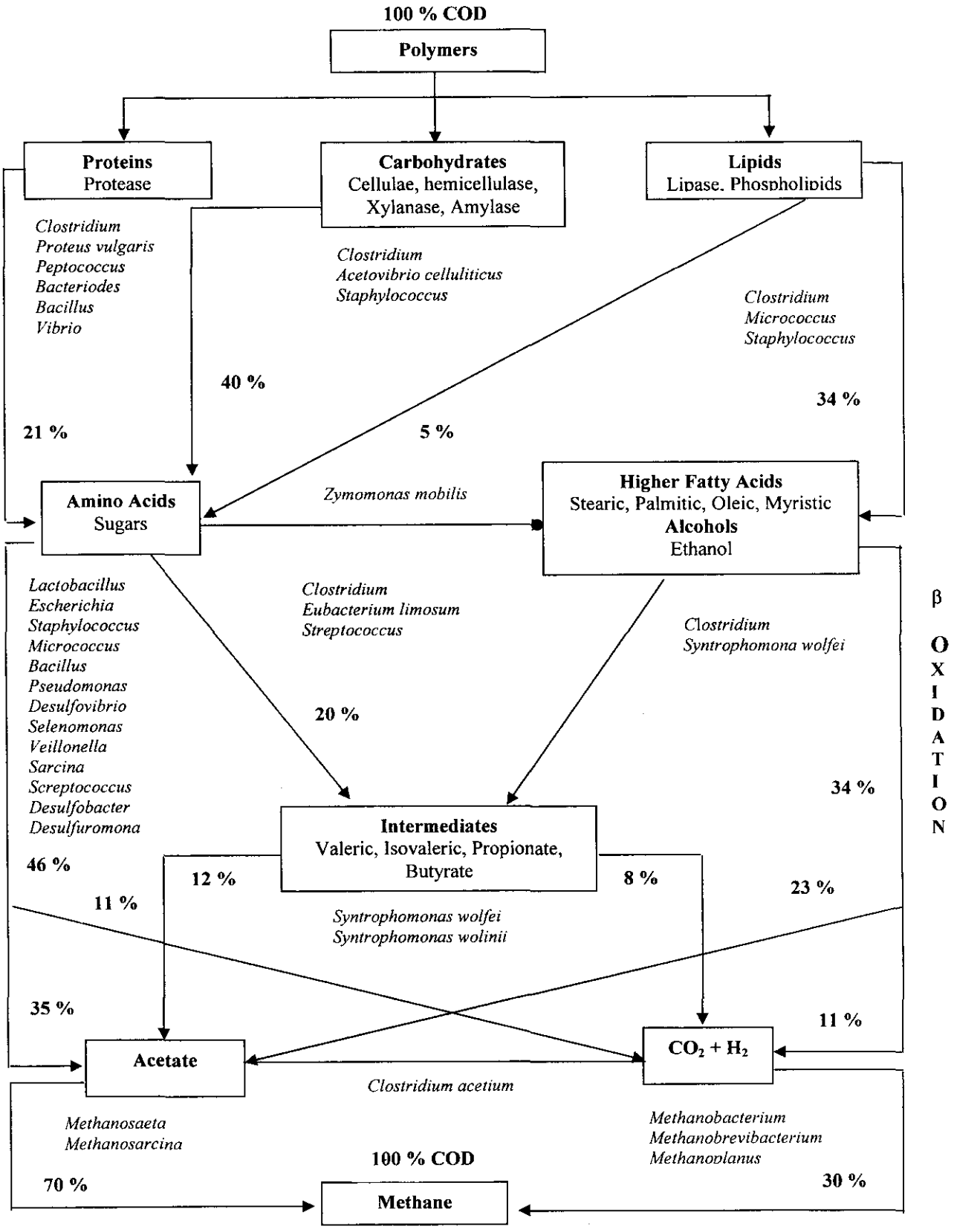

Figure 1. Carbon flow to methane in anaerobic digestion with responsible microorganisms (Anderson *et al.*, 2003).

Stable and efficient operation of anaerobic processes are dependant on the growth and maintenance of sludge granules containing the four microbial trophic groups needed for complete methanogenesis of the organic constituents of wastewater (McHugh *et al.*, 2003). Slow development of effective granular sludge has limited the application of up-flow anaerobic systems (e.g. UASB) for a long period, particularly when treating complex wastewater where the granule accumulation is slower and the granules may have a weak structure. The driving force for the development of granules under differing conditions has not been extensively investigated and the process is not fully understood. It has been extensively hypothesised that the production of extracellular polysaccharides (EPS) by acidogens may contribute to the formation of granules (Riedel and Britz, 1993), EPS plays an important part in the strength of the granules formed in the reactor (Quarmby and Forster, 1995). Granule formation rates have been maximised by increasing acidification in the reactor to increase EPS production (Batstone and Keller, 2001). EPS has a greater role to play in some parts of the granule than in others. Near the edge of the granule EPS has a greater effect on shear strength than it does in the center of the granule (Batstone and Keller, 2001).

3.3.2. Attached Growth Processes

In nature bacteria appear to prefer living on a surface in an aqueous environment rather than be free-floating. Possible reasons for this include, the possibility that the surface may provide nutrients from adsorbed materials, the continuous flow of water across the surface could be a continuous source of nutrients, and the aeration provides oxygen for the aerobic species. A solid surface provides protection for the bacteria against predation by protozoa etc. and survival may be enhanced in biofilms (Melo and Bott, 1997).

A biofilm can be defined as a complex heterogeneous structure of cells and cellular products, like extracellular polymers, which either form spontaneously as large, dense granules, or attach to a solid static surface, known as static biofilms, or on suspended carriers, called particle-supported biofilms (Nicolella *et al.*, 2000). The thickness of a biofilm can vary from a single layer to several hundred millimeters (Mueller, 1994).

Microbial biofilms are not only widely distributed in nature but are found in many industrial environments where relatively high nutrient fluxes and large surface areas are available to provide choice niches for the formation of extensive biofilms. This causes increased fluid frictional resistance in pipes, increased heat transfer resistance, biocorrosion and reduced water quality (Wood *et al.*, 1996).

Attached growth processes such as trickling filters, rotating biological contactors, biological aerated filters and fluidised-bed reactors have proven to have lower hydraulic retention times, can retain greater amounts of biomass, have been shown to be able to attain high volumetric loads, treat wastewater with high or low organic loading rates and have a greater mass transfer efficiency. However, these systems have numerous drawbacks such as long start-up periods and speed limitations in aerated filters (Dickeson and Yoshimura, 2003).

High concentrations of biomass within the reactor are achieved by using small particles, such as sand, anthracite and granular activated carbon, as support matrices (Hosaka *et al.*, 1991). The retention of biomass on the support matrix enables the uncoupling of biomass retention and hydraulic retention time, restricting biomass washout. The quantity of biomass attached to the medium in the fluidised-bed reactor is the main determination of the reactors performance and application. Diffusion of the substrate, nutrients or oxygen into the biofilm is limited to depths of around 0.7 - 120 μm. When the biofilm becomes thick the substrate is degraded rapidly depending on how fast the microorganisms can function. Further growth of the biofilm thickness will have only minimal enhancement on the removal rate of the substrate (Safferman and Bishop, 1997).

Biofilms generally consist of multispecies bacterial communities, which attach themselves to the surface of support matrices and build a layer of polysaccarides or glycocalyx to cement themselves to the surface, and are then covered with more layers of polysaccharides (Watkins and Costerton, 1990; Liu and Tay, 2002). Biological fixed-film reactors for the treatment of wastewater can be considered as catalytic reactors, and depending on their hydraulic behaviour, may be classified as a plug-flow or completely

mixed. The composition of the biofilm's microbial population is dependent on the hydraulic behaviour, pH, temperature and wastewater characteristics (Gonzalez-Martinez and Duque-Luciano, 1992). The biological fixed-film process allows the retention of a greater amount of biomass in the reactor resulting in an intensified reaction rate and lowering the required hydraulic retention times (Garcia-Calderon *et al.*, 1998). Due to biofilm formation on support matrices, solids retention becomes independent of hydraulic retention times enabling the operation of BFBRs at very low hydraulic retention times while preventing cell washout. This, in turn, enables the system to attain higher volumetric loads allowing for the treatment of wastewater containing either high or low organic loads (Bull *et al.*, 1983; Hosaka *et al.*, 1991). High concentrations of biomass within the reactor are achieved using small particles such as sand, anthracite and granular activated carbon as support matrices (Hosaka *et al.*, 1991). The biological treatment of large volumes of heavily polluted wastewater requires high performance systems such as fluidised-bed reactors. For several types of conversion, the aerobic removal of organic compounds, denitrification and nitrification, the merits of this type of reactor have been demonstrated in laboratory, pilot plant and full scale reactors (Gommers *et al.*, 1988). The quantity of biomass that attaches to a support matrix reactor determines the performance of the reactor and its application (Safferman and Bishop, 1997) and choice of support matrix is critical in order to obtain maximum performance from the associated biofilm (Edwards *et al.*, 1994). Support matrices affect fluidisation characteristics, which depend on the density and the diameter of the support matrix (Jordening and Buchholz, 2003). The microbial cells attach to the surface of the support matrix creating a large surface area for cells to attach themselves to, enabling a higher rate of transfer of oxygen and nutrients through physical forces and bind to the surface using exopolysaccharide polymers. The cells begin dividing to form a microcolony and these primary cells attract other bacteria from the planktonic phase (Blenkinsopp and Costerton, 1991). The individual bacteria in these biofilm microecosystems are incapable of degrading complex wastes. The complete degradation of industrial wastes involves complex interactions between the different species within the biofilm. Therefore biofilms are desirable in biological treatment processes as a high biomass concentration is obtained. The high biomass concentration enables larger volumes to be treated which occupying a smaller

surface area (Liu and Tay, 2002). Within the biofilm physiological co-operation between the various members of the microbial consortium enables the degradation of various substances. In thick biofilms the upper layers are aerobic while the lower layers next to the particle are anaerobic due to the oxygen depletion by the cells in the upper layers (Blenkinsopp and Costerton, 1991). Organic and inorganic molecules in the bulk liquid provide nutrients for cell growth within the biofilm. If the aeration equipment can transfer more O_2 into solution than the biomass can use then aerobic conditions will occur. However, if the oxygen demand of the system is higher than the aeration capacity to meet this requirement, microaerobic conditions will occur and thus be accompanied by products produced from partly oxidised substrates (Chu *et al.*, 1996). Nutrients may also be available in the biofilm due to cell death and metabolites of one microbial species may serve as a nutrient source for another (Blenkinsopp and Costerton, 1991). Diffusion through the biofilm is dependent on film density, age, thickness, and presence of filaments, film speciation and electrostatic interactions. The ability of oxygen to enter the biofilm is critical to the oxidation/reduction reactions of aerobic respiration and varies with the structure of the biofilm (Bishop *et al.*, 1995). The structure of the biofilm is influenced by external shear forces, internal diffusion profiles and microbial community composition. The shear forces will determine the thickness of the biofilm and the structure of the surface of the biofilm (van Loosdrecht *et al.*, 1995). As the biofilm gets older micro-gradients begin forming (Blenkinsopp and Costerton, 1991).

The formation of biofilms requires a high consumption of organic material through microbial synthesis. Specific parameters describing the biofilm are used to evaluate the start-up operation and determine the optimum function of the reactor. The parameters provide vital information regarding the bacterial initiation process and can be applied to any biofilm reactor where biomass sampling is impractical. The monitoring of parameters also provides important information regarding the biomass attachment, which could improve the start-up performance and function of the reactors (Michaud *et al.*, 2002).

For reliable treatment of industrial effluents, biological processes must be capable of treating wastewater of a variable nature and should be tolerant to erratic changes in influent strength and composition that can occur during the cleaning cycles or as a result of spillages or wastage, as well as reductions in temperature that may result from failure of equipment (Cayless *et al.*, 1989).

Materials such as sand and activated carbon are commonly used as support matrices due to economic reasons and availability (Yu *et al.*, 1999). Sand has been reported to offer better fluidisation properties than the granular activated carbon (GAC). Granular activated carbon has, however, been associated with the facilitation of biofilm formation (Edwards *et al.*, 1994). The GAC's adsorption capacity for organic compounds protects the attached biofilm from organic shock loading and is ideal for rapid biomass colonisation providing protection from shear forces (Safferman and Bishop, 1997).

3.3.2.1. Trickling Filters

Trickling filters (TF) are fixed-growth biological beds where the wastewater is evenly spread on the surface of media supporting microbial growth (Viessman and Hammer, 1998). High-rate trickling filters always include effluent recycle. The recycle increases the shear rate and controls the buildup of attached microbial slime on the filter medium (Tchobanoglous and Schroeder, 1987). Trickling filters may be packed with rocks, pumice or plastic media in the form of random packings or corrugated plastic sheets. The wastewater flows in a layer along the carrier material. This results in low oxygen transfer rates. If trickling filters are operated as single units, a distinct gradient in biomass activity is observed along the filter depth caused by nutrient depletion at the lower end (Boller *et al.*, 1994). The main reasons for the popularity of trickling filters are their simplicity, reliability, ability to treat industrial wastewater, low maintenance and operating costs, as well as the ability to withstand shock loads (Viessman and Hammer, 1998; Lessard and Le Bihan, 2003). Disadvantages in using Trickling Filters included filter clogging for high organic loads as a result of excessive slime production, odour

problems, pretreatment and primary sedimentation is necessary (Lessard and Le Bihan, 2003).

3.3.2.2. Rotating Biological Contactors

A rotating biological contactor (RBC) consists of a shaft of circular plastic discs revolving at 40 % submergence in a contour-bottom tank (Viessman and Hammer, 1998; Lessard and Le Bihan, 2003) or plastic media drums exerting different hydraulic flow patterns (Boller *et al.*, 1994). When rotated out of the tank, air enters the spaces while the liquid trickles out over films of biological growth attached to the media. Alternating exposure to organics in the wastewater and oxygen in the air is similar to dosing a trickling filter with a rotating distributor. Excess microbial solids are hydraulically scoured from the media and carried out in the process effluent for gravity separation in a final clarifier. Rotating biological contactors have a slightly better oxygen transfer rate and a well-developed biofilm with minor grazing effects lead to nitrification rates generally higher than that observed in other biofilm systems (Boller *et al.*, 1994). A RBC system has the advantage of low power consumption, low maintenance and energy costs, and good process stability. Disadvantages include no operational flexibility, need of primary sedimentation, dryness of unsubmerged biofilm and the need to be covered in cold climates (Lessard and Le Bihan, 2003). However, new RBC installations are rare because of the comparatively low cost of trickling filters (Viessman and Hammer, 1998).

3.3.2.3. Biological Aerated Filters

Biological aerated filters (BAF) have become increasingly popular in treating wastewater. Biological aerated filters were developed in order to retain suspended solids and for oxidation of carbonaceous soluble pollution in the same reactor. The water flows through a packed bed media which is generally inorganic with a particle size of between 3 – 5 mm and a specific area of 300 – 500 m^2/m^3. Aeration for oxidation occurs at the base of the biofilter. As the biofilm grows and suspended solids are retained within the biofilters, clogging occurs requiring backwashing of the reactors. Advantages of BAF

include good quality of treatment, its fast recovery after problems, quick start-up periods and the compactness of the process. Disadvantages include the high-energy consumption, large volumes of washwater needed and transient operation (Lessard and Le Bihan, 2003).

3.3.2.4. Fluidised-bed Reactors

One of the most promising wastewater treatments processes of is the high rate fixed-film process or the biofilm reactor, of which the fluidised-bed is one of the most effective (Bull *et al.*, 1983; Edwards *et al.*, 1994). The development of fluidised-bed reactors (BFBRs) for the treatment of biological wastewater can be traced back to the 1940s, although the first full-scale reactors were only commissioned in the mid 1980s (Sutton and Mishra, 1994). The first reported treatment of industrial wastewater with BFBRs occurred in the 1970s (Sadick *et al.*, 1996).

Fluidised-bed reactors have been designed for biological treatment of wastewater with a high rate of organic removal. A fluidised-bed reactor consists of a bed packed with small particles that are contained within a vertical column (Bull *et al.*, 1983). Fluidised-bed reactors can be classified into three major types. These include two-phase biological fluidised-bed reactors, comprising liquid and solid phases, three-phase biological fluidised-bed reactors comprising gas, liquid and solid phases, in one reactor (Chang and Rittman, 1994), and the down-flow fluidised-bed reactor, in which the bed expansion occurs downwards (Garcia-Calderon *et al.*, 1998). The two-phase and three-phase biological fluidised-bed reactors operate by fluidising the support matrix, consisting of the solid particles, using the liquid or gas stream flowing in the opposite direction to gravitational force (Cooper, 1981; Sadick *et al.*, 1996). These particles are expanded upwards via the flow introduced at the base of the vertical column. The flow rate is adjusted to maintain the particles in constant motion but is kept low enough to avoid particle carryover in the effluent. The particles provide a larger surface area for microbial attachment and growth, which in turn results in a high biomass concentration in the reactor. Due to the biomass retention in biofilms attached to the support particles of

the fluidised-bed, washout of the biomass at higher hydraulic and organic loading rates is significantly reduced (Borja *et al.*, 1995). However, in the down-flow fluidised-bed reactor the liquid's specific gravity is higher than that of the support matrix consisting of solid particles. In comparison to up-flow BFBRs little attention has been given to the down-flow fluidised-bed reactors (Garcia-Calderon *et al.*, 1998). Two- and three-phase BFBR process designs have been used extensively in many industries to treat effluent wastes such as petrochemical wastes, brewery wastes, as well as refinery wastes. The BFBRs have become popular due to their compactness, simplicity in construction, low maintenance and ability to handle high loading rates (Wu *et al*, 1999; Hirata *et al.*, 2000; Ochieng *et al.*, 2002, Sokol, 2003). The typical loading rates and percentage COD removals achieved using the three-phase BFBRs treating the petrochemical wastewater were found to be 6.6 - 10 kg COD/m^3.d and 76 %, respectively. The BFBR used to treat refinery wastes obtained a COD removal efficiency of 90 %, while the brewery wastes treated using a BFBR achieved a COD removal efficiency of 65 % (Wu *et al*, 1999; Sokol, 2003).

Biological fluidised-bed reactors have been employed in a wide range of applications in the industrial sector (Table 1). Currently they are being used in aerobic and anaerobic treatment of industrial wastewater (Lazarova and Manem, 1994; Yu *et al.*, 1999), as well as treatment of petroleum-contaminated wastewater (EPA, 1993; Ochieng *et al.*, 2003). Aerobic biological fluidised-bed reactors are used to treat industrial wastewater as they provide a large liquid-gas interaction and can be operated at a lower aeration rate than other aerobic bioreactors, flocs in these reactors form granules that are not expected to crumble (Tsuneda *et al.*, 2003). Disadvantages associated with the use of the aerobic fluidised-bed reactor include the need to provide sufficient aeration to satisfy the high oxygen demand (Bull *et al.*, 1983) and the high quantity of sludge produced by the aerated systems that need treatment before being disposed of (Hidalgo and Garcia-Encina, 2002). It has been shown that external dissolution of pure oxygen is the only practical method for high rate treatment in fluidised-bed reactors. The addition of pure

Table 1. Examples of large scale applications of BFBR's.

Type of BFBR	Support Medium	Application	Volumetric Loading Rate $kg/m^3.d$	COD Removal (%)	Reference
2- phase	Pumice	IW	3 (COD)	82	Sen and Demirer (2003).
Aerobic	Saponite	IW		80 - 98	Borja *et al.* (2000).
BFBR	Sand/GAC	UW, IW, NF	0.6-1.3 (NH_4-N)		Lazarova and Manem (1994).
3-phase	KMT® particles				
BFBR	polypropylene	IW		90	Sokol (2000).
	Polyethylene	IW		74	Ochieng *et al.* (2003).
	Glass beads	UW, NF	4 (COD)	70	Yu *et al.* (1999).
Inverse (down-flow) BFBR	Perlite	IW	4.5 (COD)	85	Garcia-Calderon, *et al.* (1998).

Abbreviations used: GAC – Granular Activated Carbon, IW – Industrial Wastewater, UW – Urban Wastewater, NF – Nitrification, BFBR – Biological Fluidised-Bed Reactor, COD – Chemical Oxygen Demand.

oxygen adds to the overall wastewater treatment cost, making it economically inefficient (Tsuneda *et al.*, 2003).

The major advantages of using fluidised-bed reactor over other biological systems include a higher biomass concentration, and a higher mass transfer, resulting in higher biodegradation rates (Ochieng *et al.*, 2003). Other advantages include the biomass being distributed throughout the entire volume of reactor, no cell washout, greater overall process stability, allowance for high loading rates (20 to 80 $kg/m^3.d$), and high surface areas in the region of 3 000 – 4 000 m^2/m^3 particle bed for biofilm attachment (Cooper, 1981; Borja *et al.*, 2001). These characteristics enable fluidised-bed reactors to operate at higher volumetric loadings, a fact that makes the fluidised-bed an appropriate choice for treatment of toxic effluents (Ochieng *et al.*, 2003). Disadvantages include the fact that the fluidised-beds have to have a high recycle rate to keep the support matrix in suspension, the aeration systems used are highly complex, and problems occur with the scaling-up of these reactors.

4. SASOL Scenario

The South African Coal, Oil and Gas Corporation Limited (SASOL) was founded in 1950 as a profit-orientated company designed to meet the liquid fuel needs of South Africa (Dry, 2002). The process of gasification of low-grade coal under high temperature and pressure was introduced to produce the fuel at this time (Ambaram, 2001). The Fischer-Tropsch technology applied by SASOL in the Synthol process in South Africa is the largest commercial scale application of the Fischer-Tropsch technology (Steynberg *et al.*, 1999). Currently SASOL produces 43 % of South Africa's liquid fuels and manufactures more than 120 different chemical products, some of which is exported to more than 80 different countries (Ambaram, 2001).

The SASOL Synthol process is a two-stage indirect fusion process, which produces a variety of hydrocarbon-based products from all grades of coal. Coal, together with steam and oxygen is fed into Lurgi gasifiers where the coal gasified. Purified synthesised gas is

fed into the SASOL Synthol plant where it is circulated with a powdered iron-based catalyst. The synthesis gas can be converted to fuels and chemicals either directly using the Fischer-Tropsch process or indirectly by first producing methanol and then by conversion to olefins and/or fuels. During the exothermic Fischer-Tropsch reaction, a gaseous mixture of hydrocarbons and oxygenated products are produced (Dry, 1988). The reaction that occurs can be generalised by the following equation $CO + 2H_2 \rightarrow CH_2 + H_2O$ (Dry, 1999; Rostrup-Nielsen, 2002). A condensation product of the Synthol fluidised-bed process is a dilute aqueous chemical mixture referred to as Fischer-Tropsch reaction water (Figure 2) (Dry, 1988). Almost equal volumes of oil and water are produced during the Fischer-Tropsch process. Water-soluble organic compounds such as alcohols, ketones and aldehydes are recovered by distillation. Approximately 25 - 30 ML of Fischer-Tropsch (Synthol) reaction water is produced daily at SASOL SynFuels, Secunda, South Africa. Distillation of this reaction water to remove non- and oxygenated hydrocarbons yields an organic acid-enriched effluent. This effluent contains 1 to 1.5 % v/v $C_2 - C_4$ organic acids (> 85 % acetic acid), $C_5 - C_{18}$ organic acids, including light oils, aldehydes, ketones, cresols and phenols.

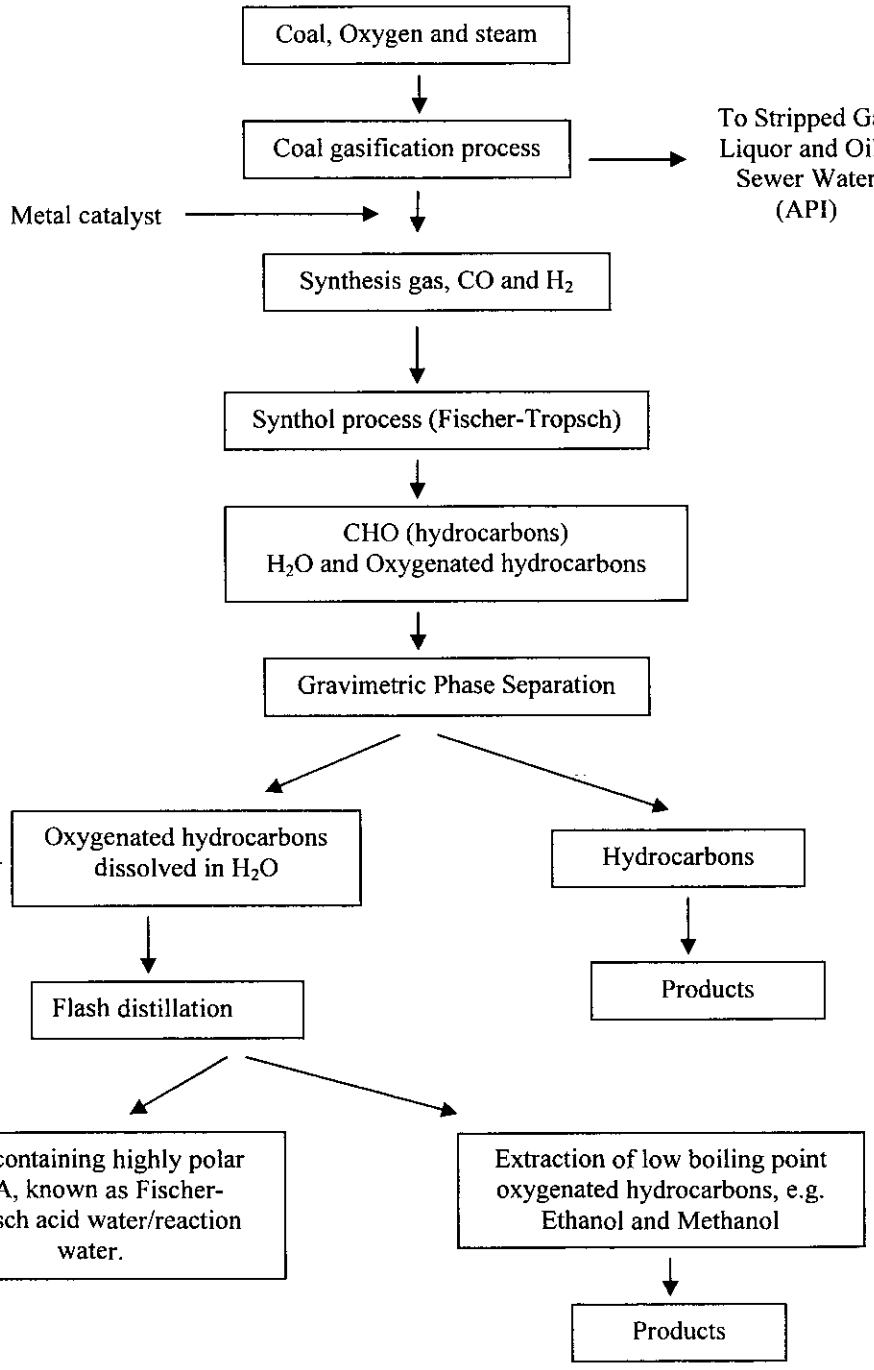

Figure 2. Schematic representation of Fischer-Tropsch reaction water production

The original design of the wastewater treatment systems for the SASOL SynFuels, Secunda, South Africa plants was based on the concept of a zero liquid effluent discharge with the re-use of purified effluents as process waters primarily in heat exchange units

and cooling towers. These plants were designed to recycle wastewaters in order to minimise raw water consumption (utility water) and reduce discharge to nearby rivers, thereby reducing pollution.

Three aqueous waste effluents, namely Fischer-Tropsch acid water, also known as reaction water, Stripped Gas Liquor (SGL) and Oily sewer water (API) are produced at SASOL SynFuels, Secunda, South Africa. These waste effluents are combined and treated biologically using ten dedicated activated sludge systems. This is based on the principle that wastewater contains a number of different organic compounds which serve as a carbon source for the microorganisms in the mixture of activated sludge (Roux, 1991; Duvenhage and Shingles, 2002). After the wastewater is treated at the SASOL SynFuels (SSF) activated sludge processes (Unit 52/252) it is used as process utility cooling water. This flow diagram is illustrated in Figure 3.

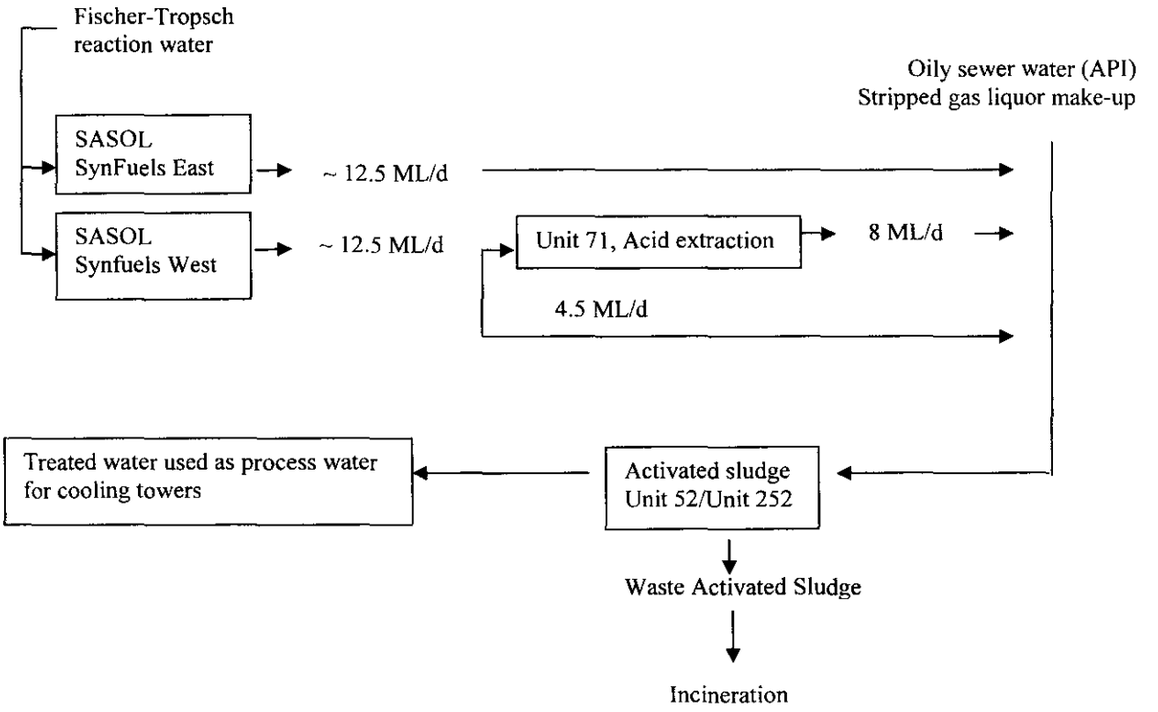

Figure 3. Illustration of the fate of Fischer-Tropsch reaction water at SASOL Synthetic Fuels, Secunda

treatment of Fischer-Tropsch reaction water alone using the activated sludge system has also proven to be very difficult and to some extent unsuccessful.

The activated sludge basins of SASOL SynFuels (SSF), Secunda, South Africa, used to treat the Fischer-Tropsch reaction water, API and SGL currently has a specific air requirement of approximately 60 - 75 m^3 air/kg COD_{rem} and a low organic loading rate of 3.5 kg COD/m^3.d making the existing activated sludge systems inefficient and costly to operate. Aeration is the major cost factor associated with the activated sludge systems currently in use at SASOL amounting to approximately R20 million per annum (pers comm: Phillips, T). The sludge generated during the aerobic activated sludge treatment process is treated by the addition of polyelectrolytes, which aid in dewatering of the sludge. The sludge is then stabilised using incineration. The ash is then disposed of in a class 1 landfill site due to the heavy metal content of the ash. Advantages of using the activated sludge process include low maintenance and simple operation. However, significant problems are continuously experienced with the biological treatment of the effluents in the activated sludge systems. These problems include sludge bulking, which results in sludge washout necessitating frequent re-inoculation of the systems. Furthermore, primarily due to shock loadings, variation in volumetric and hydraulic loadings, as well as variations in the composition of the reaction water streams, COD removal efficiencies of these systems never exceed 80 %. A possible reason for this could be shock loadings as the Fischer-Tropsch reaction water contains an average COD of 16 000 mg/L, but can vary from 12 000 mg/L to 22 000 mg/L. Such a high degree of variation will have a negative impact on the microbial population in the biological system. This can leave the system unstable, resulting in failure. The presence of toxic contaminants in the Fischer-Tropsch reaction water, API and SGL effluents occurs periodically and can also have a negative impact on the activated sludge treatment process. Even under stable operational conditions the effluent quality is not suitable for discharge to the environment, containing approximately 1 000 mg COD/L. Due to the fact that Fischer-Tropsch reaction water is easily biodegradable and constitutes 70 % of the COD load on the activated sludge basins, it is logical that the separate treatment of this wastewater stream could be significantly beneficial and the separation of the effluents may also reduce the costs of treating the effluent. However, the biological treatment of Fischer-Tropsch reaction water alone using the activated sludge system has also proven to be very difficult and to some extent unsuccessful.

In an attempt to address the problems experienced at SASOL Synthetic Fuels, Secunda, SASOL is currently in the process of making major changes to the water recovery system. Some of the proposed changes include the acid extraction from the west-side of SSF and the biological treatment of a mixture of the remainder of the reaction water. SASOL is also investigating alternative biological processes, such as the anaerobic reactors and the fixed-film biological processes. This aspect has resulted in the initiation of studies concerning the evaluation of the suitability of different reactors for the treatment of Fischer-Tropsch reaction water. Britz *et al*, (1983), obtained a 93 – 95 % COD reduction rate, with an OLR of 4.7 kg COD/m^3.d and a methane content of 90 – 96 % while using downflow fixed bed anaerobic reactors to treat a synthetic effluent analogous to Fischer-Tropsch reaction water. However, due to the low settleability of the sludge and resulting cell washout, support matrices were required in order to reduce this loss of biomass. Other reactors that were investigated by SASOL include the high-rate compact reactor, which obtained an OLR of 35 kg COD/m^3.d with an average COD removal of 70 % and a specific air requirement of 18 m^3 air/kg COD_{rem}. However, this reactor was unstable and COD removal was erratic (pers comm: Phillips. T). The biological aerated filter achieved an OLR of 35 kg COD/m^3.d, with an average COD removal of 80 % and a specific air requirement of 11 m^3 air/kg COD_{rem}. This process has however not been tested at large scale. While the anaerobic digestion was also investigated and obtained an OLR of 15 kg COD/m^3.d with an average COD removal of 92 % and had no specific air requirements. The disadvantage of the anaerobic digestion is the high initial capital costs (pers comm: Phillips.T).

Anaerobic wastewater treatment has been used extensively in municipal sewage treatment for many years. However, in recent years interest in the application of anaerobic reactors for the treatment of industrial wastewater has increased. However, due to the slow growth rates of anaerobic microorganisms granule formation requires an extended start-up period, making the microorganisms susceptible to washout. This could result in a loss of sludge, which has detrimental effects on the treatment of waste effluent. Further factors that influence granule formation and strength include the composition of

the wastewater as well as the presence of inhibitory compounds. Due to the composition of the Fischer-Tropsch reaction water (primarily volatile fatty acids) it is evident that the lack of complex substances (polysaccharides, lipids, proteins), the acidogenic trophic groups will not be maintained. It has been reported that acidogens are primarily responsible for the production of EPS, which contributes to floc and granule structure and strength. However, in the anaerobic digesters used in treating effluent analogous to that produced at SASOL SynFuels, Secunda, new granules are not formed and cell washout occurs. This indicates that the use of aerobic treatment or anaerobic digestion for the treatment of Fischer-Tropsch reaction water as generated by SASOL SynFuels, Secunda, using the suspended growth wastewater treatment systems, which includes the activated sludge systems or UASB reactors, is impractical. It is evident that the addition of support matrices will add to the surface area, which in turn will increase the growth rate of the bacteria, reducing the washout of microorganisms. This will improve the treatment levels of the anaerobic reactors making them more desirable in the treatment of the Fischer-Tropsch reaction water. High rate fixed-film biological processes, or biofilm reactors, of which the fluidised-bed reactor is one of the more effective, can be considered as a promising technology for the treatment of high-strength industrial wastewaters. These processes allow the retention of a greater amount of biomass, thereby enabling drastic decreases in hydraulic retention times. It is therefore also possible to attain higher volumetric loading rates and to treat wastewater with either high or low organic loads.

However, one major disadvantage of the process is the long start-up period. Despite the proven success of the BFBR in the aquaculture industry, very little research has been undertaken in the evaluation of the suitability of this technology for the treatment of high-strength industrial effluents, and no previously published research has been undertaken concerning the treatment of the Fischer-Tropsch reaction water. Based on the extensive literature review undertaken during this study it is hypothesised that the application of BFBRs for the aerobic and anaerobic treatment of Fischer-Tropsch reaction water could serve as a suitable alternative treatment technology for the activated sludge systems currently being employed by SASOL SynFuels, Secunda, South Africa.

5. Research Aims

The primary aim of this study was to assess the suitability of two-phase biological fluidised-bed reactors (BFBRs) for the aerobic and anaerobic treatment of a synthetic high-strength COD petrochemical effluent analogous to the Fischer-Tropsch reaction water, while comparing sand and granular activated carbon (GAC) as support matrices.

6. Research Objectives

The objectives of this study included the following:

- The characterisation of two-phase BFBRs in terms of bed expansion versus up-flow velocities;
- The characterisation and comparative evaluation of two-phase BFBRs using two different support matrices (sand and granular activated carbon);
- Optimisation and comparative evaluation of COD removal efficiencies in two-phase BFBRs while treating a synthetic effluent analogous to the Fischer-Tropsch reaction water; During this study the following was evaluated;
  - The effect of increased COD loading rates on COD removal efficiencies; and
  - The effect of increased COD loading rates on the removal efficiencies of specific volatile fatty acids.
- The evaluation and optimisation of aerobic and anaerobic treatment of a synthetic effluent analogous to Fischer-Tropsch reaction water effluent using biological fluidised-bed reactors;
  - Determination of specific air requirements and oxygen transfer efficiencies of aerobic fluidised-bed reactors using sand and GAC as support matrices; and
  - Determination of the biogas and methane yields of the anaerobic BFBR using sand and GAC as support matrices.
- Comparative evaluation of aerobic and anaerobic BFBRs to the conventional activated sludge systems currently being utilised by SASOL SynFuels, Secunda, South Africa.

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Chapter 3

Evaluation of Biological Fluidised-Bed Reactors for the Aerobic Treatment of Fischer-Tropsch Reaction Water

1. Abstract

Reaction water, a high-strength COD petrochemical effluent, is generated during the Fischer-Tropsch reaction, which occurs during the SASOL Synthol process at SASOL SynFuels, Secunda, South Africa. Together with other aqueous process effluents (Stripped Gas Liquor (SGL) and Oily sewer water (API)) this high-strength petrochemical waste effluent is currently treated using ten dedicated activated sludge basins. However, these systems are prone to difficulties resulting in low COD removal efficiencies. It is hypothesised that these problems are primarily due to shock loading, variation in volumetric and hydraulic loading, as well as variation in the composition of the process effluents and/or the presence of inhibitory compounds. Due to the fact that the reaction water contributes to 70 % of the COD load on the activated sludge basins, alternative processes are currently being investigated by SASOL SynFuels in order to improve the treatment of wastewater as well as the COD removal efficiency. High rate fixed-film processes or biofilm reactors, of which fluidised-bed reactors are considered to be the more effective, have been successfully applied for the treatment of several high-strength industrial wastewaters. The primary aim of this study was thus to evaluate the suitability of aerobic biological fluidised-bed reactors (BFBRs) for the treatment of a high-strength COD synthetic industrial effluent analogous to Fischer-Tropsch reaction water. The suitability of sand and granular activated carbon (GAC) as support matrices in the biological fluidised-bed reactors were also evaluated. COD removal efficiencies in excess of 80 % at organic loading rates of up to 30 kg COD/m^3.d could be achieved in the aerobic BFBRs using sand and GAC as support matrices. Specific air requirements were determined to be approximately 35 and 41 m^3 air/kg $COD_{removed}$ for the BFBRs using sand and GAC as support matrices, respectively. The oxygen transfer efficiencies for both reactors

were 5.4 %. However, due to plugging and subsequent channeling in the BFBR using GAC as support matrix at these high organic loading rates, the reactor had to be backwashed at regular intervals to remove excess biomass. Despite these washes, removal efficiencies recovered to previous levels within 24 hours. In contrast no problems were encountered with plug formation and channeling in the BFBR using sand as support matrix. The VFA/alkalinity ratio determines the stability of the reactor. The aerobic BFBRs containing sand and GAC as support matrices were stable until the OLR increased above 10 $kg/m^3.d$ when the BFBR using sand support matrix increased to 4, above the failure limit value of 0.3 - 0.4. The BFBR using GAC support matrix remained stable until an OLR of 15 $kg/m^3.d$ was obtained, the VFA/alkalinity valued then increased to 3. Towards the end of the study when an OLR of approximately 25 $kg/m^3.d$ was obtained both BFBRs VFA/alkalinity ratio increased even further, indicating the decrease in reactor stability. The overall performance and removal efficiency of the BFBR using sand as support matrix was more stable and consistent than the BFBR using GAC as support matrix. Although both reactors displayed high resilience and COD removal efficiencies in excess of 80 % during shock loadings, the reactor using GAC as support matrix showed higher resilience to variations in operational conditions, such as the lowering of the hydraulic retention times. Both reactors were extremely sensitive to changes in pH. The BFBR using sand as support matrix was more sensitive than the BFBR using GAC as its support matrix to any decrease in pH. pH reduction in the influent to values below the pKa values of the volatile fatty acids in the feed resulted in significant reductions in COD removal efficiencies. Maintenance of reactor pH was thus an essential facet of reactor operation. Aerobic treatment of Fischer-Tropsch reaction water using BFBRs may thus serve as a suitable alternative treatment technology for the activated sludge systems currently used by SASOL.

2. Introduction

SASOL SynFuels, Secunda, South Africa, produces three aqueous process effluents, namely the Fischer-Tropsch reaction water, Stripped Gas Liquor (SGL) and Oily sewer water (API). During the Fischer-Tropsch reaction in the SASOL Synthol

process (SASOL SynFuels, Secunda, South Africa) a mixture of CO and H_2 (syngas) is converted to a range of hydrocarbons (Dry, 2002; Rostrup-Nielsen, 2002). The Fischer-Tropsch reaction effluent contains 1 to 1.5 % v/v $C_2 - C_4$ organic acids (> 85 % acetic acid), $C_5 - C_{18}$ organic acids, including light oils, aldehydes, ketones, cresols and phenols. Approximately 25 - 30 ML of Fischer-Tropsch (Synthol) reaction water, with an average COD of 16 000 mg/L is produced daily, however, the COD may vary between 12 000 mg/L and 22 000 mg/L. Such a high degree of variation may result in shock loadings to the biological system (activated sludge systems), which will have a negative impact on the microbial populations of these systems. Biological treatment of the reaction water, SGL and API effluents currently comprises the use of ten dedicated activated sludge systems. However, the combined biological treatment of these effluent streams using activated sludge systems has proven difficult and to some extent unsuccessful and unable to achieve COD removal efficiencies above 80 %. This may be due to the presence of toxic contaminants found in the various process effluents, primarily SGL and API, having a negative impact on the activated sludge treatment processes. Low organic loading rates (3.5 kg COD/m^3.d) and high specific air requirements (60 - 75 m^3 air/kg COD_{rem}) make the activated sludge system inefficient and economically non-viable.

The low COD removal efficiency of the activated sludge systems may primarily be ascribed to the shock loadings experienced by the biological system due to variations in volumetric and hydraulic loadings, and variations in the composition of the various wastewater streams. Problems with sludge bulking and washout are also frequently experienced necessitating frequent re-inoculation of the systems. These factors result in the instability of the systems making it prone to failure. Since Fischer-Tropsch reaction water constitutes 70 % of the COD load applied into the activated sludge basins, alternative processes to improve the treatment cost and efficiency of the Fischer-Tropsch acid water stream are being investigated.

Alternative aerobic degradation processes have been investigated by SASOL SynFuels, Secunda, included the biological aerated filter (BAF), and the high-rate compact reactor (Lessard and Le Bihan, 2003). In an independent study performed by

SASOL Technology Research and Development an organic loading rate (OLR) of 35 $kg/m^3.d$ using a BAF reactor was achieved, with an average COD removal efficiency of 80 %. The specific air requirement was determined to be 11 m^3 air/kg COD_{rem}. However, this reactor has only been studied to laboratory scale (pers comm: Phillips, T). A COD removal efficiency of 70 % at an OLR of 35 $kg/m^3.d$ could be achieved in a high-rate compact reactor, while the specific air requirement was determined to be 18 m^3 air/kg COD_{rem}. Although the COD removal efficiency of this reactor was not as high as that obtained in the BAF process this reactor has been tested to pilot plant level. It was found that this process was unstable due to shock loading which resulted in erratic COD removal efficiencies (pers comm: Phillips, T).

Fluidised-bed and fixed film reactors have been used extensively in recirculating aquaculture systems, where greater ammonia removal efficiencies have been observed than in suspended growth systems, primarily due to an increase in biofilm surface area and increased mass transfer efficiencies (Summerfelt and Cleasby, 1996). The fluidised-bed reactor has shown a higher biomass concentration, limited cell wash-out, small external mass transfer resistance and an easy continuous operation compared to the activated sludge reactor and packed bed biofilm reactor (Yu *et al.*, 1999). This makes the fluidised-bed reactors one of the most promising alternative treatment technologies of wastewater (Bull *et al.*, 1983). Very little research, however, has been undertaken in the evaluation of the suitability of aerobic BFBRs for the biological treatment of high-strength petrochemical effluents. Edwards *et al.*, (1994) reported using a laboratory-scale aerobic fluidised-bed reactor to treatment a high strength synthetic chemical industrial wastewater. The authors reported a COD removal efficiency of 99 % at an organic loading rate of 9.6 kg $COD/m^3.d$ using sand as a support matrix, while a 98 % COD removal rate could be achieved at an organic loading rate of between 2 and 4 kg $COD/m^3.d$ using GAC as support matrix. However, no research has been published concerning the use of BFBRs in the aerobic treatment of Fischer-Tropsch reaction water as generated by SASOL SynFuels, Secunda, South Africa.

The aim of this study was thus to assess the suitability and to optimise the operation of two-phase biological fluidised-bed reactors (BFBRs) for the aerobic treatment of a synthetic high-strength COD petrochemical effluent analogous to the Fischer-Tropsch reaction water, using sand and granular activated carbon (GAC) as support matrices.

Specific objectives of this study included the following:

- The characterisation of two-phase BFBRs in terms of bed expansion of the support matrices (sand and granular activated carbon) versus up-flow velocities.
- The characterisation and comparative evaluation of the use of sand and GAC as support matrices in the two-phase.
- Optimisation and comparative evaluation of COD removal efficiencies of the synthetic Fischer-Tropsch reaction water. During this study the following was evaluated:
  - The effect of increased organic (COD) loading rates on COD removal efficiencies;
  - The effect of increased COD loading rates on the removal efficiencies of specific volatile fatty acids.
- Determination of specific air requirements and oxygen transfer efficiencies of the aerobic fluidised-bed reactors using sand and GAC as support matrices.

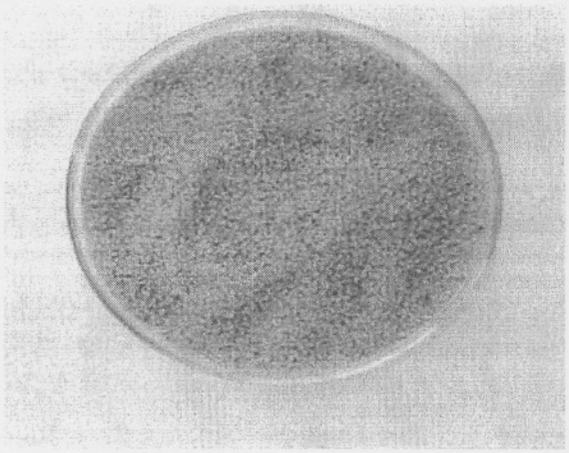
3. Materials and Methods

3.1. Physical properties and characteristics of the support matrices

The silica sand used as support matrix during this study, shown in Figure 1a, (*B and E Silica, Delmas, South Africa*) had a uniformity coefficient (UFC) of 1.09, and an equivalent diameter (D_{10}) of 0.86 mm. Furthermore, the sand had a static bed porosity of 0.746, bulk density of 1.57 g/cm^2 and a particle density of 2.5 g/ml. The GAC support matrix, shown in Figure 1b, used during this study (Filtrasorb 300; *Chematron Products (Pty) Ltd Isando, S.A.*) had a UFC of 1.9 and an equivalent diameter (D_{eq}) of 1.924 mm. Furthermore, the GAC had a static bed porosity of 0.799, bulk density of 1.43 g/cm^2, and a particle density of 2.66 g/mL. These values

were determined according to the methods described by Summerfelt and Cleasby (1996). Approximately 10.6 kg of sand and 3.6 kg GAC were used as support matrices in each of the aerobic BFBRs operated in parallel.

a)



b)

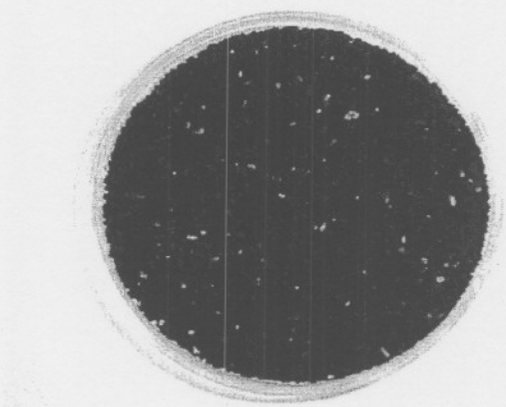


Figure 1. The support matrices used during the study: a) Sand; and b) Granular Activated Carbon.

3.2. Feed composition

The synthetic wastewater make-up used during this study was analogous to the Fischer-Tropsch reaction water generated during the Fischer-Tropsch reaction in the SASOL Synthol process. The composition of the high-strength Fischer-Tropsch reaction water (yielding a COD of 20 000 mg/L) was as follows (mg/L): Acetic acid, 9 005; Propionic acid, 2 499; Butyric acid, 1 106; Isobutyric acid, 147; Isovaleric

acid, 219. The COD of the effluent feed was gradually increased from 1 600 mg/L to 20 000 mg/L in the aerobic reactors. The pKa values of the organic acids used to make up the synthetic effluent vary from acetic acid with a pKa value of 4.76, which is the lowest value, to propionic acid with a pKa value of 4.87, the highest pKa value of the organic acids. The C:N:P ratio of the synthetic high-strength COD industrial effluent was corrected to a ratio of 100:10:1, using NH_4OH and KH_2PO_4. Once the maximum influent COD concentration (20 000 mg/L) was achieved the organic loading rate was further increased by decreasing the HRTs of the aerobic reactors to 36 h, 24 h and 8 h. The ratios between the respective VFAs were maintained during the preparation of low-strength reaction water. The pH within the reactors was maintained at 7.0 with the addition of 2N HCl or 2M NaOH using an automatic pH controller (*Hanna instruments, Germany*). During inoculation, start-up and operation, the reactors were operated at a bed height expansion of 30 %. The aerobic reactors were inoculated using 1 L of aerobic activated sludge obtained from the Flip Human Water Care Works, Krugersdorp, Gauteng, South Africa.

3.3. Reactor operation

During this study two aerobic BFBRs using sand and granular activated carbon (GAC) as support matrices were operated in parallel. A schematic representation (not to scale) of these reactors is shown in Figure 2 and an overview of the experimental set-up of the BFBR as used during this study is shown in Figure 3.

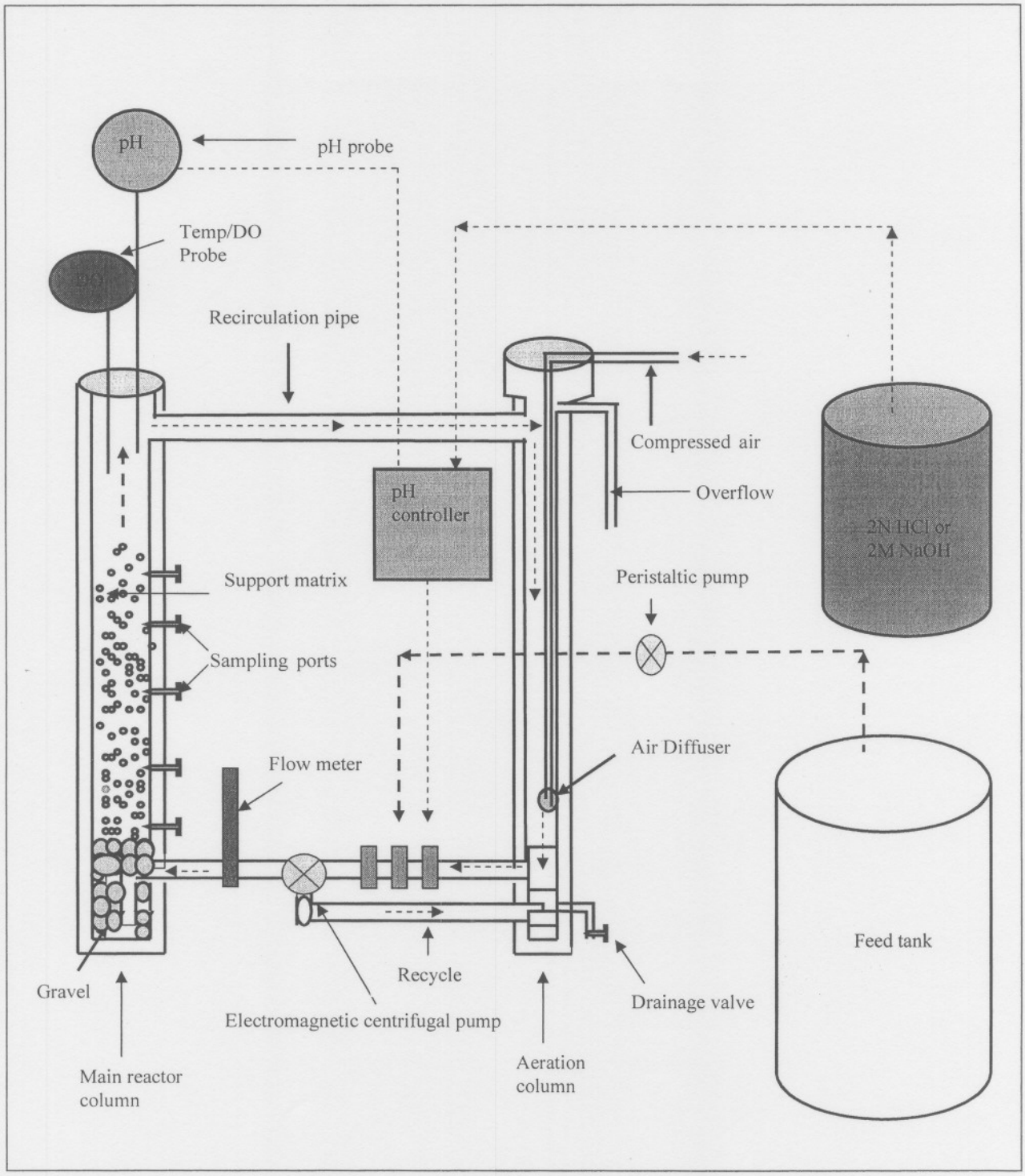


Figure 2. Schematic representation of the aerobic fluidised-bed reactors (not to scale) indicating the main reactor column and the aeration column.

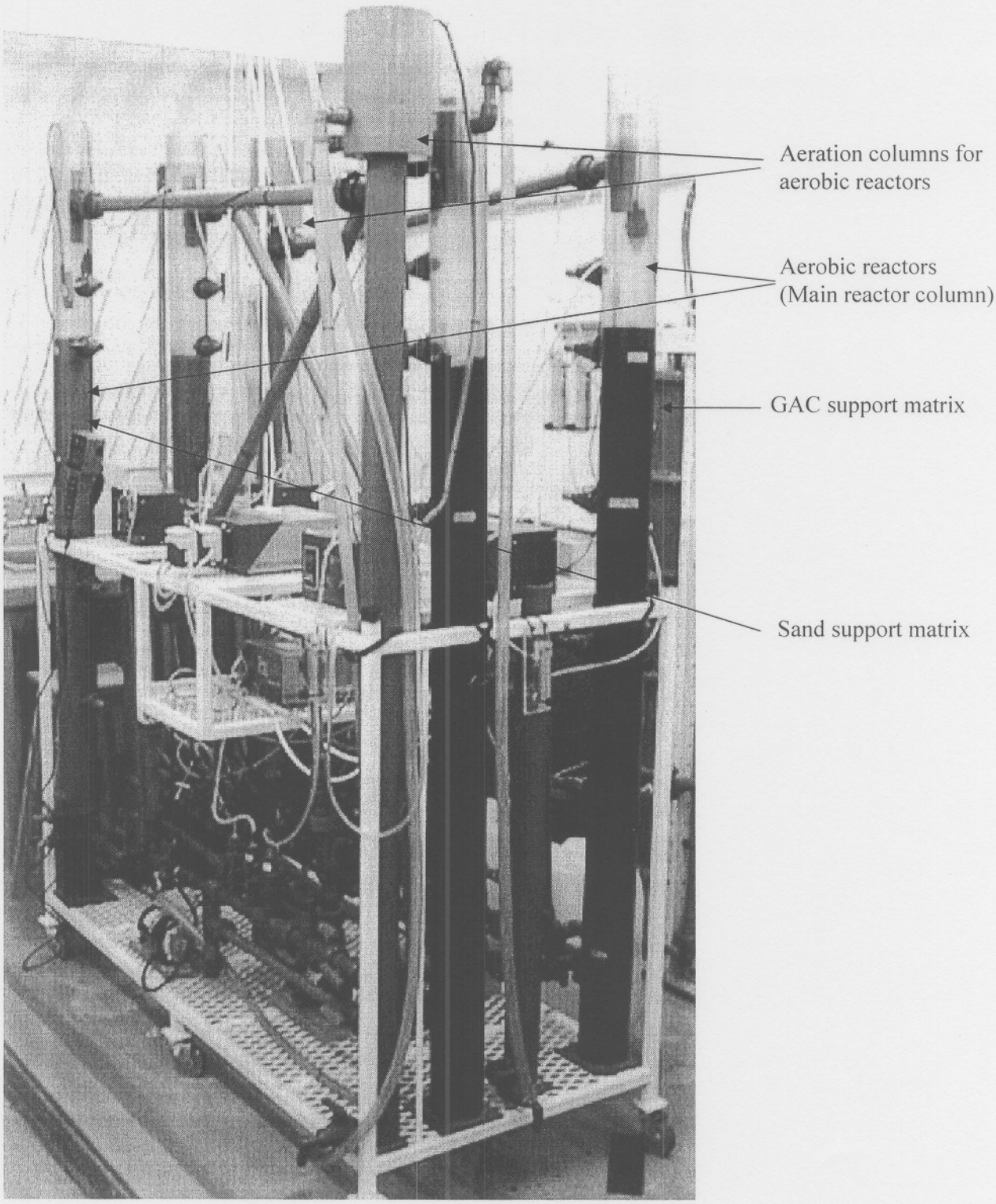


Figure 3. An overview of the experimental set-up of the BFBR as used during this study.

The main reactor columns were constructed using transparent polyvinyl chloride (PVC) piping (height 2 m, internal diameter 0.099 m). The total reactor volume was 23.485 L and the operational volume of the main reactor column was 13.765 L. The lower sections of the reactors were filled with course gravel to 25 cm in depth in order to stabilise the flow in the bottom section of the reactors after recirculation (Figure 4) (Bach *et al.*, 1998).

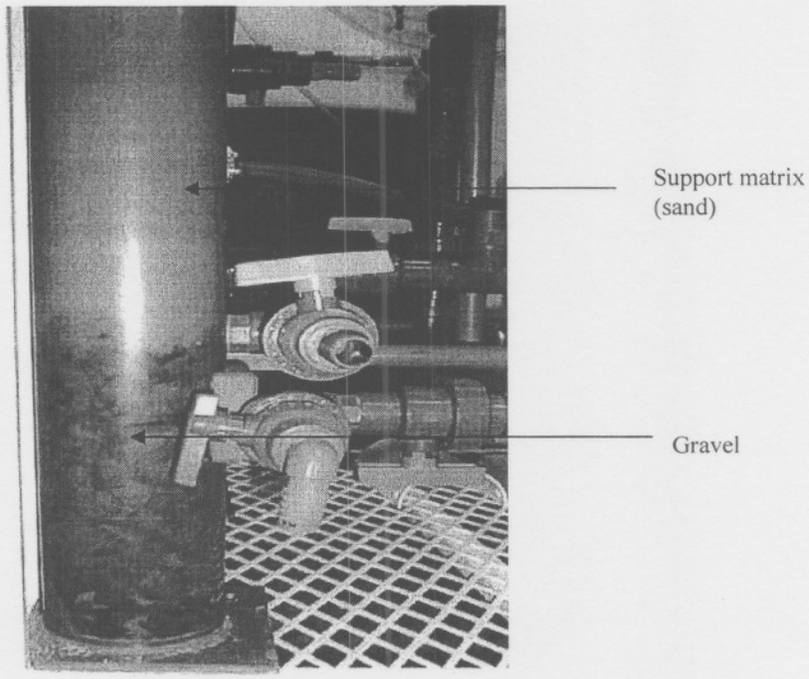


Figure 4. The bottom section of a two-phase BFBR illustrating the gravel below the support matrix (sand).

Sixty percent of the remaining height of the main reactor columns were filled with the respective support matrices. Before inoculation of the reactors, the relationship between static bed expansion and up-flow fluid velocities was determined. This enabled the calculation of the minimum up-flow liquid velocities required for the fluidisation of the support matrices. The main reactor volume was used in all subsequent calculations. Fluidisation was achieved and maintained using magnetic centrifugal pumps (*March mfg., Inc. U.S.A*). A 10 mm (diameter) filter was connected between the recirculation tube and the magnetic centrifugal pump to

prevent excess biomass and support matrix from entering the pump. The synthetic wastewater analogous to the Fischer-Tropsch reaction water was fed into the reactors using peristaltic pumps (*Watson Marlow, Germany*). The pH within the reactors was maintained at 7.0 with the addition of 2N HCl or 2M NaOH using an automatic pH controller (*Hanna instruments, Germany*). The temperature was maintained at 30 °C using a thermostatically controlled element. The dissolved oxygen (DO) and temperature within the reactors were monitored using a YSI 5100 DO and temperature probe (*Hanna instruments, Germany*).

3.4. Reactor inoculation, start-up and continuous operation

Both the aerobic reactors were initially inoculated using 1L of aerobic sludge obtained from the Flip Human Water Care Works in Krugersdorp, Gauteng, South Africa. After inoculation, the reactors were operated in batch mode for 10 days to facilitate biofilm formation on the support matrices. This was followed by continuous operation of the reactors at hydraulic retention times (HRTs) of 2 days at a bed height expansion of 30 %. The air supply to the aerobic reactors was gradually decreased in order to maintain a dissolved O_2 concentration of 0.5 mg/L in the main reactor columns. After stabilisation of the COD removal efficiency the hydraulic retention times (HRT) were decreased incrementally over time. It was assumed that steady-state conditions would be achieved after 3 HRTs. Therefore three HRTs were subsequently allowed to pass before decreasing to the proceeding HRT in order to determine the optimum organic loading rate. Table 1 shows the influent COD concentrations of both the biological fluidised-bed reactors using sand and GAC as support matrices, in relation to the hydraulic retention time in days, and the achieved organic loading rates. Once the maximal OLR had been achieved and steady-state conditions were apparent, the effect of pH shock loading on the reactor systems were evaluated by decreasing the pH of the reactor to 3.5 for an 8h cycle.

Table 1. COD feed concentrations and OLR achieved at specific HRTs at certain stages of the experiment shown in days.

Symbol	Days	HRT (days)	Target COD feed (mg/L)	OLR (kg COD/m^3.d)
A	0	2.0	1 600	0.89
B	25	2.0	3 200	2.80
C	42	2.0	6 400	4.00
D	49	2.0	9 000	5.20
E	82	2.0	12 000	7.00
F	117	1.7	16 000	6.50
G	124	1.5	18 000	9.00
H	141	1.0	20 000	10.00
I	180	1.0	20 000	20.00
J	205	0.8	20 000	25.00

3.5. Biofilm characterisation

Biofilm development on the various support matrices was also characterised using scanning electron microscopy (SEM). The samples of biofilm-coated support matrices (sand and GAC) were dehydrated with 70 % ethanol for 12 hours. The ethanol was subsequently replaced with 70, 80, 90 and 2 x 100 % acetone at 15 minute intervals each. The samples were then critical-point dried with liquid CO_2, mounted on stubs using double sided carbon tape and coated with 20 nm Au/Pd at a ratio of 70:30 (Csikor *et al.*, 1996; Chen and Chen, 2000). The samples were then viewed using a FEI: Quanta 200 E Scanning electron microscope.

3.6. Analytical methods

Routine analysis for the determination of alkalinity, total suspended solids (TSS), total solids (TS), volatile suspended solids (VSS) and volatile solids (VS) were performed according to the Standard methods for the Examination of Water and Wastewater (APHA, 1992). pH, temperature, dissolved oxygen (dO_2) and conductivity measurements were determined using a YSI 5100 DO and temperature probe. COD was determined spectrophotometrically using a MERCK Spectroquant, method number 112, using the MERCK kit 14555 for COD concentrations between 500 - 10 000 mg/L and. The VFAs were determined using steam distillation, modified from the Standard methods for the Examination of Water and Wastewater

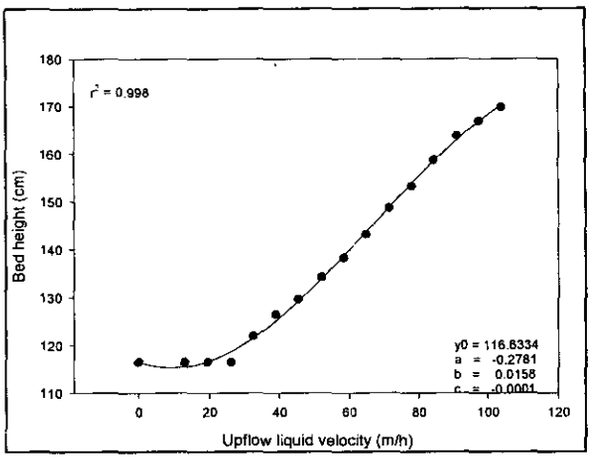
(APHA, 1992). The concentration of the individual organic acids in the influent and effluent were also determined using a Varian 3300 gas chromatograph equipped with a 6` x 4 mm ID glass column (10 % SP-1000/1 % H_3PO_4 on 100/120 Chromosorb® W AW, *Supelco*). One milliliter samples were diluted at a ratio of 50:50 using distilled water and then centrifuged in a 4 °C precooled centrifuge. Sample centrifugation took place at 13 000 x g for 15 minutes for the removal of cells from the samples prior to injection into the gas chromatograph column, with an oven temperature of 127 °C. Nitrogen (N_2) was utilised as the carrier gas at a flow rate of 86 mL/min. The detector (flame ionisation) was operated at a temperature of 160 °C. The injection volume was 1 μL and the injection temperature was 100 °C.

4. Results and Discussions

4.1. Assessment of fluidisation hydraulics.

The effect of the up-flow liquid velocity on the height of the bed of the fluidised-bed reactors is an important factor in determining the minimum up-flow liquid velocity required to fluidise the reactors. Biofilm formation on the support matrix has been repeated to result in an increased bed height at a constant up-flow velocity, mainly due to a decrease in the density of the support matrix. As a result, the bed height becomes less sensitive to the up-flow liquid velocity (Chang and Rittman, 1994). The effect of the up-flow liquid velocity on the clean bed height of the sand and GAC support matrices is shown in Figure 5a and 5b, respectively. The minimum up-flow liquid velocity required for the fluidisation of sand was determined to be 20 m/h, whereas the minimum up-flow liquid velocity required for the fluidisation of GAC was determined to be approximately 15 m/h.

a)



b)

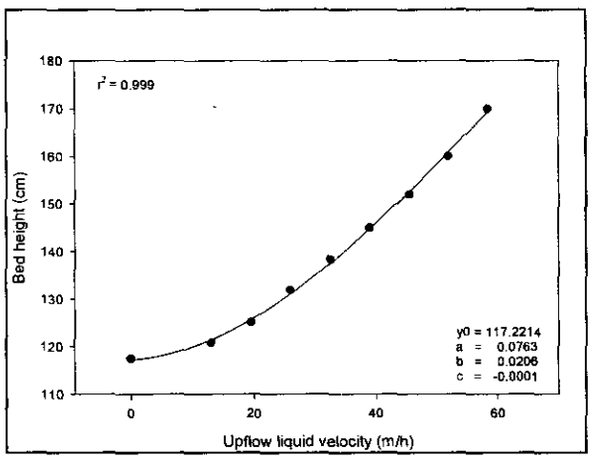


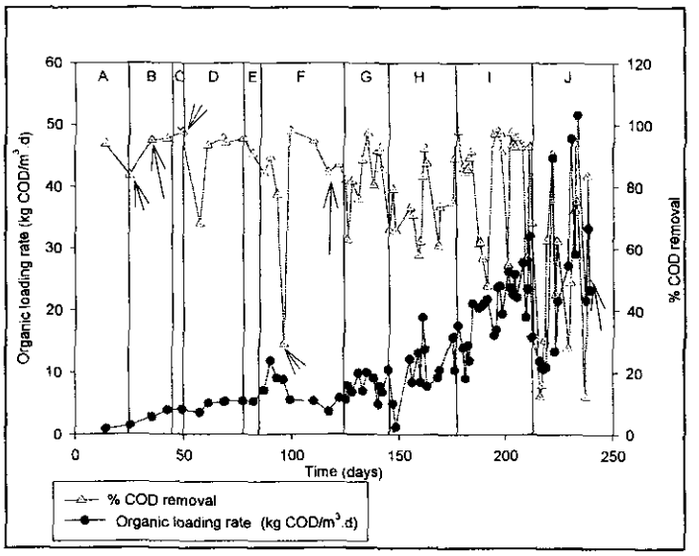
Figure 5. The effect of up-flow liquid velocity on the bed height of the various support matrices a) sand, and b) granular activated carbon.

4.2. Influence of organic loading rate has on COD removal efficiency

The effect of OLR on the percentage COD removal in the BFBRs using sand and GAC as support matrices is shown in Figure 6a and 6b, respectively. The aerobic reactor using sand as support matrix consistently achieved COD removal efficiencies in excess of 80 %. This COD removal efficiency was maintained up to an organic loading rate of 30 kg COD/m^3.d. Very few problems were experienced with plugging

and channelling in the BFBR using sand as support matrix, and the reactor (Figure 6a) required very little maintenance throughout the study. Wu *et al.*, (1998) used an internal circulating three-phase fluidised-bed bioreactor containing ceramic particles as biocarriers to treat a petrochemical wastewater and achieved a COD removal efficiency of 77 % at a COD loading rate of 6.7 COD/m^3.d. While, Yu *et al.*, (1999), achieved a COD removal efficiency of 70 %, maintaining a COD loading rate below 4 kg COD/m^3.d using a three-phase fluidised-bed reactor treating wastewater. COD removal efficiencies in excess of 80 % (Figure 6b) could also be attained in the BFBR using GAC as support matrix. An organic loading rate (OLR) of 30 kg COD/m^3.d could also be achieved in the BFBR using GAC as support matrix. However, significant problems were encountered with plugging and subsequent channeling occurred in the GAC reactor resulting in the need to frequently backwash the reactor in order to remove excess biomass (backwashes are indicated by the arrows in the graphs). Frequent bachwashes became necessary as the OLR reached 10 kg/m^3.d. The backwashes resulted in a significant decrease in the percentage COD removal. Despite these backwashes the reactor recovered rapidly to achieve a normal COD removal efficiency of above 80 % within 24 hours. Edwards *et al.*, (1994) reported achieving a COD removal rates of 99 % with an organic loading rate of 9.6 kg COD/m^3.d using a laboratory scale aerobic fluidised-bed reactor with sand as its support matrix for the biotreatment of a high-strength chemical industrial waste, while a 98 % removal efficiency at an organic loading rate of between 2 and 4 kg COD/m^3.d was achieved in a BFBR using GAC as support matrix. The results achieved in this study subsequently compare favourably with results found in literature although a different influent composition was used.

a)



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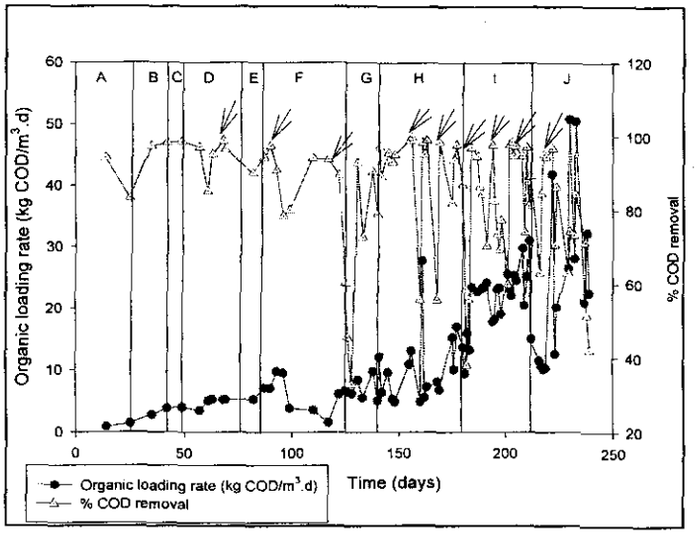
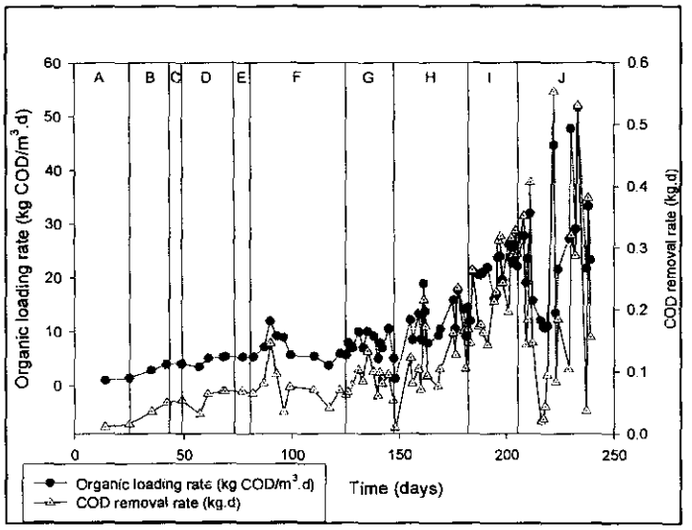


Figure 6. The effect of organic loading rate on the percentage COD removal in the BFBRs using a) sand and b) GAC as support matrices. (Arrows indicate washes). (key to symbols: A = 0.89 kg COD/m^3.d; B = 2.8 kg COD/m^3.d; C = 4.0 kg COD/m^3.d ; D = 5.2 kg COD/m^3.d; E = 7.0 kg COD/m^3.d; F = 6.5 kg COD/m^3.d; G = 9 kg COD/m^3.d; H = 10 kg COD/m^3.d; I = 20 kg COD/m^3.d; J = 25 kg COD/m^3.d)

4.3. COD reduction

The effect of the OLR on the COD removal rate for the BFBRs using sand and GAC as support matrices are shown in Figure 7a and 7b, respectively.

a)



b)

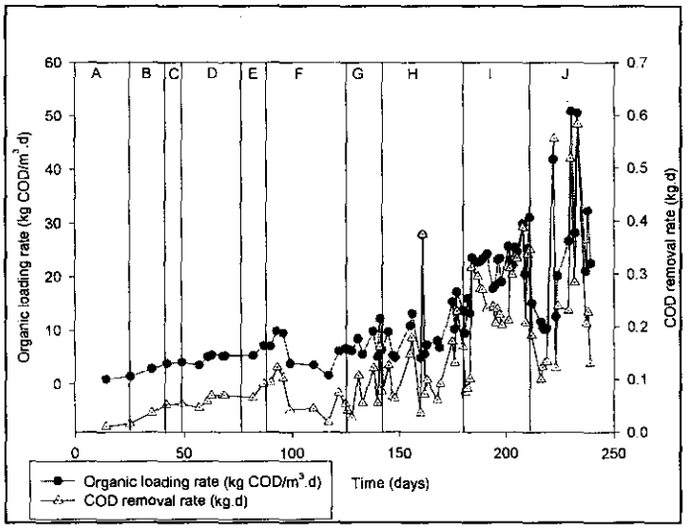


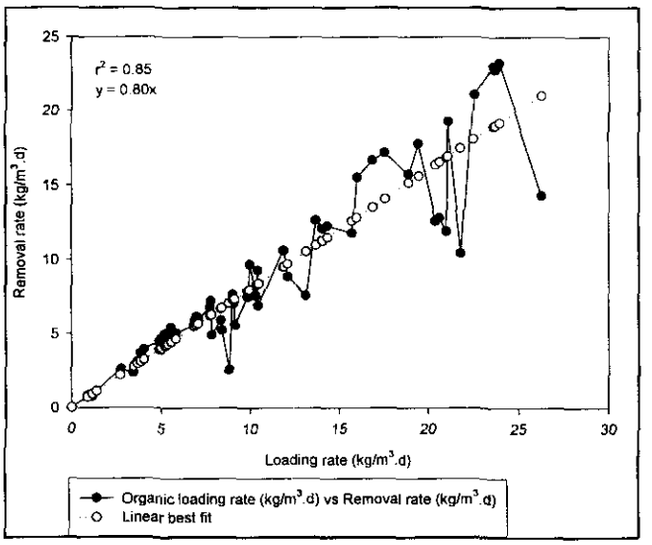
Figure 7. The effect of organic loading rate (kg COD/m^3.d) on the COD removal rate (kg/d) in the BFBRs using a) sand and b) GAC as support matrices. (key to symbols: A = 0.89 kg COD/m^3.d; B = 2.8 kg COD/m^3.d; C = 4.0 kg COD/m^3.d ; D = 5.2 kg COD/m^3.d; E = 7.0 kg COD/m^3.d; F = 6.5 kg COD/m^3.d; G = 9 kg COD/m^3.d; H = 10 kg COD/m^3.d; I = 20 kg COD/m^3.d; J = 25 kg COD/m^3.d).

It was evident that as the organic loading rate increased so did the COD removal rate in both aerobic BFBRs. pH shock loadings were introduced into both of the aerobic reactors on approximately day 200. Both COD removal rates and organic loading rates of these reactors became erratic after the introduction of these shock loadings. This erratic behaviour noticed in both of the aerobic BFBRs indicates that the microorganisms in the reactors were negatively affected by changes in pH, however, once the pH had been returned to stable conditions (6.5 –7.0) the reactors recovered within 24h. The optimum OLR achieved by both aerobic BFBRs was 25 kg COD/m^3.d, with a maximum COD removal rate of 0.35 kg/d in the BFBR using sand as support matrix and 0.4 kg/d in the BFBR using GAC as support matrix. Although the BFBR using GAC as support matrix obtained a higher COD removal rate and a higher average COD removal efficiency throughout the study, once the OLR reached above 10 kg COD/m^3.d plugging and subsequent channeling occurred, this increased the maintenance of the reactor which was time consuming. No such problems were experienced in the BFBR using sand as support matrix.

4.4. COD loading and removal

In the aerobic BFBRs as the loading rate was increased throughout the study, the removal rate increased as is illustrated in Figure 8a and 8b. The BFBR using sand as a support matrix achieved an average COD removal rate throughout this study of approximately 80 % (r^2 = 0.85) during the whole study, while the BFBR using GAC as support matrix achieved an average removal rate throughout this study of around 85 % (r^2 = 0.91) throughout the whole study.

a)



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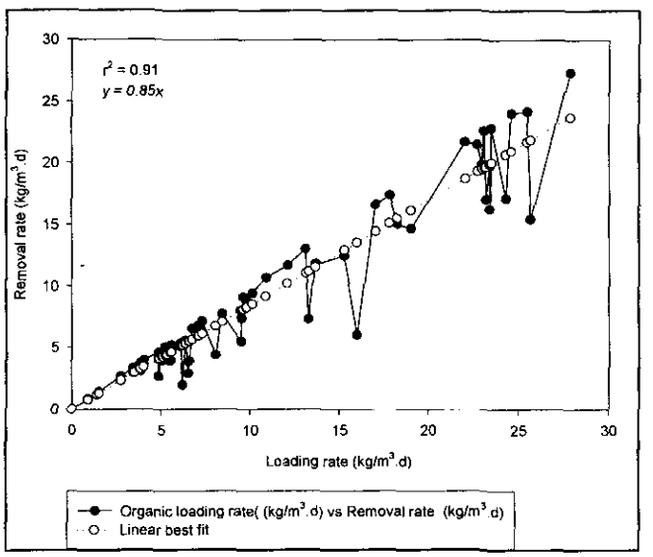


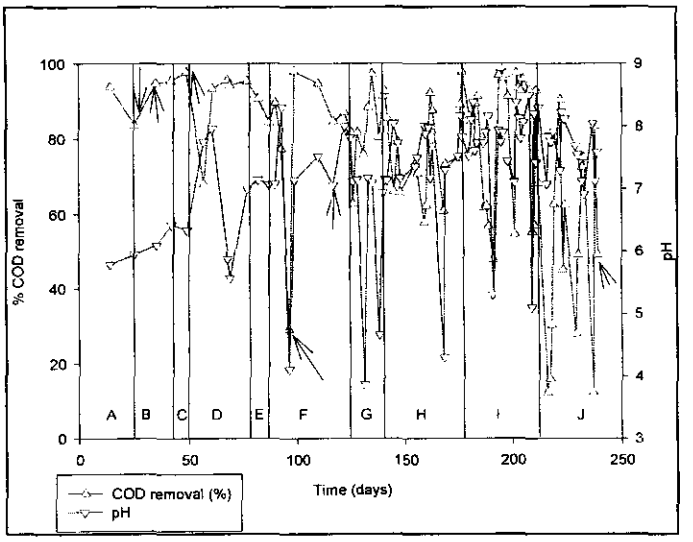
Figure 8. Organic loading rate (kg/m^3.d) vs Removal rate (kg/m^3.d) a) BFBR using sand as support matrix, and b) BFBR using GAC as support matrix.

4.5. Effect of changes in pH on COD performance

Figure 9a illustrates the percentage COD removal in relation to the pH values of the BFBR using sand as support matrix. It was observed that the COD removal efficiency remained in excess of 80 % when the pH of the reactor was maintained

between 6.5 – 7.0. pH shock loadings were introduced near the end of the study (on day 200), and the COD removal rates dropped to 50 % removal. When the pH dropped below the pKa value of the organic acid with the highest pKa value (propionic acid), that organic acid becomes toxic to the microorganisms significantly affecting the composition of the microorganisms in the system resulting in the lowering of the COD removal rates achieved in the aerobic fluidised-bed reactors. It was observed that when the pH within the reactor was decreased the operation of the reactors became very erratic and COD removal efficiencies decreased almost immediately. Alkalinity, COD, SS and volatile acid results also became increasingly erratic. However, when the pH of the reactor using sand as support matrix was returned to 6.5 – 7.0 the COD removal efficiency recovered to previous levels (> 85 %). Figure 9b shows the effect of pH on the percentage COD removal in the BFBR using GAC as its support matrix. The pH shock loadings introduced towards the end of the study resulted in COD removal efficiencies dropping to below 60 %. The COD removal efficiencies never recovered to previous percentage COD removal efficiencies.

a)



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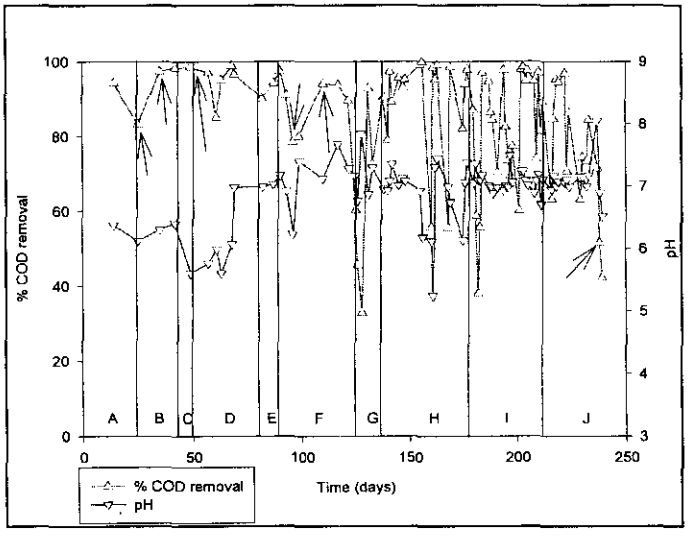


Figure 9. The effect of pH on the percentage COD removal in the BFBRs using a) sand and b) GAC as support matrices. (Arrows indicate washes). (key to symbols: A = 0.89 kg COD/m^3.d; B = 2.8 kg COD/m^3.d; C = 4.0 kg COD/m^3.d ; D = 5.2 kg COD/m^3.d; E = 7.0 kg COD/m^3.d; F = 6.5 kg COD/m^3.d; G = 9 kg COD/m^3.d; H = 10 kg COD/m^3.d; I = 20 kg COD/m^3.d; J = 25 kg COD/m^3.d).

4.6. Volatile fatty acids

The VFA/alkalinity ratio is a measure of process stability, when the ratio is less than 0.3 - 0.4 the process is considered to be operating favourably without the risk of acidity. When the VFA concentration increases, the alkalinity concentration decreases. Alkalinity is used as a buffer against the acidity, so the decrease in alkalinity results in high acid concentrations within the reactor which prevents the microorganisms in the system from functioning resulting in reactor failure (Borja *et al.*, 2001). In Figure 10 it is seen that the BFBR using GAC as a support matrix is more stable than the BFBR using sand as a support matrix. Both BFBRs were fairly stable until an OLR of 10 $kg/m^3.d$ was achieved, then the VFA/alkalinity value of the BFBR containing sand as a support matrix increased to around 4. It was noticed that the pH value decreased significantly to approximately 4 around the same time (100 days). This may be a result of an increase in the COD load (16 000 mg/L) and decreased in the HRT (1.7 days), leading to some biomass washout and the remainder of the bacteria having to adapt to the change in environment. This is assumed to have reduced the ability of the bacteria in breaking down the VFA, which will then accumulate increasing the level of acidity in the reactor and reducing the ability of the alkalinity to buffer this reaction. The reactor containing GAC support matrix remained stable until an OLR of above 15 $kg/m^3.d$ was obtained. The VFA/alkalinity ratio of this reactor then increased to approximately 3. This is thought to be as a result of backwashing due to excessive biomass build up in the reactor causing plugging. The viable bacteria used to treat the effluent are washed out leading to an increase in the VFA concentration, reducing the stability of the reactor. When the OLR reached 25 $kg/m^3.d$ the VFA/alkalinity ratio for both reactors had reached above the suggested failure limit value mentioned above. The BFBR using sand as a support matrix reached a VFA/alkalinity ratio value of above 9, while the BFBR using GAC as a support matrix reached a VFA/alkalinity ratio value of approximately 6.

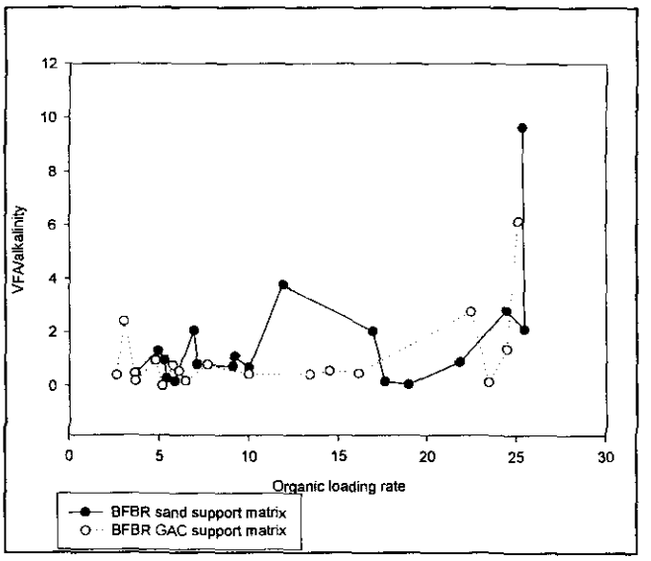


Figure 10. The VFA/Alkalinity ratio versus the OLR (kg COD/m^3.d).

The removal of the individual volatile fatty acids in both the BFBRs using sand and GAC as support matrices are indicated in Appendix A. It is evident that the VFA removal from the BFBR using sand as a support matrix took longer to stabilise than in the BFBR using GAC as a support matrix. This is thought to be due to the fact that the sand particles have a higher shear force, resulting in the biofilm having a lower formation rate as well as lower biomass concentration. It is illustrated in Figure 15 that the BFBR using sand as support matrix had higher shear forces than the BFBR using GAC as support matrix. The SEM of the sand particle shows that the biofilm grew only in the cracks and crevasses, which protected the microorganisms from other sand particles. While the biofilm on the GAC particle grew all over it as these mircoorganisms did not need protection from other GAC particles. The biomass both aerobic BFBRs is illustrated in Figure 11b and Figure 12b, which shows the TS and VS concentrations, respectively. Both Figures illustrate that the BFBR using sand as support matrix had lower biomass values compared to the BFBR using GAC as support matrix. The TS values of the sand support matrix started at approximately 150 mg/g and decreased steadily to approximately 50 mg/g, while the GAC support matrix had TS values that began at approximately 400 mg/g and decreased to approximately 150 mg/g. The VS values gave the same trend with the sand support

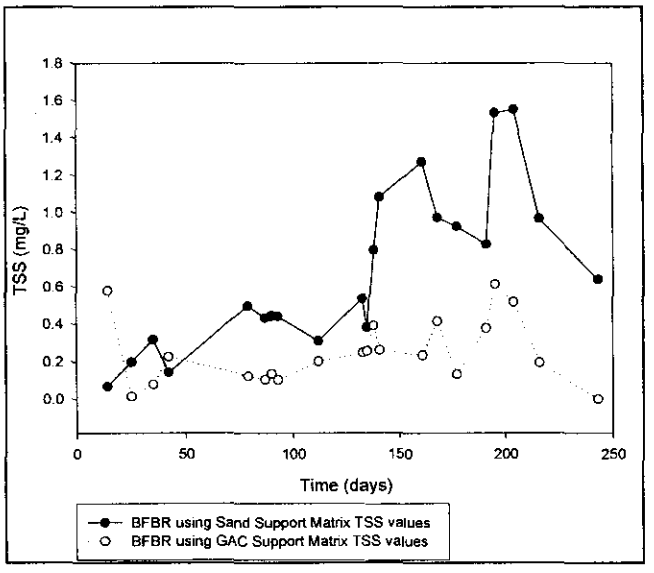
matrix remaining around 5 mg/g throughout the study, while the GAC support matrix began at a VS value of approximately 40 mg/g and decreased steadily to approximately 10 mg/g. In both The BFBR using GAC as a support matrix responded by day 50, reaching removal rates in excess of 80 % of all the volatile fatty acids in the feed while the BFBR using sand as a support matrix took over 100 days to reach removal rates of above 80 %. It has been reported that the adsorption capacity of GAC for organic compounds is ideal for rapid biomass formation and by providing protection from shear forces (Safferman and Bishop, 1997). The overall removal of acetic acid and propionic acid appears less sensitive to operation fluctuations of the reactors compared to isobutyric, isovaleric and butyric acids. Edwards *et al.*, (1994) reported that it took a reactor using sand as support matrix approximately 100 days to reach a consistent chemical removal, whilst their reactor using GAC as support matrix took around 40 days. These results correlate to the start-up periods for the two reactors during this study. The rapid biomass formation in the BFBR using GAC as support matrix lead to large amounts of biomass being formed in the reactor, which resulted in plugging and channelling and the need to backwash the reactor regularly. After a backwash the removal percentage would drop significantly but this would recover to above 80 % removal rates within 24h. Once the BFBR using sand as support matrix stabilised very few problems were experienced and removal efficiency in excess of 80 % of all of the VFAs was observed for the remainder of the study.

4.7. Biomass measurements

During this study both total suspended solids (TSS) and total solids (TS) were measured for the planktonic and sessile phases of the BFBRs using sand and GAC as support matrices. In comparison to the BFBR using GAC as support matrix, the BFBR using sand as support matrix had significantly higher TSS values were in the planktonic phase. This may be ascribed to the high shear forces in the BFBR using sand as support matrix. In contrast, the BFBR containing GAC as support matrix had significantly higher TS values than the BFBR containing sand as a support matrix. This may be ascribed to the larger surface area of the GAC enabling more biofilm attachment and the lower levels of shear forces due to the decrease in up-flow velocities. The TSS and TS values as determined in the planktonic and sessile phase

of both reactors respectively are shown in Figure 11. The TSS values in the planktonic phase of the BFBR using sand as a support matrix reached a maximum value of 1.6 mg/L, while the BFBR using GAC as a support matrix reached a maximum value of 0.6 mg/L, both at an OLR of approximately 20 000 mg/L. The TS values obtained in the sessile phase of the BFBR using GAC as support matrix began at 400 mg/g and decreased steadily to 150 mg/g, with the highest value being 450 mg/g. While the BFBR using sand as a support matrix had TS values that began at 150 mg/g and decreased to 50 mg/g through the study, achieving a maximum TS value of 150 mg/g. Once pH shock loadings were introduced (day 200), of the experiment the TSS values for the planktonic phase dropped. It is evident from the results presented in Figure 9a and 9b that a direct inverse relationship existed between the TS levels on the various support matrices and the TSS levels in the planktonic phase of the respective BFBRs. The TS results obtained during this study indicate that the biofilm development on the GAC support matrix was more sensitive to decreased hydraulic retention time. The TS values dropped significantly from levels in excess of 400 mg/g during the start-up phase of the reactors to relatively stable levels (~ 190 mg/g) during the operation of the reactors at high OLR. In contrast the TS levels of the BFBR using sand as support matrix remained relatively constant throughout the study (~ 100 mg/g). In contrast to the observed TS values, the TSS values obtained in the BFBR using sand as support matrix increased significantly from approximately 0.1 mg/L to approximately 1.5 mg/L. While the BFBR using GAC as support matrix remained constant at approximately 0.2 mg/L but increased slowly to approximately 0.6 mg/L through the study.

a)



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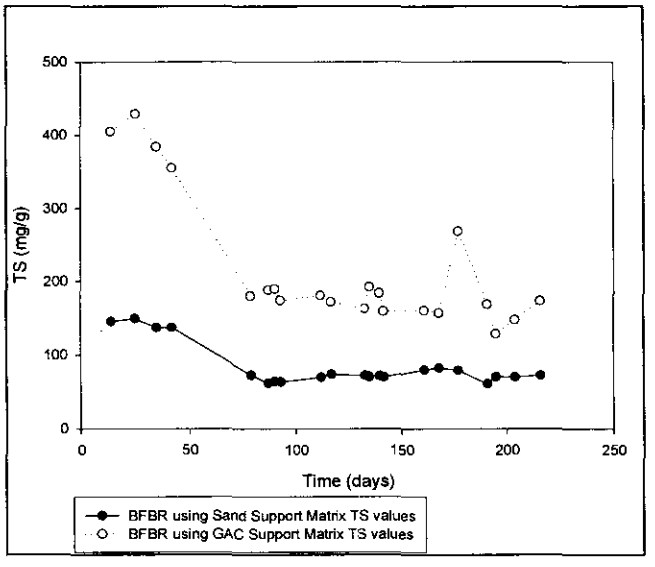
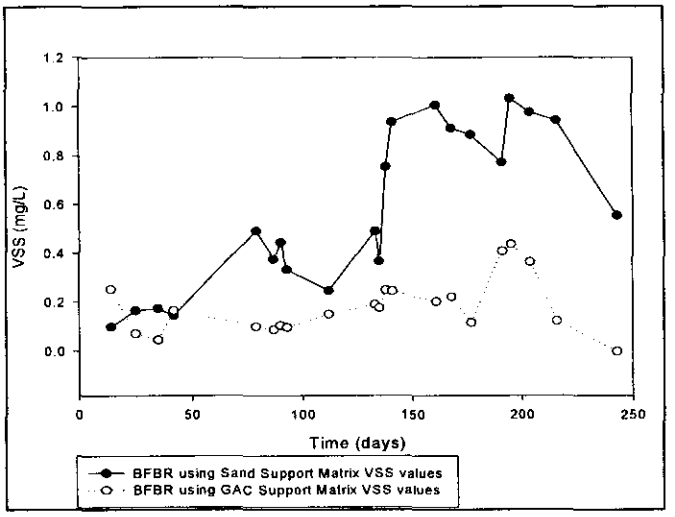


Figure 11. a) TSS concentrations (mg/L); and b) TS concentrations (mg/g) for the planktonic and sessile phases of the aerobic BFBRs using sand and GAC as support matrices, respectively.

a)



b)

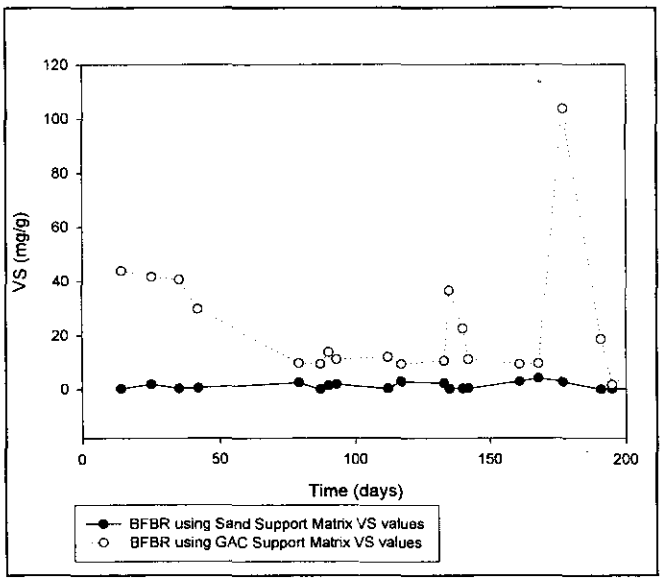


Figure 12. a) VSS concentrations (mg/L) for the planktonic phase; and b) VS concentrations (mg/g) for the sessile phase of the aerobic BFBRs using sand and GAC as support matrices.

Volatile suspended solids (VSS) and volatile solids (VS) were also determined on the planktonic and sessile phases of the BFB reactors, respectively. The VSS values for

both reactors followed the same pattern as the TSS values. The VS values of the sessile phase were higher than the VSS values of the planktonic phase. In the planktonic phase the BFBR using sand support matrix has a higher VSS value than the BFBR using GAC support matrix, as illustrated in Figures 12a and 12b. In the planktonic phase the sand support matrix obtained a maximum value of 1 mg/L, while the GAC support matrix reached a maximum VSS value of 0.4 mg/L. In the sessile phase the GAC reactor achieved VS values that began at 40 mg/g and decreased to 10 mg/g for the remainder of the study, and obtained a maximum VS value of 100 mg/g. While the BFBR using sand as support matrix obtained VS values that remained constant at approximately 5 mg/g throughout the study. The TS and VS values indicate that the BFBR using sand as support matrix has a lower biomass concentration than the BFBR using GAC as support matrix. It was evident that in both BFBRs the TSS and VSS values started low and increased over time, while the TS and VS values started high and decreased through the study. This is thought to be as a result of the increase in HRTs, which lead to increased shear forces breaking up the biofilm found on the support matrices. The biofilm then moves into the planktonic phase resulting in the increase of the TSS and VSS values.

In determining the VSS/TSS ratio of the BFBR the correlation between the biomass growth and the quality of the biomass is determined (Amatya, 1996). The VSS/TSS ratios of the planktonic phase is illustrated in Figure 13. It has been reported that a VSS/TSS of approximately 1 indicates that the suspended solids have a high organic fraction. At the time of reactor start-up the aerobic BFBR using sand as a support matrix had a very high VSS/TSS value of 1.58. This could indicate that the inoculum initially used contained a high inorganic content. This value dropped below 0.5 within 40 days of reactor operation and then began to increase, stabilising around day 80, and remaining constant between 0.8 and 1.0. However, the aerobic BFBR using GAC as a support matrix had an initial start-up VSS/TSS value of 0.8. There was a steady increase in the VSS/TSS ratio as the granules grew bigger in the reactor during operation and the VSS/TSS values stabilised at approximately 1.0 (day 70).

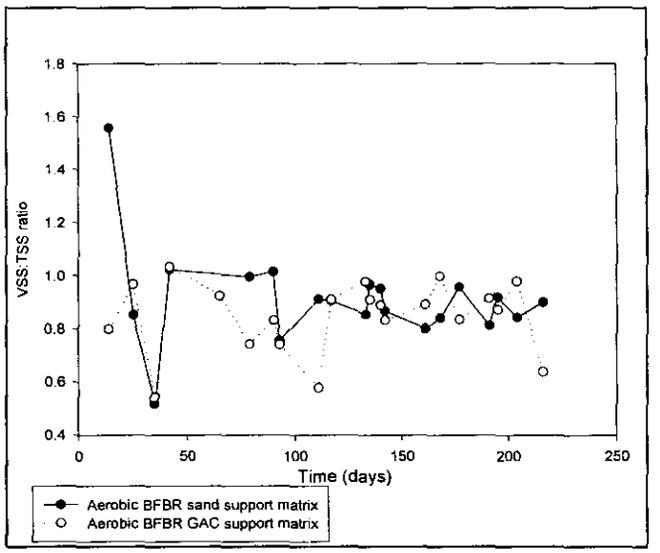


Figure 13. VSS/TSS ratio in the aerobic BFBRs during reactor operation period

4.8. Oxygen utilisation

The dissolved oxygen (dO_2) was measured in order to maintain the airflow in the reactor above 0.5 mg/L. This was achieved by adjusting the compressed airflow (L/min). The airflow was altered in order to determine which flow rate allowed the bacteria in the reactors to function at their optimal levels. Aeration was maintained at 15 L/min in an attempt to achieve a final dO_2 concentration of between 0.5 to 2 mg/L. Aeration is possibly the largest cost aspect during operation of aerobic reactors making them less cost effective than anaerobic reactors. It was therefore essential to determine the lowest aeration levels of the reactors while maintaining a high COD removal rate. The dO_2 levels achieved in the BFBRs are shown in Figure 14. The specific air requirements of the aerobic BFB reactors using sand and GAC as support matrices were calculated to be approximately 35 m^3 air/kg COD_{rem} and 41 m^3 air/kg COD_{rem}, respectively. The oxygen transfer efficiency for both reactors was determined to be approximately 5.4 %. In comparison to the activated sludge treatment system currently in use at SASOL SynFuels, Secunda the specific air requirements of the BFBR is favourable as the activated sludge system requires a specific air volume of 75 m^3 air/kg COD removed at a maximum OLR of 3.5 kg COD/m^3.d. However, when compared to the high-rate compact reactor and the biological aerated filter which obtained specific air requirements of 18 m^3 air/kg COD

removed (OLR = 35 kg COD/m^3.d) and 11 m^3 air/kg COD removed (OLR = 35 kg COD/m^3.d), respectively, both the aerobic BFBRs had significantly higher specific air requirements and a lower OLR (25 kg COD/m^3.d).

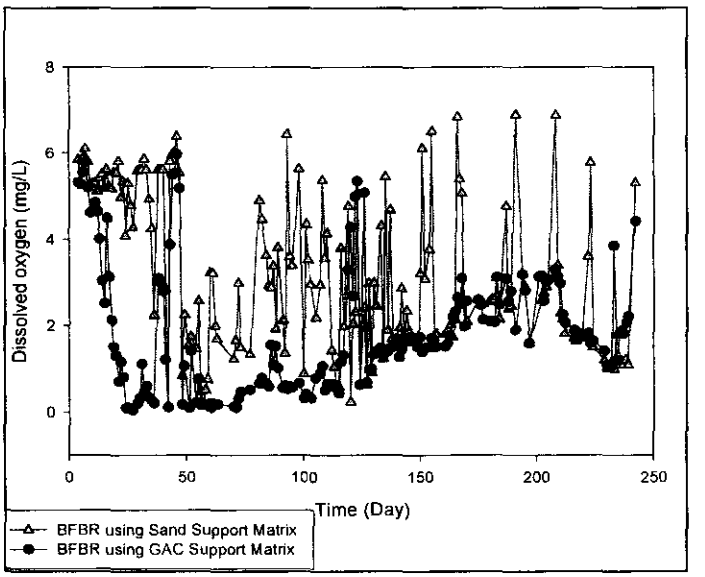
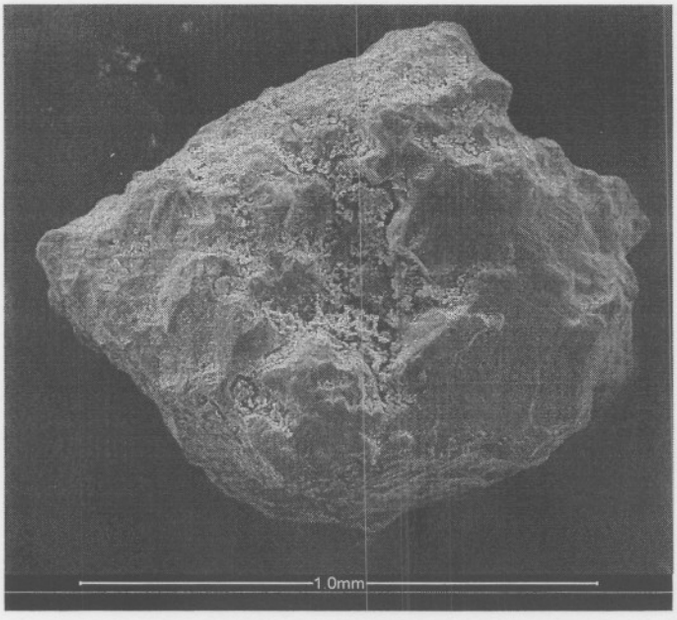


Figure 14. Time course analysis of the DO concentration in the aerobic BFBRs using sand and GAC as support matrices.

4.9. Scanning electron microscopy

Biofilm formation occurred on both sand and GAC support matrices, and gradually increased over time due to increased OLR. However, initial biofilm formation took longer on the sand support matrix than on the GAC support matrix. This was evident in the fact that the GAC reactor produced more biofilm and required more backwashes than the sand reactor, as illustrated in Figure 6. Examination of the electron micrograph indicates that biofilm formation on the sand support matrix was restricted to the crevasses and cavities (Figure 15a) of the sand particles possibly due to the high shear forces associated with the fluidisation of sand, while the biofilm formation on the GAC support matrix grew uniformly on the particles (Figure 15b). Due to the irregularity and high porosity of GAC it has been reported to be a better immobilisation matrix than sand (Texeira and Oliveira, 1998). GACs adsorption capacity to absorb organic compounds has also been reported to protect the attached

a)



b)

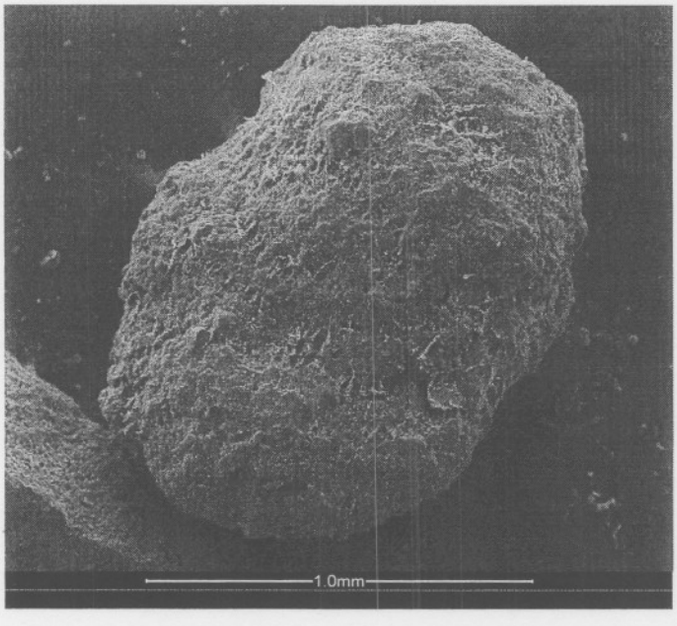
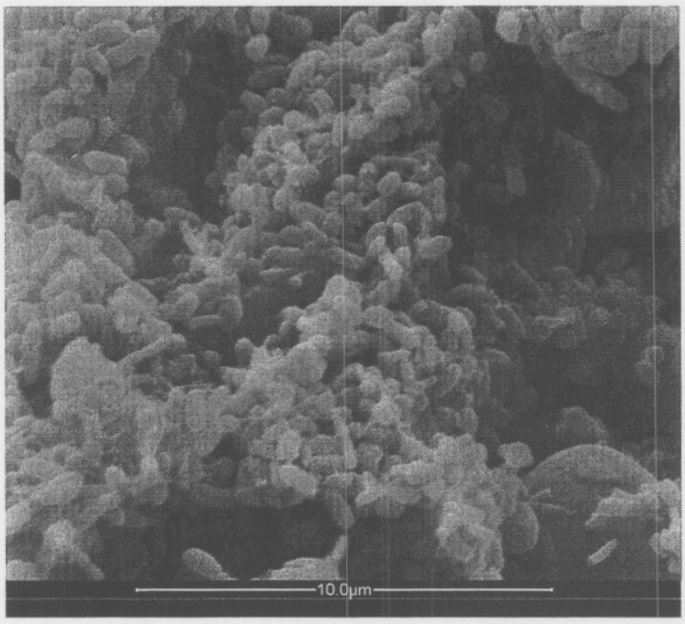


Figure 15. Scanning Electron Micrographs illustrating biofilm growth on the surface of the a) sand; and b) GAC support matrices after 110 days of reactor operation.

biofilm from shock organic loading and is ideal for rapid biomass colonisation providing protection from shear forces (Safferman and Bishop, 1997). The increase of biofilm formation on the support matrices over time corresponded with an increase in the expanded bed height despite the constant up-flow velocity. These results confirmed previous reports that biofilm formation resulted in the development of a less dense support matrix, culminating in an increase in bed height (Summerfelt and Cleasby, 1996). The bed height was kept constant by reduction in the up-flow liquid velocities.

The morphology and diversity of the bacterial biofilm development on the sand and GAC support matrices is shown in Figure 16a and 16b, respectively. The morphology of the microorganisms found in both aerobic BFBRs is rod-shaped (bacil) and yeast cells are evident in both scanning electron micrographs. The morphology of the microorganisms found in the anaerobic BFBR (Chapter 4) which are coccoid.

a)



b)

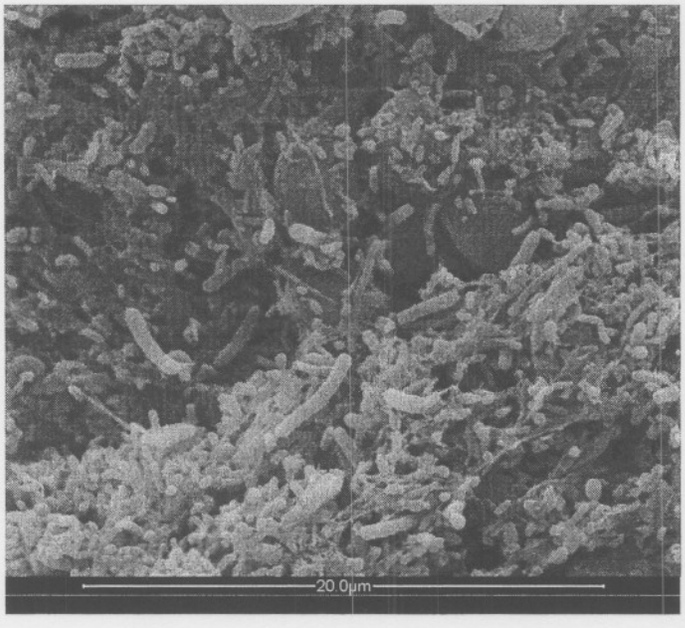


Figure 16. Scanning Electron Micrographs illustrating the bacterial morphology and diversity on the a) sand; and b) GAC support matrices, respectively.

5. Conclusions

The main conclusions that were drawn from this study are the following:

- The BFBR containing sand as a support matrix required a longer start-up period (70 days) possibly due to the large shear forces associated with sand as the immobilisation matrix. However, once the reactor had stabilised very few problems occurred for the duration of this study. Biofilm grew on the GAC support matrix of the aerobic BFBR within 50 days of the start-up of the reactor and high removal rates were achieved. However, the biofilm accumulated rapidly resulting in the need to backwash the reactor regularly. The washes had very little effect on the overall removal of the VFAs in the reactor but increased the maintenance requirement, which was time consuming.

- Both the BFBRs containing sand and GAC as support matrices were successful in achieving COD removal rates in excess of 80 % throughout the study, until pH shock loadings were introduced. The average removal rate of the BFBR using sand as a support matrix was approximately 80 %, while the average removal rate of the BFBR using GAC as support matrix was approximately 85 %. The maximum OLR achieved for both reactors was approximately 30 kg COD/m^3.d. This OLR was higher than the OLRs achieved in most available literature, whilst still maintaining removal rates of above 80 %. In comparison to the activated sludge reactor which is currently in use at SASOL SynFuels, Secunda, which has an OLR of 3.5 kg COD/m^3.d with and average COD removal efficiency of 80%, the BFBR was favourable as it was able to achieve a much higher OLR and a higher COD removal efficiency. While both the high-rate compact and BAF reactors achieved OLR of 35 kg COD/m^3.d, with COD removal efficiencies of 70 % and 80% respectively. Both of these reactors performed better than the aerobic BFBR.

- It was determined that pH played an important role in the function of the BFBRs. If the pH was decreased below the pKa value of the organic acids present in the

feed, the removal rates dropped significantly to approximately 50 % for both BFBRs. However, once the pH was returned to between 6.5 and 7 the reactors recovered within 24 hours to achieving removal rates of above 80 %.

- The VFA/alkalinity ratio determined that both reactors were stable (0.3 - 0.4) until an OLR of 10 kg/m^3.d was obtained, then the VFA/alkalinity ratio of the BFBR using sand as a support matrix increased significantly to 4. This correlates with a significant decrease in the pH to a pH of approximately 4. This drop in pH is thought to be caused by the decrease in HRT (1.7 days) on day 100 and the increase in the concentration of the COD load (16 000 mg/L) of the reactor in order to achieve higher OLR. The decrease in HRT may have lead to biomass washout reducing the amount of bacteria in the reactor able to breakdown the increased concentrations of organic acids. This in turn may result in the reactor becoming less stable. The BFBR using GAC as support matrix remained stable until an OLR of 15 kg/m^3.d was obtained, the VFA/alkalinity ratio increased to 3. This is thought to be due to the backwashing of the reactor to prevent plugging due to excess biomass. The backwashing may have resulted in an accumulation of VFAs in the reactor leading to increased acidity and decreased stability. When an OLR of 25 kg/m^3.d the VFA/alkalinity ratios of the BFBRs using sand and GAC as support matrices to 9 and 6, respectively. This is thought to be due to the shock loadings introduced at the end of the study reducing the ability of the microorganisms from operating at their optimal levels resulting in a decrease in the stability of the reactors.

- The TSS values in the planktonic phase of the BFBR using sand as a support matrix reached a maximum value of 1.6 mg/L, while the BFBR using GAC as a support matrix reached a maximum value of 0.6 mg/L, both at an OLR of approximately 20 000 mg/L. The TS values (sessile phase) of the BFBR using GAC as support matrix began at 400 mg/g and decreased steadily to 150 mg/g, with the highest value being 450 mg/g. While the BFBR using sand as a support matrix had TS values that began at 150 mg/g and decreased to 50 mg/g through the study, achieving a maximum TS value of 150 mg/g. Once pH shock loadings

were introduced (day 200) the TSS values (planktonic phase) decreased significantly. The TS results obtained during this study indicate that the biofilm development on the GAC support matrix was more sensitive to decreased up-flow liquid velocity. The TS values dropped significantly from levels in excess of 400 mg/g during the start-up phase of the reactors to relatively stable levels (~ 190 mg/g) during the operation of the reactors at high OLR. In contrast the TS levels of the BFBR using sand as support matrix remained relatively constant throughout the study (~ 100 mg/g). In contrast to the observed TS values, the TSS values obtained in the BFBR using sand as support matrix increased significantly from approximately 0.1 mg/L to approximately 1.5 mg/L. While the BFBR using GAC as support matrix increased slowly to approximately 0.6 mg/L during the study. The VSS (planktonic phase) and VS (sessile phase) values for both reactors followed the same pattern as the TSS and TS values. The VS values of the sessile phase were higher than the VSS values of the planktonic phase. In the planktonic phase the BFBR using sand support matrix has a higher VSS value than the BFBR using GAC support matrix. In the planktonic phase the sand support matrix obtained a maximum value of 1 mg/L, while the GAC support matrix reached a maximum VSS value of 0.4 mg/L. In the sessile phase the GAC reactor achieved VS values that began at 40 mg/g and decreased to 10 mg/g for the remainder of the study, and obtained a maximum VS value of 100 mg/g. While the BFBR using sand as support matrix obtained VS values that remained constant at approximately 5 mg/g throughout the study. The TS and VS values indicate that the BFBR using sand as support matrix has a lower biomass concentration than the BFBR using GAC as support matrix. It was evident that in both BFBRs the TSS and VSS values started low and increased over time, while the TS and VS values started high and decreased through the study. This is thought to be as a result of the decrease in HRTs, which lead to increased shear forces breaking up the biofilm found on the support matrices. The biofilm then moves into the planktonic phase resulting in the increase of the TSS and VSS values.

- The VSS/TSS ratios illustrate the biomass growth and quality. The results obtained in this study indicate that the sand support matrix with its rough surface protected the microorganisms in the biofilm from they hydraulic shear enabling

the VSS/TSS ratio to stabilise around day 80 between 0.8 and 1. The VSS/TSS ratio of the BFBR using GAC as a support matrix stabilised at approximately 0.9 on around day 90 after increasing gradually through the start-up of the reactor.

- The dissolved oxygen (dO_2) was measured in order to maintain the air flow in the reactor above 0.5 mg/L. Aeration was maintained at 15 L/min in an attempt to achieve a final dO_2 concentration of between 0.5 to 2 mg/L. The specific air requirements of the aerobic BFB reactors using sand and GAC as support matrices were calculated to be approximately 35 m^3 air/kg COD_{rem} and 41 m^3 air/kg COD_{rem}, respectively. The oxygen transfer efficiency for both reactors was determined to be approximately 5.4 %. In comparison to the activated sludge treatment system currently in use at SASOL SynFuels, Secunda the specific air requirements of the BFBR is favourable as the activated sludge system requires a specific air volume of 75 m^3 air/kg COD removed at a maximum OLR of 3.5 kg COD/m^3.d. However, when compared to the high-rate compact reactor and the biological aerated filter which obtained specific air requirements of 18 m^3 air/kg COD removed (OLR = 35 kg COD/m^3.d) and 11 m^3 air/kg COD removed (OLR = 35 kg COD/m^3.d), respectively, both the aerobic BFBRs had significantly higher specific air requirements and a lower OLR (25 kg COD/m^3.d).

- A higher removal efficiency and a more stable reactor operation was achieved with the use of sand as support matrix during aerobic treatment, as plugging and subsequent channeling at high OLR occurred in the BFBR using GAC as support matrix resulting in the need for frequent backwashing.

COD removal efficiencies and OLR compare favourably with activated sludge systems and application of aerobic BFBR could serve as a suitable alternative treatment technology for the treatment of Fischer-Tropsch reaction water.

In contrast to other treatment processes being investigated by SASOL SynFuels, Secunda the aerobic BFBR does not compare as favourably. The high-rate compact reactor and the biological aerated filter reactor both achieve higher OLR than the

BFBR while maintaining high COD removal efficiencies. The anaerobic digestion also achieves a higher average COD removal efficiency at a higher OLR than the anaerobic BFBR.

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Chapter 4

Evaluation of Biological Fluidised-Bed Reactors for the Anaerobic Treatment of Fischer-Tropsch Reaction Water

1. Abstract

A high-strength COD petrochemical effluent, known as reaction water is generated during the Fischer-Tropsch reaction in the SASOL Synthol process, SASOL SynFuels, Secunda, South Africa. The effluent together with two other aqueous process effluents (Stripped Gas Liquor (SGL) and Oily sewer water (API)) are currently treated using ten dedicated activated sludge basins. However, biological treatment of these effluents has proven to be difficult with low COD removal efficiencies (< 80 %). It is hypothesised that these difficulties are due to shock loadings, presence of toxic compounds variation in volumetric and hydraulic loadings, as well as variations in the composition of the process effluents. Due to these major limitations, and the fact that the Fischer-Tropsch (Synthol) reaction water constitutes 70 % of the COD load in the activated sludge process, possible alternative biological treatment processes are being investigated in order to optimise operational costs and effluent treatment efficiencies. Low organic loading rates (3.5 kg COD/m^3.d) and high specific air requirements (60 - 75 m^3 air/kg COD_{rem}) currently make the existing activated sludge systems inefficient and economically non-viable. However, various studies concerning the aerobic and anaerobic treatment of Fischer-Tropsch reaction water in suspended growth wastewater treatment systems have proven unsuccessful. High rate fixed-film processes or biofilm reactors, of which the fluidised-bed reactors have been reported to be one of the most effective, are seen as a promising alternative process for the treatment of high-strength industrial wastewaters. The primary aim of this study was to evaluate the suitability of biological fluidised-bed reactors (BFBRs) for the anaerobic treatment of a high strength COD industrial effluent. The suitability of two different biofilm support matrices, sand and granular activated carbon (GAC)

were also evaluated during this study. The COD removal efficiencies averaged 60 % at organic loading rates lower than 10 kg COD/m^3.d in the anaerobic BFBR using GAC as a support matrix. The removal efficiency decreased to 50 % as organic loading rates were increased to 20 kg COD/m^3.d. In contrast, removal efficiencies remained very low (approximately 30 %) in the anaerobic BFBR using sand as support matrix, possibly due to the high shear force levels caused by the up-flow liquid velocity and the reactor never stabilised. Further studies concerning the use of sand as support matrix were subsequently terminated. The biogas and methane yields of the anaerobic BFBR using GAC as support matrix were determined to be approximately 0.38 m^3 biogas/kg COD_{rem} (0.30 m^3 biogas/$m^3_{reactor\ vol}$.d), and 0.20 m^3 CH_4/kg COD_{rem} (0.23 m^3 CH_4/$m^3_{reactor\ vol}$.d), respectively. The maximum theoretical methane yield is 0.35 m^3 CH_4/g COD_{rem}. Although the methane content of the biogas was initially low (< 30 %), the methane content gradually increased to 60 % at organic loading rates of 20 kg COD/m^3.d. Methane obtained during this study increased until a OLR of 8 kg/m^3.d was achieved and then leveled off and remained constant at approximately 2 m^3 CH_4/$m^3_{reactor\ vol}$.d for the remainder of the study. At an OLR of 12 kg/m^3.d the stability of the reactor decreased significantly, indicated by a dramatic increase of the VFA/alkalinity ratio and COD removal efficiencies dropped to 50 %. Biomass values obtained at the beginning of the study were high at 50 mg/g TS but decreased steadily throughout the study to below 10 mg/g due to biomass washout as a result of decreased HRT in order to increase OLR. Anaerobic treatment of Fischer-Tropsch reaction water using BFBR may thus serve as a suitable alternative treatment technology for the activated sludge systems currently used by SASOL.

2. Introduction

During the Fischer-Tropsch reaction in the Synthol process (SASOL SynFuels, Secunda, South Africa), a mixture of CO and H_2 (syngas) is converted to a range of hydrocarbons. The reaction can be represented as $CO + 2H_2 \rightarrow CH_2 + H_2O$ (Dry, 1999). During this process, an aqueous stream, referred to as Fischer-Tropsch

(Synthol) reaction water, is generated. Approximately 25 - 30 ML of this reaction water is produced daily. Distillation of the reaction water to remove non- and oxygenated hydrocarbons yields on organic acid-enriched stream. This effluent contains 1 to 1.5 % v/v $C_2 - C_4$ organic acids (> 85 % acetic acid), and $C_5 - C_{18}$ organic acids, including light oils, aldehydes, ketones, cresols and phenols. The Fischer-Tropsch reaction water has an average COD of 16 000 mg/L, but this can vary between 12 000 mg/L and 22 000 mg/L.

Together with Fischer-Tropsch reaction water, two other aqueous process effluents are generated by SASOL SynFuels, Secunda. These include Stripped Gas liquor (SGL) and Oily sewer water (API). Biological treatment of these combined process effluents currently includes the use of ten dedicated activated sludge systems. After treatment the effluent is used as utility cooling water within the SASOL SynFuels (SSF) system. However, the biological treatment of these process effluents in activated sludge systems, has proven to be very difficult and to some extent unsuccessful. Problems with sludge bulking and cell washout are frequently experienced, necessitating frequent re-inoculation of the systems. The high degree of variation in the COD concentrations usually results in shock loadings to the biological system with a negative impact on the microbial populations in the system. These factors result in instability of the activated sludge system, making them prone to failure. Due to these shock loadings, as well as variation in volumetric and hydraulic loadings, and constant variations in the composition of the process effluents, COD removal efficiencies of these activated sludge systems never exceed 80 %. Furthermore, it is hypothesised that the presence of toxic compounds in the various process effluents (primarily SGL and API) may have a negative impact on the activated sludge treatment process. Low organic loading rates (3.5 kg COD/m^3.d) and high specific air requirements (60 - 75 m^3 air/kg COD_{rem}) currently make the existing activated sludge systems inefficient and economically non-viable.

Due to these major limitations, and the fact that the Fischer-Tropsch reaction water constitutes 70 % of the COD load in the activated sludge process, possible alternative

biological treatment processes are being investigated in order to optimise operational costs and effluent treatment efficiencies. One possibility includes the dedicated treatment of reaction water alone. Various studies evaluating the anaerobic treatment of SASOL Fischer-Tropsch reaction water in suspended growth wastewater treatment systems have proven unsuccessful. The upflow anaerobic sludge blanket (UASB) process is one of the most extensively applied anaerobic treatment systems in the world (Lettinga *et al.*, 1997; Britz *et al.*, 2002). Previous studies by Britz *et al.* (2002) on the treatment of Fischer-Tropsch reaction water using UASB reactors were unsuccessful primarily due to the disintegration of existing granules and the lack of formation of new granules. In contrast Augoustinos *et al.* (1989) reported COD removal efficiencies in excess of 80 % could be achieved using hybrid anaerobic digesters while treating a synthetic effluent analogous to the Fischer-Tropsch reaction water. These results suggest that immobilisation of the biomass onto a support matrix in attached growth systems could be essential for the biological treatment of Fischer-Tropsch reaction water. It is thus hypothesised that biological treatment of Fischer-Tropsch reaction water in attached growth systems (fixed-film) could be a suitable alternative treatment technology. However, Joubert and Britz, (1987) while treating a similar synthetic effluent to the effluent used in this study reported a 90 % reduction in COD at an organic loading rate of 15 kg COD/m^3.d using a hybrid anaerobic digester. These results suggest that fixed-film or biofilm reactors could possibly be used for the treatment of Fischer-Tropsch reaction water alone. The use of anaerobic digestion for the treatment of high-strength organic wastewater has only recently become increasingly popular due to a better understanding of the anaerobic process (Britz *et al.*, 1990). It is hypothesised that the absence of complex organic matter (carbohydrates, proteins, lipids) in the Fischer-Tropsch reaction water prevents the growth of acidogenic bacteria, which are primarily responsible for the production of extracellular polysaccharides (EPS). Numerous reports have suggested that EPS is essential for the formation of granular sludge (Riedel and Britz, 1993). The lack of EPS production by the acidogens may contribute to the lack of floc and granule formation, which results in the washout of the microbial biomass at low HRTs.

High rate fixed-film processes or biofilm reactors, of which fluidised-bed reactors have been reported to be one of the most effective have been described as a promising alternative for the treatment of wastewater (Bull *et al.*, 1983a). The fluidised-bed reactor presents a series of advantages over other anaerobic processes, such as high OLR and short HRT (Garcia-Calderon *et al.*, 1998). Other advantages include high biomass retention, good mixing properties and the absence of plugging in the anaerobic processes due to the lower quantity of biomass produced (Buffiere *et al.*, 1998; Hidalgo and Garcia-Encina, 2002).

Very little research has been undertaken in the evaluation of the suitability of anaerobic BFBRs for the biological treatment of high-strength petrochemical effluents. However, no research has been published concerning the use of BFBRs in the anaerobic treatment of Fischer-Tropsch reaction water as generated by SASOL SynFuels, Secunda, South Africa.

Thus the aim of this study was to assess the suitability of two-phase biological fluidised-bed reactors (BFBRs) for the anaerobic treatment of a synthetic high-strength COD petrochemical effluent analogous to the Fischer-Tropsch reaction water as generated by SASOL SynFuels, Secunda.

Specific objectives of this study included the following:

- The characterisation of two-phase BFBRs in terms of bed expansion versus up-flow velocities;
- The comparative evaluation of the use of the two different support matrices (sand and granular activated carbon) in the two-phase BFBRs;
- Optimisation and comparative evaluation of COD removal efficiencies from the synthetic Fischer-Tropsch reaction water industrial effluent. During this study the following was evaluated:
  - The effect of increased COD loading rates on COD removal efficiencies;

- The effect of increased COD loading rates on the removal efficiencies of volatile fatty acids;

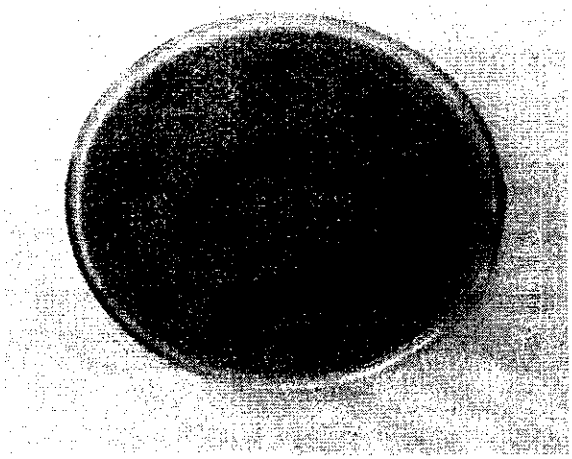
- The evaluation and optimisation of the anaerobic treatment of the synthetic reaction water analogous to the Fischer-Tropsch water process effluent using biological fluidised-bed reactors;
  - Determination of the biogas and methane yields of the anaerobic BFBR using sand and GAC as support matrices.

3. Materials and Methods

3.1. Physical properties and characteristics of the support matrices

The silica sand and granular activated carbon (GAC) used as support matrices during this study, are shown in Figures 1a and 1b, respectively. The sand (*B and E Silica, Delmas, South Africa*) had a uniformity coefficient (UFC) of 1.09, and an equivalent diameter (D_{10}) of 0.86 mm. Furthermore, the sand had a static bed porosity of 0.746, bulk density of 1.57 g/cm^2 and a particle density of 2.5 g/mL. The GAC support matrix, used during this study (Filtrasorb 300; *Chematron Products (Pty) Ltd Isando, S.A.*) had a UFC of 1.9 and an equivalent diameter (D_{eq}) of 1.924 mm. Furthermore, the GAC had a static bed porosity of 0.799, bulk density of 1.43 g/cm^2 and a particle density of 2.66 g/mL. These values were determined according to the methods described by Summerfelt and Cleasby (1996). Approximately 10.6 kg of sand and 3.6 kg GAC were used as support matrices in each of the anaerobic BFBRs operated in parallel.

a)



b)

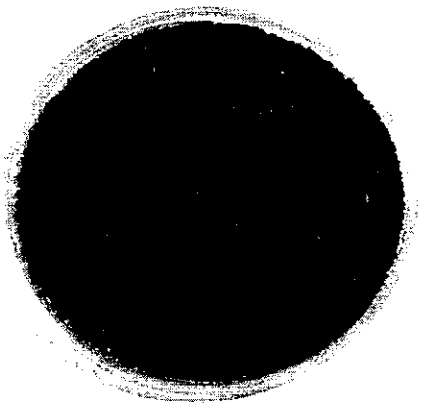


Figure 1. The support matrices used during the study: a) sand; and b) granular activated carbon.

3.2. Feed composition

The synthetic wastewater make-up used during this study was analogous to the reaction water as generated during the Fischer-Tropsch reaction in the SASOL Synthol process. The composition of the synthetic Fischer-Tropsch reaction water (yielding a COD of 18 000 mg/L) were as follows (mg/L): Acetic acid, 9 005; Propionic acid, 2 499; Butyric acid, 1 106; Isobutyric acid, 147; Isovaleric acid, 219. The pKa values of the organic acids used to make up the synthetic effluent vary from acetic acid with a pKa value of 4.76, which is the lowest value, to propionic acid with a pKa value of 4.87, the highest pKa value of the organic acids. The C:N:P ratio of the synthetic high-strength COD industrial effluent was corrected to a ratio of

100:10:1, using NH_4OH and KH_2PO_4. One milliliter of a micronutrient solution (Table 1, du Preez, 1980) was added for every one liter of feed.

Table 1. The micronutrients used in the anaerobic feed (Du Preez, 1980).

Compound	Concentration (g/L)
$FeSO_4.7H_2O$	14.0
$MnSO_4.5H_2$	4.0
$ZnSO_4.7H_2O$	4.0
$CuSO_4.5H_2O$	0.8
$CoCl_2.6H_2O$	0.8
$NaMoO_4.2H_2O$	0.4
H_3BO_3	0.8
KI	0.2
HCl conc.	50 mL
H_2O	950 mL

During this study the total concentrations of the organic acids were gradually increased from 1 600 mg/L to 18 000 mg/L in the anaerobic reactors. Relative ratios of the various organic acids were kept constant. Once the maximum influent COD concentration was achieved (18 000 mg/L) the organic loading rate was further increased by decreasing the HRTs of the anaerobic reactors to 24h and 19h.

3.3. Reactor operation

Two anaerobic BFBRs using sand and granular activated carbon (GAC) as support matrices were operated in parallel. These reactors are shown in Figure 2 and Figure 3.

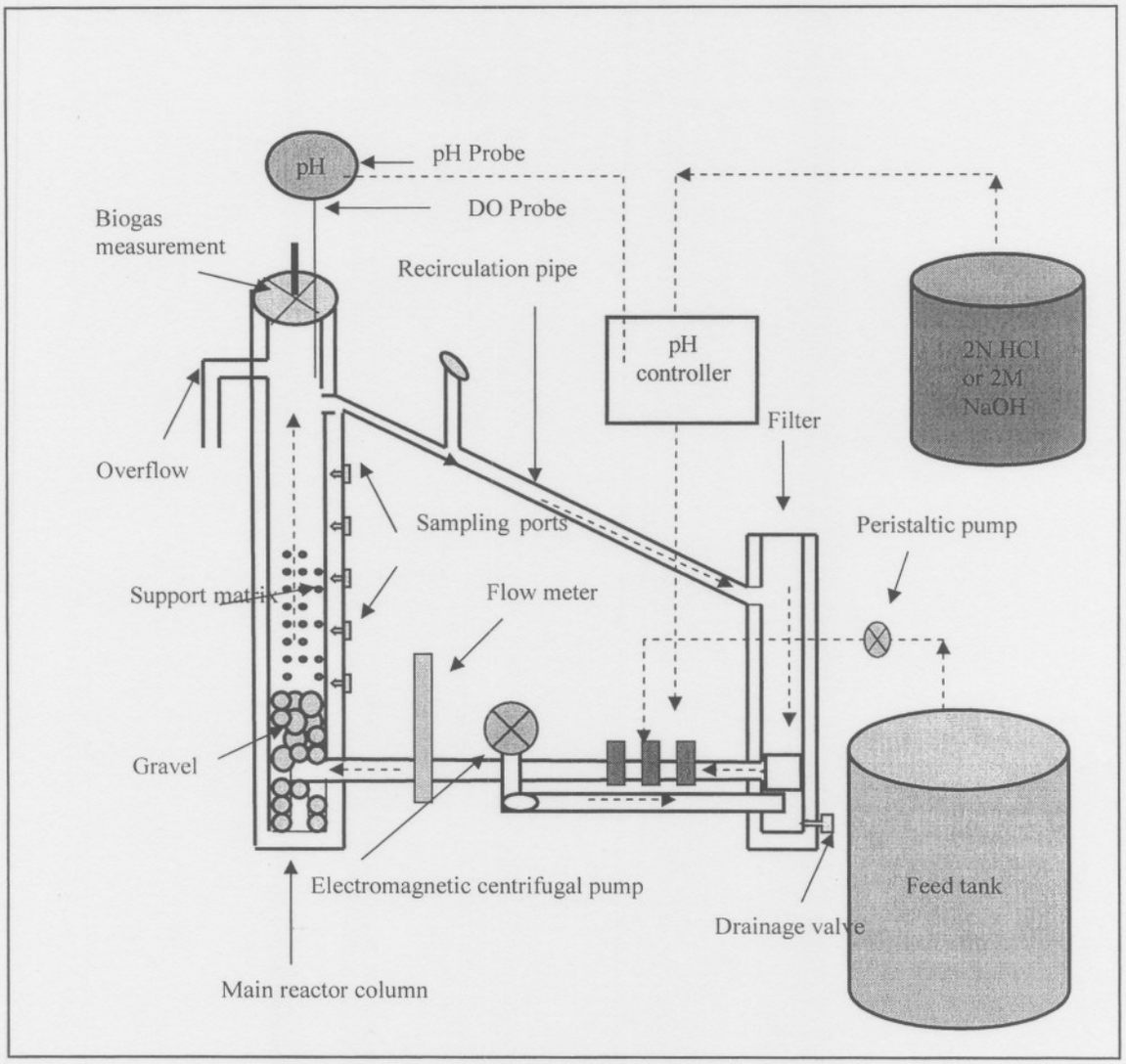


Figure 2. Schematic representation of the anaerobic biological fluidised-bed reactor (not to scale).

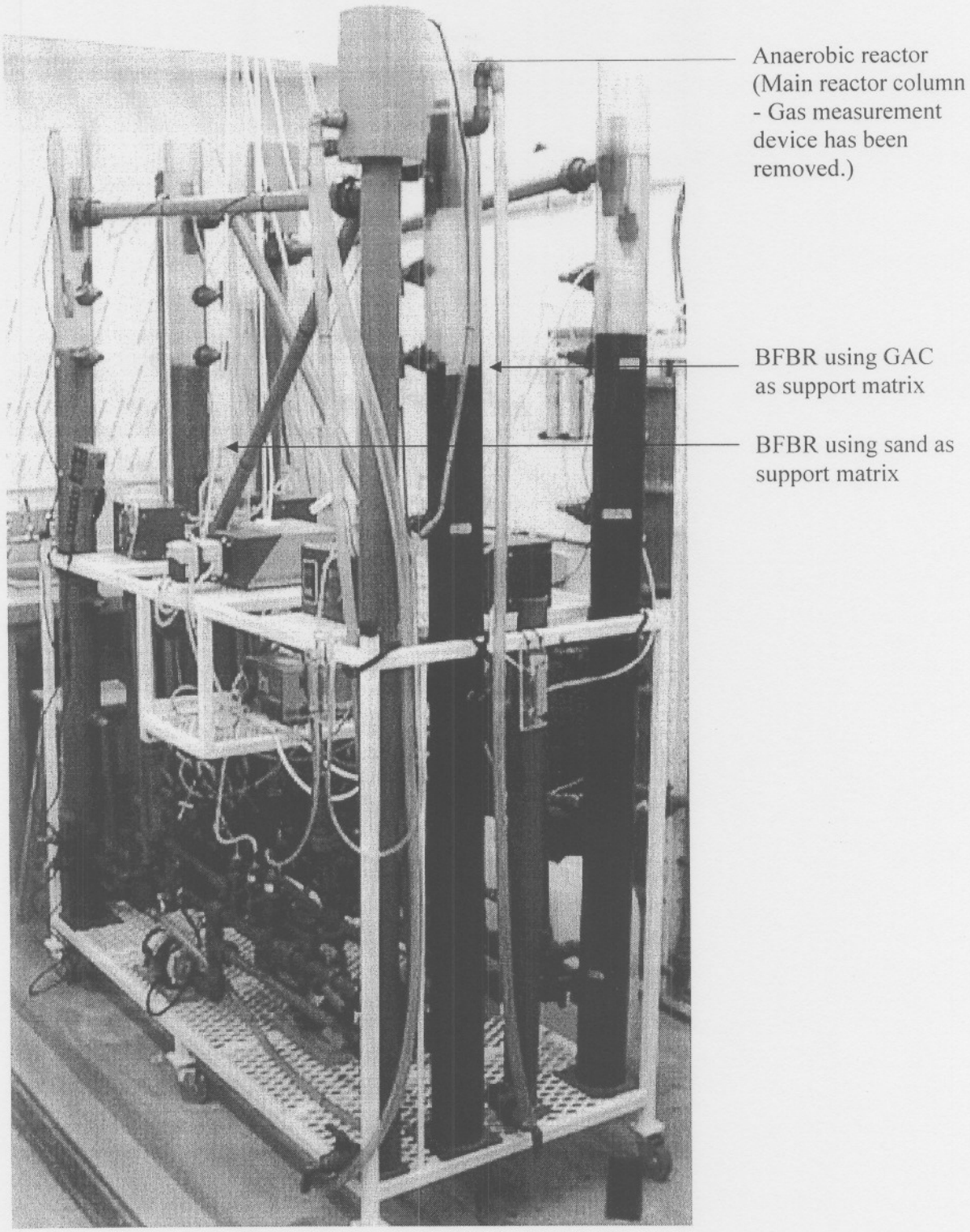


Figure 3. An overview of the experimental set-up of the anaerobic BFBRs.

The lower sections of the reactors were filled with course gravel (1.5 cm diameter), as shown in Figure 4, to prevent unstable flow in the bottom section of the reactors. Sixty percent of the remaining height of the main reactor columns were filled with the respective support matrices. Before inoculation of the reactors, the influence of up-flow fluid velocities on bed expansion were determined. This enabled the calculation of the minimum up-flow liquid velocities required for the fluidisation of support matrices.

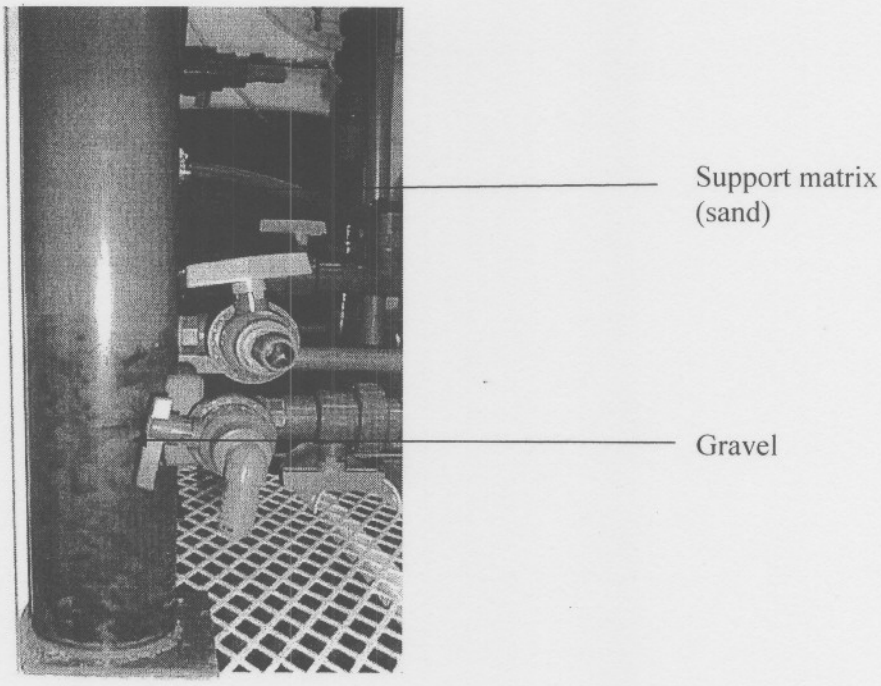


Figure 4. The bottom section of a two-phase BFBR illustrating the gravel below the support matrix (sand).

The main reactor columns were constructed using transparent polyvinyl chloride (PVC) piping (height 2 m, internal diameter 0.099 m). The total reactor volume was 23.485 L with an operational volume of 13.765 L in the main reactor. The main reactor volume was used in all subsequent calculations. Fluidisation was achieved and maintained using magnetic centrifugal pumps (*March mfg., Inc U.S.A*). The synthetic wastewater analogous to the Fischer-Tropsch reaction water was fed into the reactors using peristaltic pumps (*Watson Marlow, Germany*). The temperature within

the reactors was monitored using a YSI 5100 DO and temperature probe (*Hanna instruments, Germany*). The temperature of the main reactor column was maintained at 30 °C using a thermostatically controlled element. The pH within the reactors was maintained at 7.0 with the addition of 2N HCl or 2M NaOH using an automatic pH controller (*Hanna Instruments, Germany*).

3.4. Reactor inoculation, start-up and continuous operation

Both the anaerobic reactors were initially inoculated using 1L of anaerobic/anoxic sludge obtained from the Flip Human Water Care Works in Krugersdorp, Gauteng, South Africa. After inoculation, the reactors were operated in batch-mode for 10 days to facilitate biofilm formation on the support matrices. This was followed by continuous operation of the reactors at hydraulic retention times (HRTs) of 2 days at a bed height expansion of 30 %. The hydraulic retention times (HRTs) were decreased incrementally over time. The reactors were operated at a specified organic loading rate until all parameters had stabilised (steady-state) and a minimum of three hydraulic retention times had passed before HRT was decreased in order to obtain the optimum organic loading rates (OLR). Table 2 represents a summary of the hydraulic retention times, COD influent and the organic loading rate (OLR) obtained at certain stages of the experiment illustrated in days. Once the maximum OLR had been achieved and steady-state conditions were apparent, the effect of pH shock loading on the reactor systems were evaluated by decreasing the pH of the reactor to 3.5 for an 8h cycle.

Table 2. Experimental parameters used to obtain specific OLR.

Symbol	Days	HRT (days)	Target COD Feed (mg/L)	OLR (kg COD/m^3.d)
A	0	2.00	1 600	0.89
B	25	2.00	3 200	2.80
C	42	2.00	6 400	3.80
D	49	2.00	9 000	4.00
E	79	2.00	12 000	4.80
F	117	1.50	13 000	7.20
G	124	1.50	16 000	7.60
H	141	1.50	18 000	10.00
I	177	1.00	18 000	20.00
J	196	0.80	18 000	22.00
K	205	0.77	18 000	25.00

3.5. Biofilm characterisation

Biofilm development on the various support matrices was characterised by scanning electron microscopy (SEM). The samples of biofilm-coated support matrices (sand and GAC) were dehydrated with 70 % ethanol for 12 hours. The ethanol was subsequently replaced with 70, 80, 90 and 2 x 100 % acetone for 15 minutes each. The samples were then critical point dried with liquid CO_2, mounted on stubs using double-sided carbon tape and then coated with 20 nm Au/Pd at a ratio of 70:30 (Csikor *et al.*, 1996; Chen and Chen, 2000). The samples were then viewed under a FEI: Quanta 200 E Scanning electron microscope.

3.6. Analytical methods

Routine analysis such as alkalinity, total suspended solids (TSS), total solids (TS), volatile suspended solids (VSS) and volatile solids (VS) were conducted according to the Standard methods for Examination of Water and Wastewater (APHA, 1992). Volatile solids were used to calculate the estimated biomass concentrations. COD was determined using a MERCK Spectroquant, method number 112, using the MERCK kit 14555 for COD concentrations between 500 - 10 000 mg/L. Total volatile fatty acids were determined using steam distillation, modified from the Standard methods for Examination of Water and Wastewater (APHA, 1992). The

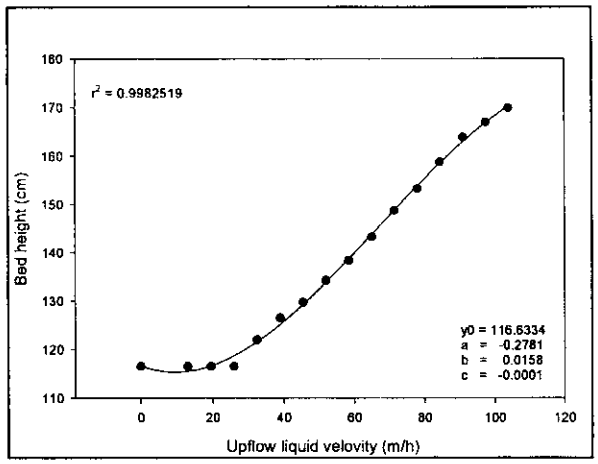
concentration of the individual organic acids in both the influent and effluent were measured by means of a Varian 3300 gas chromatograph equipped with a 6' x 4 mm ID glass column (10 % SP-1000/1 % H_3PO_4 on 100/120 Chromosorb® W AW, *Supelco*). Oven temperature was maintained at 127 °C. Nitrogen (N_2) at a flow rate of 86 mL/min was used as carrier gas. The detector (flame ionisation) temperature was maintained at 160 °C. The injection volume was 1 μL. An acidic saturated brine displacement system was used to determine the quantification of biogas produced by the anaerobic reactors, which proved to be unreliable. Gas samples were collected from the reactor in 5 mL gas-tight sampling syringes (Hamilton Series #1005) equipped with Teflon plunger-heads. Biogas samples were analysed for methane content using an Agilent HP 6850 gas chromatograph equipped with a 1 mL heated (70 °C) gas sample loop and flame ionisation detector (FID). A HP-5 (Agilent column (30 m x 0.25 mm x 0.25 μm)) was used with H_3 as the carrier gas at a flow rate of 1 mL/min. The column temperature was maintained at 70 °C, the injector at 160 °C and the detector at 280 °C. All samples were injected in split mode with a split ratio of 5:1.

4. Results and Discussions

4.1. Assessment of fluidisation hydraulics

The effect of the up-flow liquid velocity on the height of the bed of the fluidised-bed reactors (bed expansion) plays an important part in the prediction of the minimum up-flow liquid velocities required for fluidisation, as well as in the prediction of biofilm formation on the support matrices. It has been reported that biofilm formation on the support matrix results in an increased bed height at a constant up-flow liquid velocity, mainly due to a decrease in the density of the support matrix. The bed height subsequently becomes less sensitive to the up-flow liquid velocity (Chang and Rittman, 1994). The effect of the up-flow liquid velocity on the clean bed height of the sand and GAC support matrices are shown in Figures 5a and 5b, respectively. The minimum upflow liquid velocity required for the fluidisation of sand and GAC were calculated to be 20 m/h and 15 m/h, respectively.

a)



b)

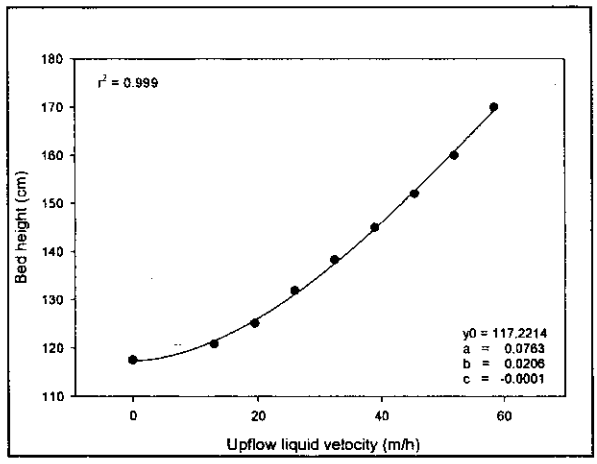


Figure 5. The effect of up-flow liquid velocity on the bed height of a) sand support matrix; and b) GAC support matrix.

4.2. Termination of BFBR using sand as support matrix

Despite several attempts at reinoculation and start-up, the anaerobic fluidised-bed reactor using sand as a support matrix never stabilised and removal efficiencies remained very low (< 30 %), possibly due to high shear force levels in the sand which disrupted biofilm establishment on the support matrix. Further studies concerning the use of sand as support matrix were subsequently terminated.

4.3. Influence of organic loading rate on COD removal efficiency

An average COD removal efficiency of 60 % at an OLR of 0.5 – 10.0 mg/mL could be achieved in the anaerobic fluidised-bed reactor containing GAC as support matrix (Figure 6), and no problems were experienced with clogging and plugging. However, when the organic loading rates increased to 20 kg COD/m^3.d the removal efficiency became erratic and dropped below 40 %. The anaerobic BFBR was highly sensitive to dramatic variations in organic loading rates and removal efficiencies decreased significantly after any shock loading. Furthermore, the anaerobic BFBR struggled to recover to previous removal efficiency levels after shock loadings. Joubert and Britz (1987) used an anaerobic hybrid reactor to treat a synthetic organic acid substrate similar to the wastewater used during this study and attained a 90 % COD reduction at a loading rate of 15 kg COD/m^3.d.

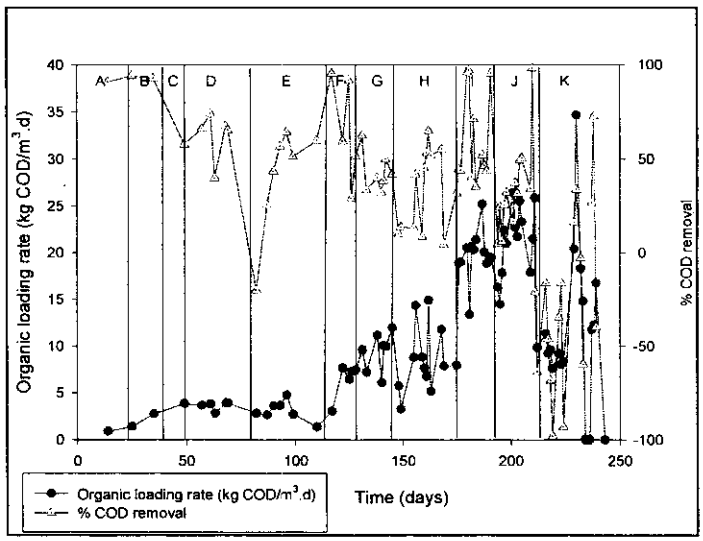


Figure 6. The effect of the organic loading rate on the percentage COD removal in the anaerobic BFBR using GAC as support matrix. (key to symbols: A = 0.89 kg COD/m^3.d; B = 2.8 kg COD/m^3.d; C = 3.8 kg COD/m^3.d; D = 4.0 kg COD/m^3.d; E = 4.8 kg COD/m^3.d; F = 7.2 kg COD/m^3.d; G = 7.6 kg COD/m^3.d; H = 10 kg COD/m^3.d; I = 20 kg COD/m^3.d; J = 22 kg COD/m^3.d; K = 25 kg COD/m^3.d).

4.4. COD reduction

In this study an OLR up to 10 kg COD/m^3.d was achieved as previously mentioned with very few problems occurring. The COD removal rate (kg/m^3.d) reached 0.3 kg/m^3.d when the OLR reached a level of 25 kg COD/m^3.d, however, the reactor's COD removal became erratic at such a high OLR and dropped to nearly 0 kg/m^3.d removal, this is shown in Figure 7. At this high OLR the anaerobic reactor was highly sensitive to environmental changes and COD removal efficiencies could not recover. Bull *et al.*, (1983b), achieved loading rates of 3.2 and 5.0 kg COD/m^3.d when using an anaerobic fluidised-bed reactor to treat a high strength dairy type waste water. The authors reported that 5 kg COD/m^3.d was the highest possible COD loading for an unconditionally stable reactor.

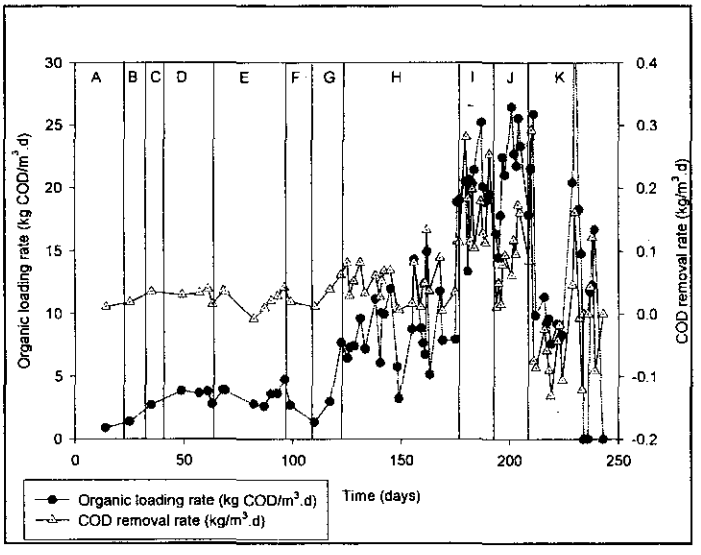


Figure 7. The effect of the organic loading rate on the COD removal rate in the anaerobic BFBR using GAC as support matrix. (key to symbols: A = 0.89 kg COD/m^3.d; B = 2.8 kg COD/m^3.d; C = 3.8 kg COD/m^3.d; D = 4.0 kg COD/m^3.d; E = 4.8 kg COD/m^3.d; F = 7.2 kg COD/m^3.d; G = 7.6 kg COD/m^3.d; H = 10 kg COD/m^3.d; I = 20 kg COD/m^3.d; J = 22 kg COD/m^3.d; K = 25 kg COD/m^3.d).

4.5. COD loading and removal

The removal rate versus the organic loading rate is illustrated in Figure 8. Based on the results presented in this figure it is evident that a slight linear relationship existed between these two parameters ($r^2 = 0.54$) and as the OLR increased the COD removal rate increased gradually. However, when the OLR reached 15 kg/m^3.d the removal rate decreased significantly. This is thought to have occurred as a result of pH problems experienced at this stage during the operation of the reactors. The pH dropped below the pKa value of the organic acids as a result the organic acids became toxic to the microorganisms which resulted in inhibition of microbial activity and a drop in removal rates. The removal rate recovered to levels prior to the pH shock after the reactor pH had been corrected. However, further increase of the OLR above 20 kg/m^3.d resulted in a further decrease in removal efficiency (Figure 7) and removal rate (Figure 8). The average COD removal efficiency (%) obtained through out the study was determined to be approximately 44 % in the anaerobic BFBR using GAC as a support matrix. The low r^2 value, 0.54, can be explained by the erratic data acquired, although a clear tendency can be observed, which is represented by the linear best fit curve (Figure 8).

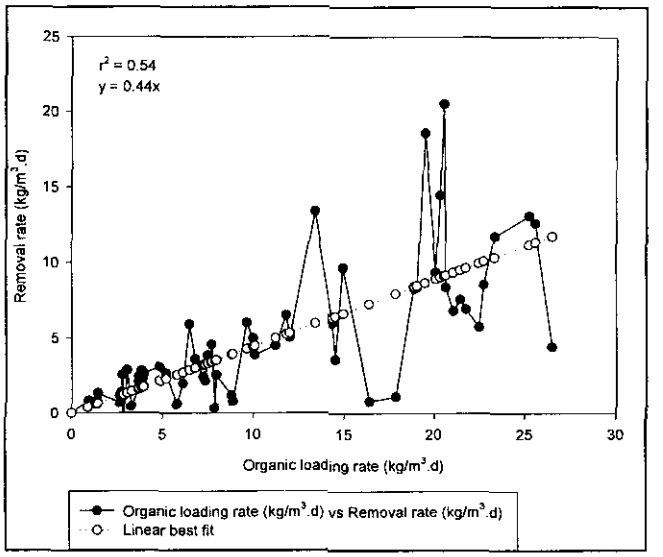


Figure 8. Organic loading rate (kg/m^3.d) versus Removal rate (kg/m^3.d) in the anaerobic BFBR using GAC as support matrix.

4.6. Effect of changes in pH on the COD performance

The effect pH has on the percentage COD removal was tested and the results are shown in Figure 9. It was observed that in the anaerobic GAC BFBR the bacteria were highly sensitive to pH changes and took approximately 5 days to recover to the previous COD removal percentages. On day 200, pH shock loadings were introduced and it is evident in Figure 9 that the % COD removal decreased with the lowering of the pH to 5, and when the pH was returned to 6.5 - 7 the % COD removal went up to 50 %. Bull *et al.*, (1983a), treating a synthetic meat extract wastewater using an unheated anaerobic fluidised-bed reactor found that long term operation at a lowered pH may lead to reactor failure due to inhibition.

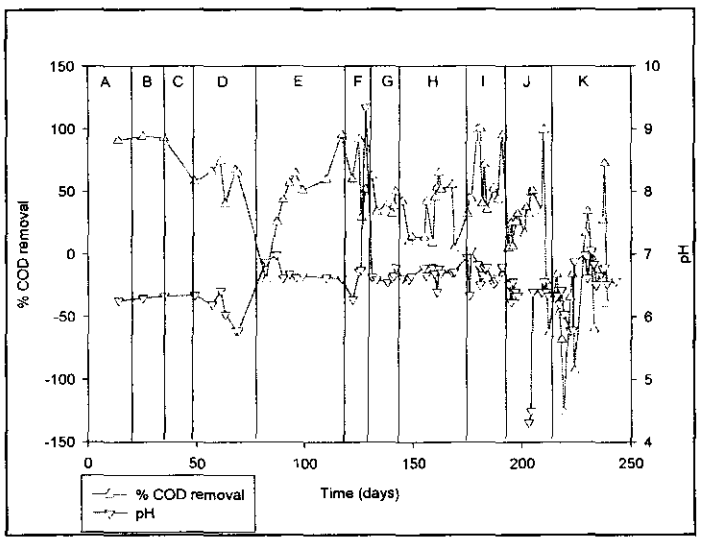


Figure 9. COD removal (%) and pH vs Time (days). (key to symbols: A = 0.89 kg COD/m^3.d; B = 2.8 kg COD/m^3.d; C = 3.8 kg COD/m^3.d; D = 4.0 kg COD/m^3.d; E = 4.8 kg COD/m^3.d; F = 7.2 kg COD/m^3.d; G = 7.6 kg COD/m^3.d; H = 10 kg COD/m^3.d; I = 20 kg COD/m^3.d; J = 22 kg COD/m^3.d; K = 25 kg COD/m^3.d).

It has been reported that methanogens are extremely sensitive to pH in the anaerobic reactors and are inhibited at low pH values (Kasan, 1986). Acidification of anaerobic reactors is generally experienced during shock loads. Under these conditions the acidogens process the excess substrate rapidly, developing excess organic acids. The

methanogens, are unable to metabolise the organic acids fast enough to prevent a decrease in the pH. When the pH decreases, the methanogens are affected first, further reducing their ability to break down the acids. Under severe or prolonged overloading bacterial activity is inhibited. This process is referred to as pickling (Viessman and Hammer, 1998) and may result in severe shock loadings in the reactor. During this study the pH was maintained at a pH of between 6.5 – 7, as shown in Figure 12. However, when the pH of the reactor dropped below 5, the percentage methane dropped below 20 % and the percentage methane of biogas was between 60 - 80 %.

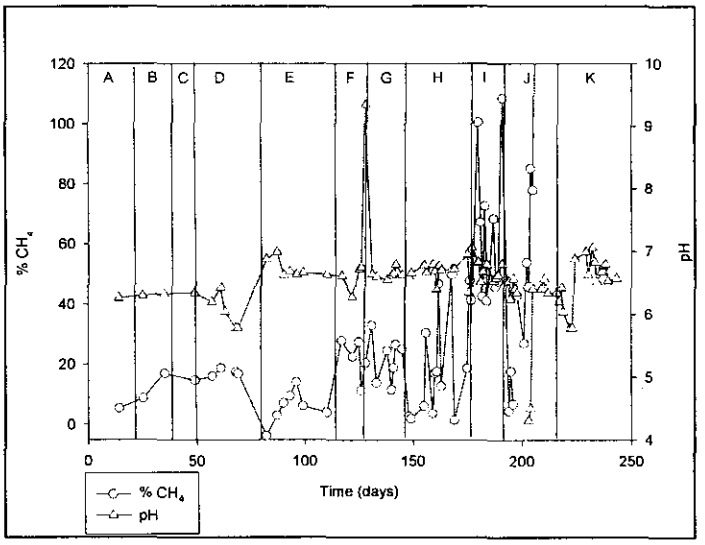


Figure 12. The effect of pH on methane content (%). (key to symbols: A = 0.89 kg COD/m^3.d; B = 2.8 kg COD/m^3.d; C = 3.8 kg COD/m^3.d; D = 4.0 kg COD/m^3.d; E = 4.8 kg COD/m^3.d; F = 7.2 kg COD/m^3.d; G = 7.6 kg COD/m^3.d; H = 10 kg COD/m^3.d; I = 20 kg COD/m^3.d; J = 22 kg COD/m^3.d; K = 25 kg COD/m^3.d).

4.7. Volatile fatty acids

The VFA/alkalinity ratio can be used to determine the measure of process stability. When the VFA/alkalinity ratio is less than 0.3 - 0.4 the process is considered to be operating favourably without risk of acidification (Borja *et al.*, 2001). As illustrated in Figure 10, the VFA/alkalinity values obtained in this study were below the

suggested failure limit value until the organic loading increased to above 12 kg COD/m^3.d, when a considerable increase to 5 in the VFA/alkalinity ratio was observed. The change in VFA/alkalinity ratio at this stage may be due to the fact that the methanogens did not have time to adapt to the increase in OLR as well as the decrease in the HRT. The results obtained suggest that the anaerobic reactor was experiencing acidification, which may have attached the performance of the bacteria as reflected in the decrease in COD removal efficiency.

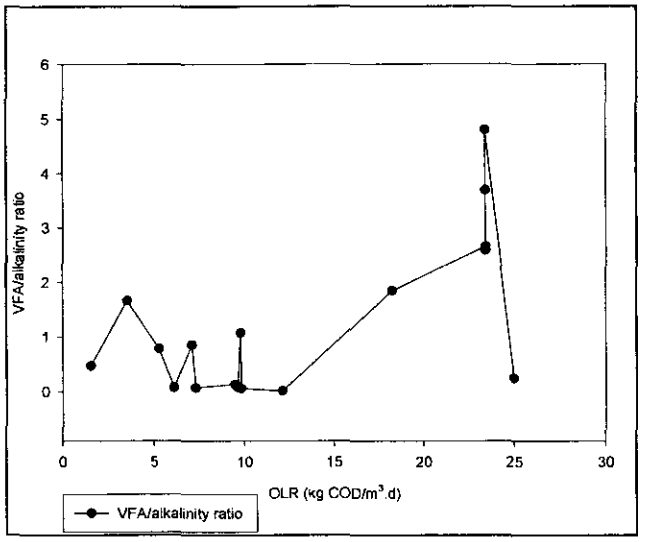


Figure 10. The VFA/Alkalinity ratio versus the organic loading rate (kg COD/m^3.d).

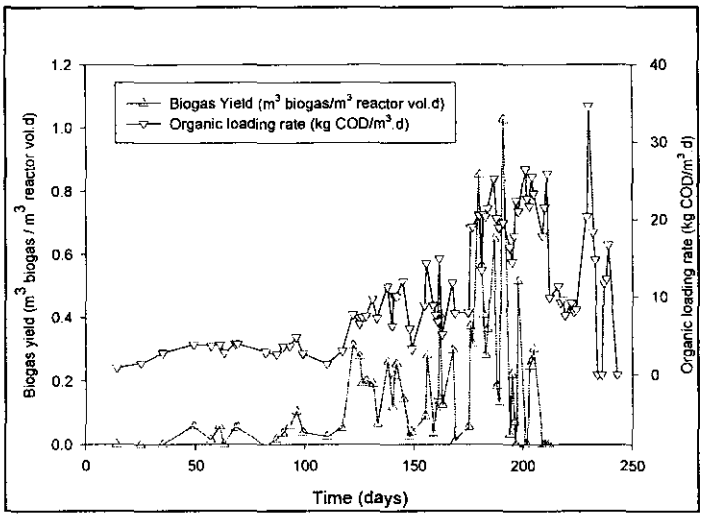
The reduction in individual volatile fatty acids (VFA) in the anaerobic BFBR using GAC as support matrix is shown in Appendix B. Based on the results obtained it is evident that the anaerobic BFBR using GAC as support matrix responded almost immediately to the feed, reaching removal efficiencies of approximately 60 % for all the volatile fatty acids in the feed. Compared to the other VFAs, acetic acid removal efficiency was slightly lower. When the pH dropped below the pKa value of the organic acid with the highest pKa value, that specific organic acid became toxic to the bacteria in the reactor, significantly affecting the composition of the microorganisms in the system resulting in the lowering of the COD removal rates achieved in the anaerobic fluidised-bed reactors. The adsorption capacity of GAC for organic

compounds could prevent some toxicity, although it is hypothesised that the adsorption capacity of GAC for organic compounds would already have been saturated after the extended period of operation (Safferman and Bishop, 1997).

4.8. Biogas and methane yield

At organic loading rates of 20 kg COD/m^3.d, the biogas and methane yields of the anaerobic BFBR using GAC as support matrix were determined to be 0.38 m^3 biogas/kg COD_{rem} (0.30 m^3 biogas/$m^3_{reactor\ vol}$.d), and 0.2 m^3 CH_4/kg COD_{rem} (0.23 m^3 CH_4/$m^3_{reactor\ vol}$.d), respectively. The effect of the OLR on the biogas yield is illustrated in Figure 11a, while the effect on the methane yield is illustrated in Figure 11b. The methane yield obtained during this study was very similar to the methane yield obtained by Joubert and Britz, (1987), who achieved a methane yield of 0.254 m^3 CH_4/$m^3r_{eactor\ vol}$.d at a loading rate of 15 kg COD/m^3.d using an anaerobic hybrid reactor treating a synthetic fatty acid substrate analogous to the Fischer-Tropsch reaction water. Although the methane content of the biogas was initially low (< 30 %), the methane gradually increased to 60 % at organic loading COD/m^3.d rates of 20 kg COD/m^3.d.

a)



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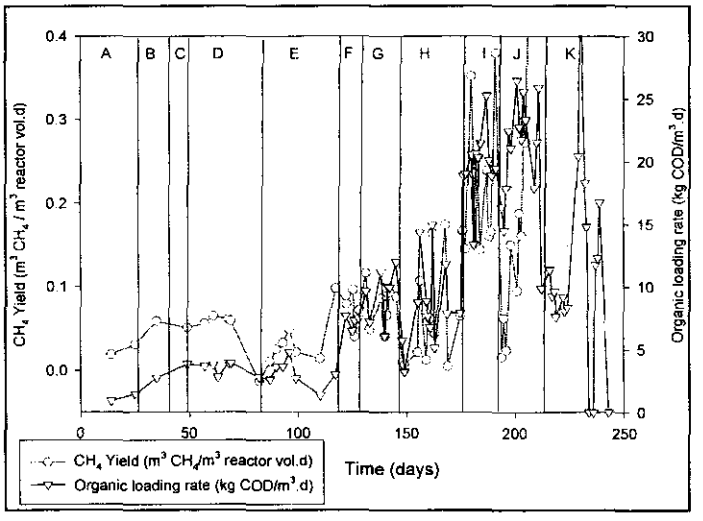
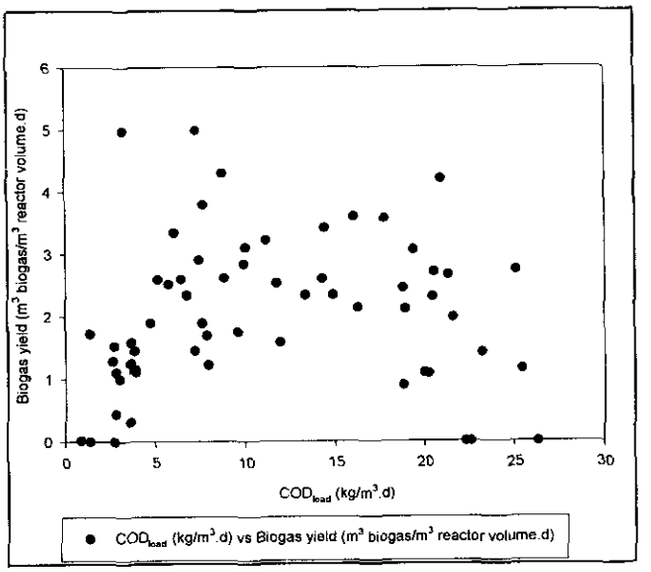


Figure 11. The effect of the organic loading rate on a) the biogas yield; and b) the methane yield. (key to symbols: A = 0.89 kg COD/m^3.d; B = 2.8 kg COD/m^3.d; C = 3.8 kg COD/m^3.d; D = 4.0 kg COD/m^3.d; E = 4.8 kg COD/m^3.d; F = 7.2 kg COD/m^3.d; G = 7.6 kg COD/m^3.d; H = 10 kg COD/m^3.d; I = 20 kg COD/m^3.d; J = 22 kg COD/m^3.d; K = 25 kg COD/m^3.d).

Scatter plots of biogas yield and methane yield against OLR, is shown in Figure 13a and 13b, respectively. The results obtained were highly erratic. The use of an acidic saturated brine displacement system for the quantification of the biogas

a)



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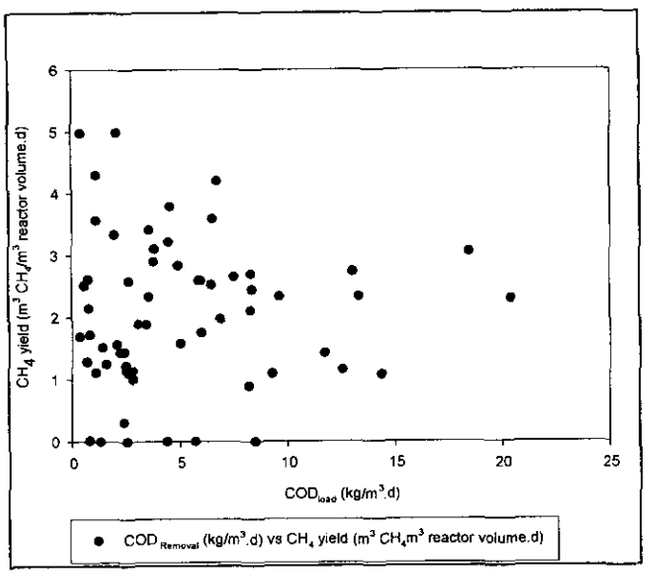


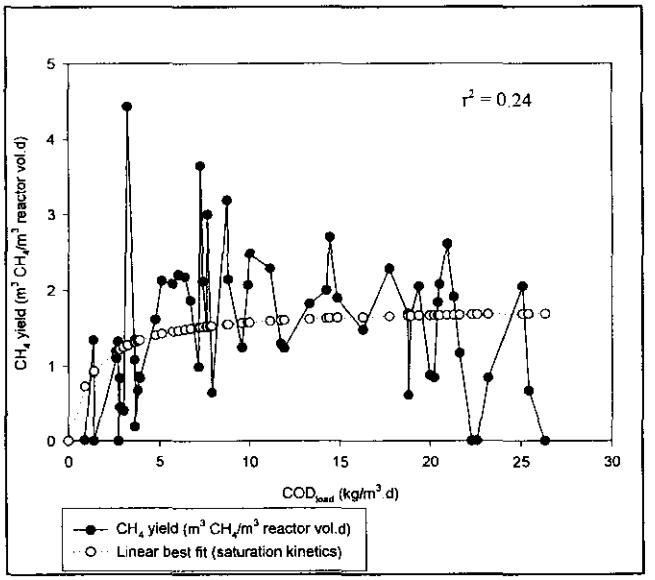
Figure 13. The effect of OLR (kg/m^3.d) on a) the biogas yield, and b) the methane yield.

produced, which proved not to be completely reliable is thought to be the reason for the erratic results obtained. Another possible reason for the erratic results obtained may be the decrease in pH below the pKa values of the organic acids (also reflected in

the VFA/alkalinity ratios) towards the end of the study. This may have affected the results obtained further, causing inhibition of methanogens due to toxicity. Due to the erratic nature of the results it was difficult to determine the relationships existing in the data, although it appeared as if the biogas and methane yields were not enhanced with further increases in the OLR. The data was subsequently re-plotted according to saturation kinetics.

The effect of the OLR on the methane yield is illustrated in Figure 14a. As the OLR ($kg/m^3.d$) increases it is expected that the methane ($m^3\ CH_4/m^3_{reactor\ vol}.d$) levels will also increase. Based on the results obtained it is however, evident that methane yield reached a saturation level, at approximately 5 $kg/m^3.d$ OLR ($r^2 = 0.24$) and leveled off even though the OLR continued to increase. This could be seen as a limiting factor in using anaerobic BFBRs for the production of methane as an alternative energy source. Possible reasons for methane saturation could include the loss of the biomass, inhibition or toxicity, all of which reduce the ability of the methanogens to produce methane. In order to prevent this leveling-off of the methane production more biomass would be required. Another possible explanation for the methane reaching saturation point is diffusion limitation. In the case of the diffusion limitation not enough acetate is passing through the biofilm to the methanogens for the conversion to methane. Towards the end of the study the methane values dropped, this is thought to have occurred due to toxic inhibition resulting from a drop in the pH levels. As a result of erratic results obtained using saturation kinetics, the stoichiometric conversion of COD removed to methane yield was also calculated. These values are presented in Figure 14b. Assuming stoichiometric conversion it is evident that the methane yield reached saturation levels at approximately 8 $kg/m^3.d$ OLR ($r^2 = 0.38$) confirming results obtained in this study.

a)



b)

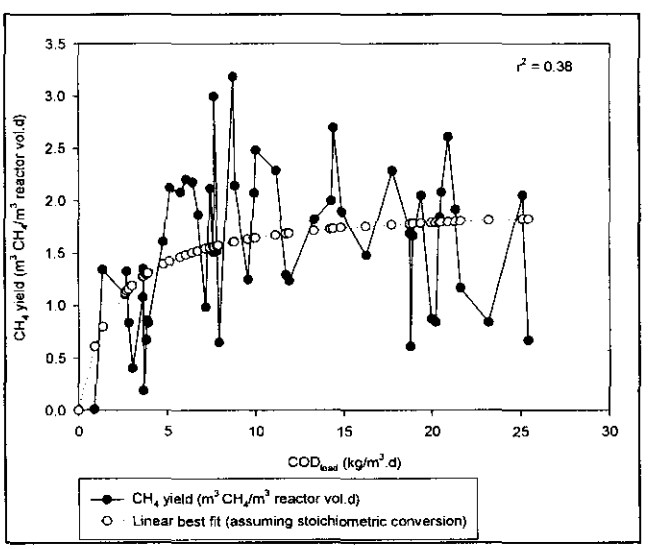


Figure 14. The effect of COD_{load} (kg/m^3.d) on methane yield (m^3 $CH_4/m^3_{reactor\ vol}$.d), a) saturation kinetics, and b) assuming stoichiometric conversion.

The effect the organic loading rate has on the methane yield using saturation kinetics is illustrated in Figure 15. The methane yield peaked at 1.2 m^3 CH_4/kg COD_{rem}.d, at an organic loading rate of approximately 6 kg/m^3.d and gradually decreased as the organic loading rate increased. At an OLR of approximately 8 kg/m^3.d there was a significant decrease in the methane yield (0.25 m^3 CH_4/kg COD_{rem}.d), this is thought to have been as a result of a drop in the pH of the reactor. The methane yield recovered to approximately 0.6 m^3 CH_4/kg COD_{rem} as the pH returned to 6.5. At an OLR of 15 kg/m^3.d pH shock loadings were introduced. As the pH dropped below the pKa values of the organic acids toxic inhibition occurred due to the organic acids becoming toxic to the microorganisms. Methanogens are highly sensitive to environmental changes and as a result a significant decrease in the methane production occurred.

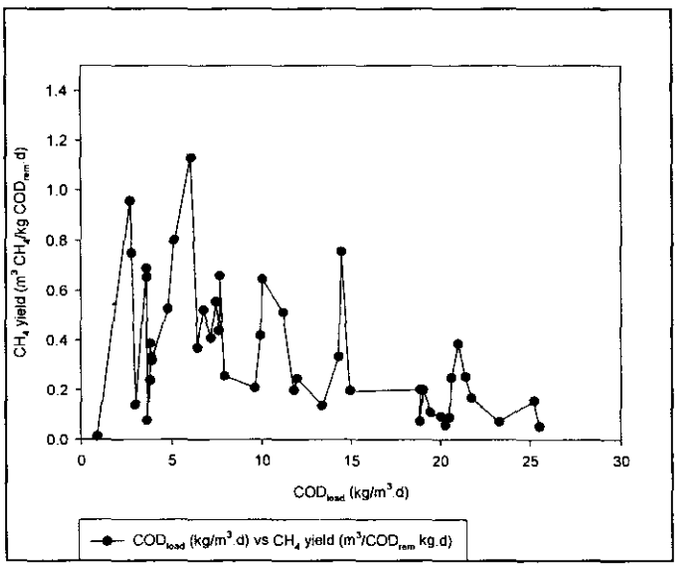
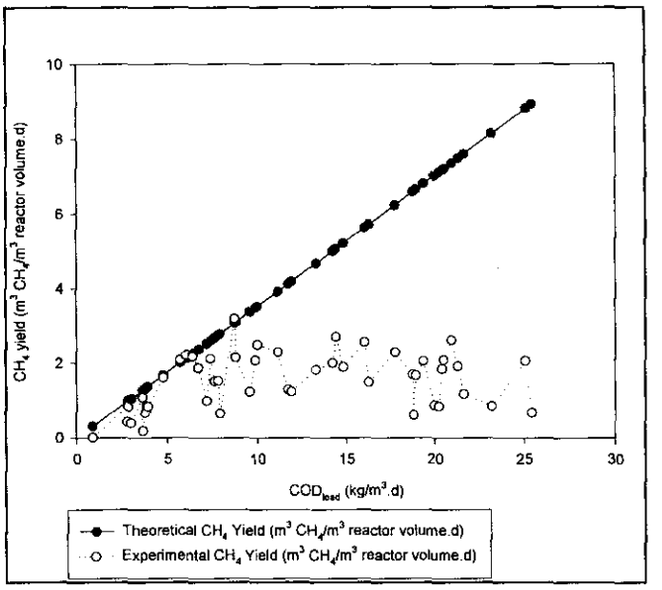


Figure 15. The effect of COD_{load} (kg/m^3.d) on methane yield (m^3 CH_4/kg COD_{rem}.d) saturation kinetics.

The maximum theoretical CH_4 yield and the CH_4 yield obtained experimentally in the study are presented in Figure 16a and 16b, respectively. The figure illustrates that the

a)



b)

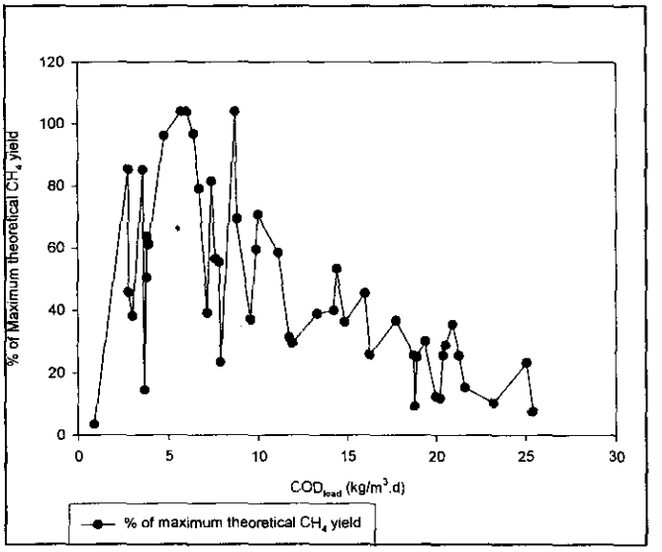


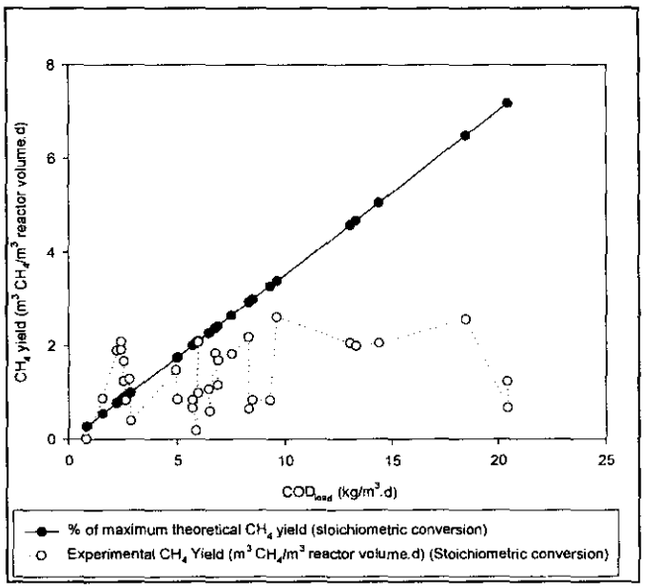
Figure 16. a) Maximum theoretical CH_4 yield vs. experimental CH_4 yield, and b) percentage difference between the theoretical CH_4 yield and experimental CH_4 yield.

CH_4 yield obtained during the study levels off at an OLR of approximately 8 $kg/m^3.d$ and remains constant despite further increases in the OLR. This leveling-off is thought to be a result of the limitation in biomass production preventing more

methane from being produced by the methanogens. In order to increase the methane production it will be necessary to increase the biomass concentrations in the BFBRs. Figure 16b illustrated the percentage of the maximum theoretical methane yield obtained during this study. At an OLR of 6 $kg/m^3.d$, 100 % of the maximum theoretical methane yield could be achieved. However, as the OLR was further increased, the percentage methane yield decreased significantly.

Figures 17a and 17b illustrate the stoichiometric conversion of the saturation kinetics used in Figures 16a and 16b. However, according to the stoichiometric conversion the CH_4 yield leveled off at around an OLR of 9 $kg/m^3.d$. In Figure 17b yields above 100 % of the maximum theoretical methane yield were obtained. There are a number of possible explanations for this. Firstly, adsorption of the volatile fatty acids onto the GAC support matrix after the 10 day batch period may not have reached saturation point. As a result, during the initial loading rates adsorption continues not degradation as the maximum theoretical methane yield is calculated according to stoichiometrical conversion this results in apparent greater methane production than is theoretically possible at that specific loading rate. Also, a significant portion of the COD may be used to establish and develop the biofilm onto the support matrix. This heightens COD removal resulting in biomass production and not biogas production, therefore, as stated above, as the maximum % of theoretical CH_4 yield is calculated according to stoichiometrical conversion, a false impression is given that more CH_4 is produced than is theoretically possible at those specific COD loadings. Mass transfer limitations are also negligible during the initial loading rates as the biofilm is still developing.

a)



b)

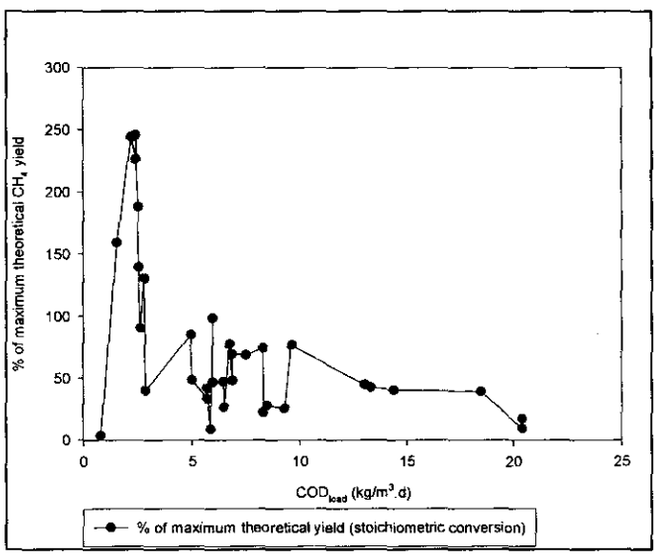


Figure 17. Stoichiometric conversion a) maximum theoretical CH_4 yield vs experimental CH_4 yield, and b) percentage of maximum theoretical CH_4 yield vs experimental CH_4 yield.

4.9. Biomass measurements

Figure 18 illustrates the biomass present in the BFBR using GAC as support matrix plotted against the OLR ($kg/m^3.d$). The estimated biomass concentrations were determined using VS concentrations, started high due to the BFBR being run in batch mode for 10 days to allow the reactors to stabilise and for the biomass to form before moving to the continuous mode in which the reactors where maintained for the duration of the study. The estimated biomass concentrations obtained at the beginning of the study were around 50 mg/g but decreased steadily to below 10 mg/g over time. This is thought to be due to biomass washout as the HRT is decreased in order to achieve higher OLRs.

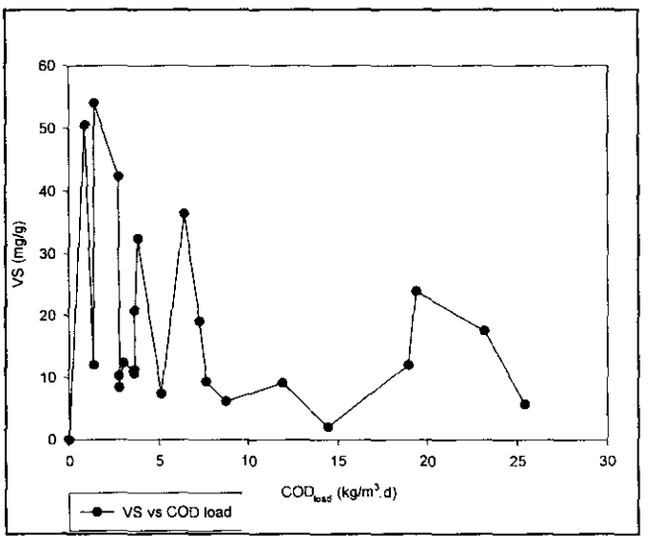
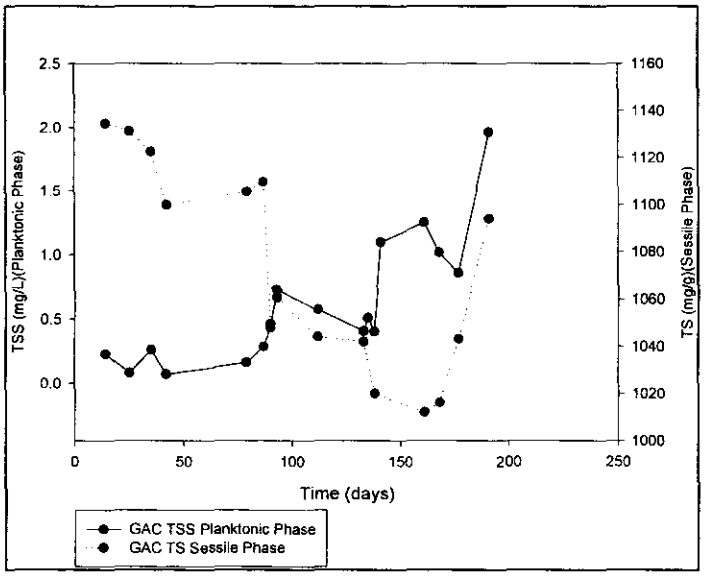


Figure 18. The effect of COD_{load} ($kg/m^3.d$) on the estimated biomass concentration illustrated as VS (mg/d).

As expected due to the reactor being run in batch mode for 10 days prior to the start of the study, the total solids (TS) concentrations in the sessile phase of the anaerobic BFBR containing GAC as support matrix were greater than the values of the total suspended solids (TSS) in the planktonic phase. However, the TSS values increased over time while the TS values decreased as indicated in Figure 19a. This indicates that shear forces in the reactor may cause the biofilm to break up and move into the planktonic phase, eventually leading to biomass washout and reducing the efficiency

of the reactor. The TS values started at 1130 mg/g and decreased steadily to values below 1020 mg/g. The TSS values began at approximately 0.3 mg/L and increased

a)



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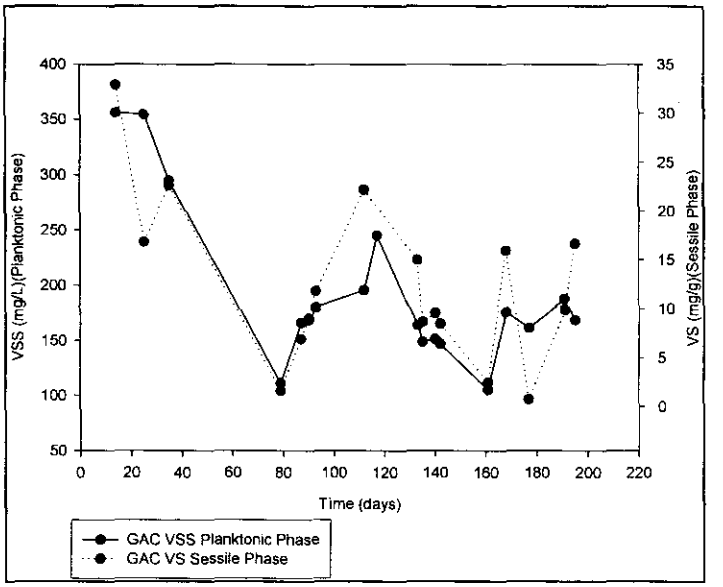


Figure 19. a) TSS and TS concentrations, as well as, b) VSS and VS concentrations for the planktonic phase (mg/L) and the sessile phase (mg/g) of the BFBR using GAC as support matrix, respectively.

over time to approximately 2 mg/L. Borja *et al.*, 2001, reported a TSS concentration of 970 mg/L treating wastewater from the production of proteins from extracted sunflower flour using a mesophilic anaerobic fluidised-bed reactor. Christensen *et al.*, 1984, obtained TSS concentrations ranging from 475 – 630 mg/L using an upflow anaerobic sludge blanket reactor to treat wastewater streams containing high concentrations of soluble organics and low solids concentrations.

The volatile suspended solids (VSS) were measured in the planktonic phase and volatile solids (VS) were measured in the sessile phase of the reactor. As expected, the sessile phase (VS) had higher values than the planktonic phase (VSS). The sessile phase reached a maximum value of 25 mg/g, while the planktonic phase had a VSS concentration of around 350 mg/L, shown in Figure 19b. Based on the results presented in Figure 19, it is evident that as the OLR was increased by reduction of the HRT there was a drop in the TS and VS values in the sessile phase, while the TSS and VSS values in the planktonic phase increased. This is primarily due to biomass detachment from the support matrices causing washout of the biomass. Borja *et al.*, 2000, reported a VSS concentration of 540 mg/L treating wastewater from the production of proteins from extracted sunflower flour using a mesophilic anaerobic fluidised-bed reactor.

The VSS/TSS ratio is frequently used to determine the correlation between the biomass growth and the quality of the biomass in the reactor during operation. This ratio as measured throughout the study of the anaerobic BFBR using GAC as a support matrix is illustrated in Figure 20. During reactor start-up the VSS/TSS ratio was very low at 0.4. Gradually the ratio increased over time to approximately 1.1 on day 90, and then decreased and stabilised at an average VSS/TSS ratio of 0.8.

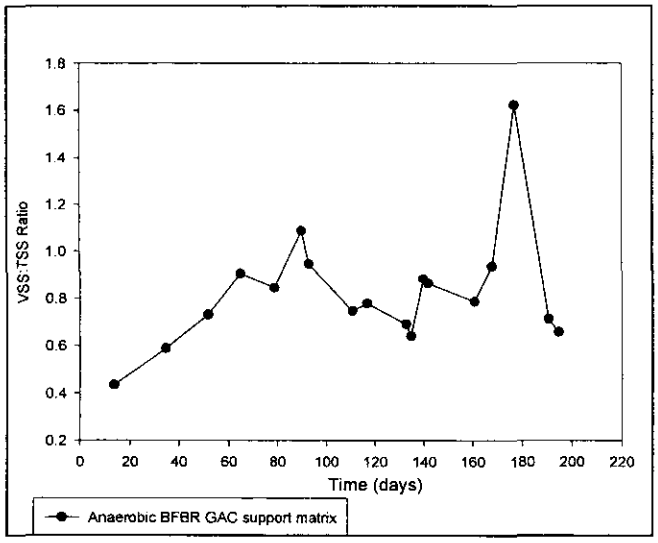
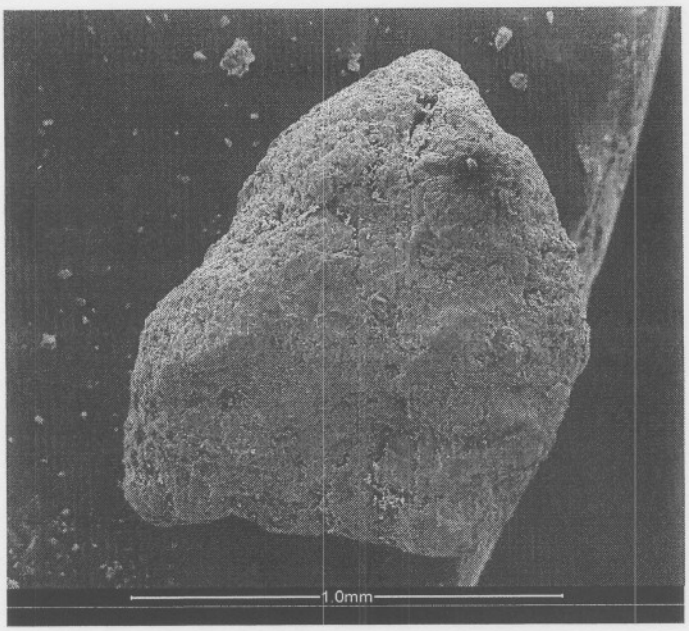


Figure 20. VSS/TSS ratio of the anaerobic BFBR using GAC as support matrix.

4.10 Scanning electron microscopy

The adsorption capacity of GAC for organic compounds has been reported to protect the attached biofilm from organic shock loading and is ideal for rapid biomass colonisation due to the porous nature of the material which provides protection from shear forces (Safferman and Bishop, 1997). The increase in biofilm formation on the support matrices over time corresponded with an increase in the expanded bed height despite the constant up-flow liquid velocity. These results confirmed previous reports that biofilm formation results in a less dense support matrix, culminating in an increase in bed height (Summerfelt and Cleasby, 1996). The morphological diversity of bacteria, shown in Figures 21a and 21b, found in the biofilm of the GAC support matrix consisted mainly of coccoid bacteria surrounded by extensive layers of extracelluar polysaccharides (EPS).

a)



b)

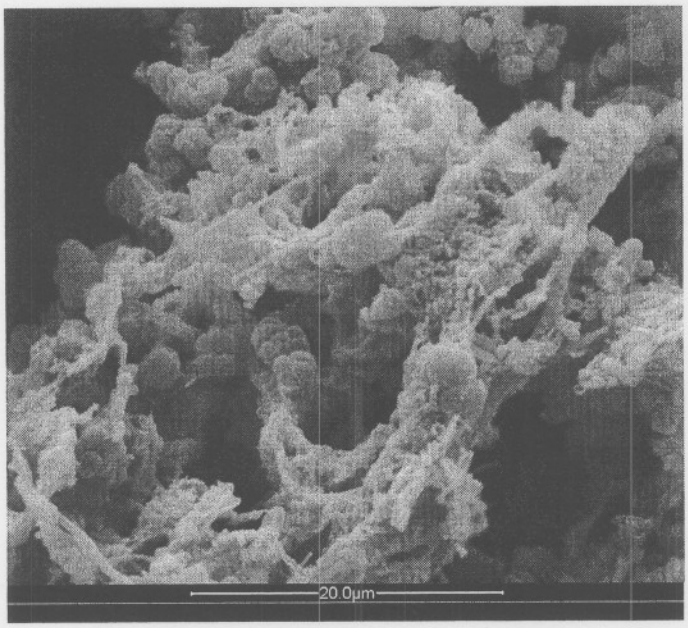


Figure 21. Scanning Electron Micrographs illustrating a) the bacterial biofilm growth, and b) morphological diversity of the bacterial biofilm on the Granular Activated Carbon support matrix.

5. Conclusions

The main conclusions that were drawn from this study are:

- Despite several attempts at reinoculation and start-up the anaerobic fluidised-bed reactor using sand as a support matrix never stabilised and removal efficiencies remained very low (approximately 30 %). This could be ascribed the high shear force levels in the sand primarily due to the increased up-flow liquid velocity required to fluidise sand and the smooth surface of individual sand particles, when compared to GAC. Further studies concerning the use of sand as support matrix were subsequently terminated;

- GAC proved to be the better support matrix for the anaerobic treatment of Fischer-Tropsch reaction water in BFBRs than the sand support matrix;

- During this study COD removal efficiencies in excess of 60 % at an OLR of approximately 10 kg COD/m^3.d could be achieved using an anaerobic BFBR using GAC as support matrix. When the OLR was increased to 15 kg COD/m^3.d the COD removal efficiency decreased to approximately 50 % and stabilised. However when the OLR was further increased to 20 kg COD/m^3.d the COD removal efficiency dropped to below 40 % and did not recover. This significant reduction in COD removal efficiency and lack of system recovery at the high OLR (> 20 kg/m3.d) can be attributed to loss of biomass (washout) caused by the reduction in HRT. These results are confirmed by the decrease in the TS values of the support matrix and the increase in TSS of the planktonic phase. This indicates that the anaerobic reactor functioned better at lower OLR. A possible reason for this could be the increase in TSS and VSS values over time as a result of decreased hydraulic retention times (HRT) leading to cell washout;

- An average COD removal efficiency of 44 % was obtained during this study. Although the experimental data obtained was highly erratic, a clear trend could be observed during this study. The COD removal efficiency decreased noticeably

towards the end of the study. This is thought to have occurred primarily due to acidification (as illustrated by the increase in VFA/alkalinity ratio) possibly due to washout of biomass at the low HRTs;

- The VFA/alkalinity ratio provided information to determine if the biological process was stable. The results obtained indicated that the reactor started off stable (VFA/alkalinity ratio < 0.3 – 0.4), however, as the OLR increased (12 $kg/m^3.d$) so did the VFA/alkalinity ratio (4.9), indicating that the process was becoming increasingly unstable. An increase in the VFA/alkalinity ratio has been reported to lead to reactor failure. Reactor failure at high OLR (> 20 $kg/m^3.d$) was possibly due to acidification and the washout of biomass due to the decreased HRT;

- The anaerobic BFBR was very sensitive to pH changes. Reduction in pH values to below the pKa values of the organic acids present in the feed resulted in a significant reduction in COD removal efficiency. It is thus essential that pH be monitored carefully and maintained at values > 5.0. When pH levels dropped below the pKa value of the organic acids, the removal efficiencies decreased to below 50 % for the anaerobic reactor. The anaerobic reactor struggled to recover to its previous removal efficiencies for approximately 5 days after a pH shock loading;

- The anaerobic reactor does not require oxygen to enable bacteria to function and therefore is a more economic alternative to the aerobic reactors. The anaerobic reactor also produces methane, which may be used as an alternative energy source. As expected the biogas yield increased with the increase of the OLR. When an OLR of 10 kg $COD/m^3.d$ was achieved the biogas yield was 0.2 m^3 $biogas/m^3_{reactor\ vol}.d$, however, when the OLR increased to 20 kg $COD/m^3.d$ the biogas yield increased to 0.6 m^3 $biogas/m^3_{reactor\ vol}.d$. The methane yield was also determined and found that when the OLR was 10 kg $COD/m^3.d$ the methane yield was 0.1 m^3 $CH_4/m^3_{reactor\ vol}.d$, and when the OLR was increased to 20 kg

COD/m^3.d the methane yield increased to 0.23 m^3 $CH_4/m^3_{reactor\ vol}$.d. The maximum theoretical methane yield of a consortium of anaerobic bacteria is 3.51 m^3 CH_4/kg COD_{rem}. Reaching this value indicates that all the carbon would be used by the biofilm for anaerobic respiration, growth and maintenance (Michaud *et al.*, 2002). pH affected the percentage methane obtained, when the pH was stable at around 6.5 – 7 the percentage methane was in excess of 80 %, however when the pH dropped below 5 the percentage methane dropped below 20 %;

- The methane yield obtained during the study increased as the OLR increased and reached 100 % maximum theoretical methane yield at around a OLR of 6 kg/m^3.d. Yields above 100 % of the maximum theoretical methane yield were also obtained. There are a number of possible explanations for this. Firstly, adsorption of the volatile fatty acids onto the GAC support matrix after the 10 day batch period may not have reached saturation point. As a result, during the initial loading rates adsorption continues not degradation as the maximum theoretical methane yield is calculated according to stoichiometrical conversion this results in apparent greater methane production than is theoretically possible at that specific loading rate. However, at an OLR of approximately 8 kg/m^3.d the methane yield leveled off and remained constant (0.20 m^3 $CH_4/m^3_{reactor\ vol}$.d), even though the OLR was increased further. This is thought to be due to the washout of biomass at this stage, which is confirmed by the reduction in TS on the support matrix. This limits the ability of the methanogens to reduce the acetate to methane. Therefore, in order to increase the methane yield it is necessary to increase the biomass levels within the BFBR;

- Due to the BFBRs being run in batch mode for 10 days prior to the start of the study biomass formed and the reactor stabilised. This resulted in high biomass values of 50 mg/g being obtained at the start of the study, which decreased steadily to below 10 mg/g. This may be due to the decrease in the HRT which lead to biomass washout. The TS concentrations in the sessile phase were higher at the start of the study and decreased slowly, while the TSS concentrations of the

planktonic phase increased over the same period. The same pattern is seen in the VS concentrations (sessile phase) and the VSS concentrations (planktonic phase). The increase in TSS and VSS concentrations could be as a result of the decreased HRT eventually resulting in biomass washout and decreased COD removal efficiency. The VSS/TSS ratio is frequently used to determine to the relationship of the biomass growth and biomass quality. The VSS/TSS ratio started very low at 0.4 and increased gradually until day 90 when the ratio stabilised just below 1.1, and then stabilised at an average VSS.TSS ratio of 0.8. The VSS/TSS ratio decreased significantly over a period of time, this is thought to be a result of the biomass being washout; and

- The biofilm in the anaerobic BFBR using GAC as support matrix formed almost immediately achieving high removal rates from early on in the study. This reactor experienced no problems with plugging, thereby requiring low maintenance as far as backwashing the reactor. However, with the methanogens being sensitive to the environmental changes the reactor needs to monitored constantly.

The activated sludge system, which is currently in use at SASOL SynFuels, Secunda has an OLR of 3.5 kg COD/m^3.d with an average COD removal efficiency of 80 %. The anaerobic BFBR is able to achieve a higher OLR (10 kg COD/m^3.d) with a 60 % COD removal efficiency. Therefore the anaerobic biological fluidised-bed reactor can be successfully applied as a competitive alternative treatment process for the treatment of the Fischer-Tropsch reaction water generated by SASOL SynFuels, Secunda, South Africa.

In contrast, Joubert and Britz, (1987) reported a 90 % reduction in COD at an organic loading rate of 15 kg/m^3.d using a hybrid anaerobic digester treating a synthetic effluent analogous to Fischer-Tropsch reaction water. In an independent investigation undertaken by SASOL Research and Development Technology it was reported that a 92 % COD removal efficiency at an OLR of 15 kg COD/m^3.d using anaerobic digestion was obtained. Both of these treatment processes achieved higher COD

removal efficiencies than the anaerobic BFBR used in this study, making them a more competitive alternative for the treatment of the high-strength COD petrochemical wastewater produced by SASOL SynFuels, Secunda during the Synthol process, to the anaerobic BFBR.

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Chapter 5

General Discussion and Conclusions

1. Background

During the Fischer-Tropsch reaction in the Synthol process (SASOL SynFuels, Secunda, South Africa), a mixture of CO and H_2 (syngas) is converted to a range of hydrocarbons. During this process, an aqueous stream, referred to as Fischer-Tropsch (Synthol) reaction water, is also generated. This effluent contains 1 to 1.5 % v/v $C_2 - C_4$ organic acids (> 85 % acetic acid), $C_5 - C_{18}$ organic acids, including light oils, aldehydes, ketones, cresols and phenols. Approximately 25 - 30 ML of Fischer-Tropsch reaction water, with an average COD of 16 000 mg/L is produced daily at SASOL SynFuels, Secunda South Africa.

Together with Fischer-Tropsch reaction water, two other aqueous process effluents are also generated by SASOL SynFuels, Secunda, South Africa. These include Stripped Gas liquor (SGL) and Oily sewer water (API). The biological treatment of these combined process effluents currently includes the use of ten dedicated activated sludge systems. After biological treatment the effluent is used as utility cooling water within the SASOL SynFuels (SSF) system. However, the biological treatment of the Fischer-Tropsch reaction water using the activated sludge systems has proven to be very difficult and to some extent unsuccessful. Problems with sludge bulking and sludge washout are frequently experienced, necessitating frequent reinoculation of the systems. Although the Fischer-Tropsch reaction water contains an average COD of 16 000 mg/L, this can vary between 12 000 mg/L and 22 000 mg/L. Such a high degree of variation usually results in shock loadings to the biological system with a negative impact on the microbial populations in the system. These factors result in instability of the activated sludge system, making them prone to failure. Due to these shock loadings, as well as variation in volumetric and hydraulic loadings, as well as constant variations in the composition of

the reaction water streams, COD removal efficiencies of these activated sludge systems never exceed 80 %. Furthermore, the presence of toxic compounds in the various process effluents (primarily SGL and API) may have a negative impact on the activated sludge treatment process. Low organic loading rates (3.5 kg COD/m^3.d) and high specific air requirements (60 – 75 m^3 air/kg COD_{rem}) also make the existing activated sludge systems inefficient and costly to operate. Aeration is the major cost factor associated with the activated sludge systems currently in use at SASOL amounting to approximately R20 million per annum (pers comm: Phillips, T). In an attempt to address the problems associated with the biological treatment of these effluents using activated sludge systems, alternative biological treatment processes for the treatment of the Fischer-Tropsch acid water effluents are being investigated. Focusing particularly on the optimisation of operational costs and effluent treatment efficiencies of Fischer-Tropsch reaction water alone, since this process effluent constitutes 70 % of organic load treated by these activated sludge systems.

Various studies evaluating the anaerobic treatment of SASOL Fischer-Tropsch reaction water in suspended growth wastewater treatment systems have proven unsuccessful. The upflow anaerobic sludge blanket (UASB) process is one of the most extensively applied anaerobic treatment systems in the world (Lettinga *et al.*, 1997; Britz *et al.*, 2002). Previous studies by Britz *et al.* (2002) using UASB reactors were unsuccessful primarily due to the disintegration of existing granules and the lack of formation of new granules. It is hypothesised that the absence of complex organic matter (carbohydrates, proteins, lipids) in the Fischer-Tropsch reaction water prevents the growth of acidogenic bacteria, which are primarily responsible for the production of extracellular polysaccharides (EPS). Numerous reports have suggested that EPS is essential for the formation of granular sludge (Riedel and Britz, 1993). The lack of EPS production by the acidogens may contribute to the lack of floc and granule formation, which results in the washout of the microbial biomass at low HRTs. In contrast to the UASB Augoustinos *et al.* (1989) reported COD removal efficiencies in excess of 80 % could be achieved using hybrid anaerobic digesters while treating a synthetic effluent analogous to the Fischer-Tropsch reaction water. These results suggest that immobilisation of the biomass onto a support

matrix in attached growth is essential for the biological treatment of Fischer-Tropsch reaction water. It is thus hypothesised that biological treatment of Fischer-Tropsch reaction water in attached growth systems (fixed-film) could be a suitable alternative treatment technology.

High rate fixed-film processes or biofilm reactors, of which the fluidised-bed reactors are considered one of the most effective, have been described as a promising alternative for the treatment of wastewaters (Bull *et al.*, 1983; Edwards *et al.*, 1994). Biological fluidised-bed reactors are an example of advanced wastewater treatment processes that are becoming increasingly used in industries (Marin *et al.*, 1999). Fluidised-bed reactors consist of a bed packed with small particles contained in a vertical column. These particles are expanded upwards via the up-flow liquid velocity of the media introduced at the base of the vertical column. The flow rate is adjusted to maintain the particles in suspension but is kept low enough to avoid particle carry over in the effluent. This arrangement of the particles provides a large surface area (3 000 – 4 000 m^2/m^3) for microbial growth as a thin biofilm layer around the support matrix (Cooper, 1981; Bull *et al.*, 1983; Borja *et al.*, 2001). This process allows the retention of a greater amount of biomass in the reactor resulting in an intensified reaction rate (Garcia-Calderon *et al.*, 1998). The increased amount of biomass thereby enables a drastic decrease in the hydraulic retention times of the reactor, enabling the achievement of significantly higher organic and volumetric loading rates. Particles frequently used as support matrices include sand, anthracite and granular activated carbon (Hosaka *et al.*, 1991). In order to achieve faster stabilisation of fluidised-bed reactors it is important to understand the hydrodynamics of fluidisation, the characteristics of the support matrices and the size of the bed. It is also important to consider the cost and availability of the support matrices used in biological fluidised-bed reactors since these aspects are crucial in determination of the economics of the process (Marin *et al.*, 1999; Summerfelt and Cleasby, 1996).

The biological treatment of large volumes of heavily polluted wastewater (domestic and industrial) requires high performance systems such as the fluidised-bed reactor (Gommers *et al.*, 1988; Sutton and Mishra, 1994). Conventional aerobic treatment

systems have a number of drawbacks. Trickling filters take up too much space and cause secondary problems such as odour and are prone to fly infestation. Activated sludge processes generate large amounts of biosolids and need careful monitoring as they are susceptible to shocks caused by sudden changes in loading rates. Rotating biological contactors are hardier and more compact, but are expensive and prone to mechanical problems. Reactors using fixed submerged media perform as well at low loadings but are easily plugged by excessive biomass build-up (Dickeson and Yoshimura, 2003). Anaerobic treatment processes have become increasingly popular as more is known about them. However, disadvantages of using the anaerobic processes include long start-up periods due to the slow growth rate of the anaerobic microorganisms and the lack of granule formation on certain industrial effluents (Riedel and Britz, 1993). As a result aerobic and anaerobic BFBRs could be successfully applied as a competitive alternative treatment technology for the above mentioned processes.

However, limited research has been undertaken to evaluate the suitability of using fluidised-bed reactor technology in the treatment of high strength industrial effluents, and no research has been done concerning the treatment of the Fischer-Tropsch reaction water.

The primary aim of this study was therefore to assess the suitability of two-phase biological fluidised-bed reactors (BFBRs) for the aerobic and anaerobic treatment of a synthetic high-strength COD petrochemical effluent analogous to the Fischer-Tropsch reaction water.

2. General Discussions and Conclusions

2.1. Aerobic Biological Fluidised-Bed Reactors

The support matrices evaluated during this study were sand and GAC. These were chosen due to their local availability and economical costs. The minimum up-flow velocities required for the fluidisation of the sand and GAC support matrices in the aerobic BFBRs were determined to be 20 m/h and 15 m/h, respectively. In comparison to

the aerobic BFBR using GAC as support matrix the aerobic BFBR using sand as support matrix required a significantly longer period for the establishment of biofilm. Biofilm establishment required 40 days and 100 days on the GAC and sand support matrices, respectively. This may be attributed to the high shear forces associated with the higher up-flow liquid velocity in the BFBR using sand as support matrix. Once both the aerobic BFBRs had stabilised COD removal efficiencies in excess of 80 % were achieved throughout the study, until shock loadings were introduced. The aerobic BFBR using sand as its support matrix experienced fewer problems with plugging and required very little maintenance throughout the study, a possible reason could be the constant high shear forces experienced within the reactor. The high shear forces also resulted in the biofilm formation being restricted to the cracks and crevices of the sand particles as revealed by the scanning electron micrograph (SEM). In comparison the BFBR using GAC as its support matrix experienced significant problems with plugging and subsequent channeling at OLRs above 15 kg COD/m^3.d. This may be ascribed to the high biomass yield under aerobic conditions and the retention of the biomass on the GAC particles. In contrast to the sand support matrix biofilm covered the GAC particle completely, as revealed by the SEM. This plugging resulted in the need for frequent backwashes of the support matrix in order to remove excess biofilm. Although the backwashes resulted in a substantial decrease in the COD removal efficiencies, the efficiencies recovered within 24 hours.

During this study the VFA/alkalinity ratio was determined as a measure of reactor stability. It has been reported that a ratio of less than 0.3 – 0.4 is indicative of a stable process. An increase in this ratio is indicative of acidification and possible reactor failure. Alkalinity is used as a buffer to maintain favourable conditions within the reactor (Borja *et al.*, 2001). During this study the VFA/alkalinity ratio for both aerobic BFBRs was 0.3 - 0.4 until an OLR of 10 kg/m^3.d was achieved. Above an OLR of 12 kg/m^3.d the VFA/alkalinity ratio of the aerobic BFBR using sand as a support matrix increased significantly to 4. This correlated with a significant decrease in the pH of this specific reactor (< 5). This decrease in pH is thought to be caused by the decrease in HRT (1.7 days) on day 100 and the increase in the COD load (16 000 mg/L) to obtain higher OLRs.

The decrease in HRT resulted in biomass washout, reducing the amount of bacteria in the reactor able to breakdown the increased organic acid concentrations. This in turn resulted in the stability of the reactor decreasing. The aerobic BFBR using GAC as support matrix remained stable until an OLR of 15 $kg/m^3.d$ was obtained, after which the VFA/alkalinity ratio increased to 3. This is thought to be as a result of backwashing the reactor to prevent plugging caused by an excess of biomass. The backwashing resulted in a reduction of biomass in the reactor, culminating in an accumulation of VFAs, increased acidity and decreased reactor stability. At an OLR of 25 $kg/m^3.d$, the VFA/alkalinity ratios of the aerobic BFBRs using sand and GAC as support matrices increased to 9 and 6, respectively. This is thought to have been as a result of pH shock loadings at the end of the study, which reduced the ability of the microorganisms to operate at their optimal levels. These results indicate that reactor operation was very unstable at high OLRs.

At high OLRs the TSS values (planktonic phase) obtained in the BFBR using sand as support matrix reached a maximum of 1.6 mg/L, while the TSS values within BFBR using GAC as support matrix reached a maximum of 0.6 mg/L at an OLR of 20 000 $kg/m^3.d$. The TS values obtained in the sessile phase of the aerobic BFBR using GAC as support matrix decreased steadily from 400 mg/g to 150 mg/g during this study. In the aerobic BFBR using sand as a support matrix had TS values also decreased from 150 mg/g to 50 mg/g through the study. The high TSS values in the planktonic phase and decrease in the TS value on the support matrices obtained at the elevated OLRs may be attributed to the dissolution of biofilm from the support matrices due to the low HRTs. During this study the VSS/TSS ratios were also determined (Amatya, 1996). This ratio stabilised after 70 - 80 days of operation at values of between 0.8 and 1.

During this study the specific air requirements for the BFBRs using sand and GAC as support matrices were determined to be approximately 35 m^3 air/kg COD_{rem} and 41 m^3 air/kg $COD_{rem,}$ respectively. The aerobic BFBRs using sand and GAC as support matrices achieved average COD removal efficiencies of approximately 80 % and 85 %, respectively. The COD removal efficiencies achieved in the aerobic reactors throughout the study were consistent. The OLRs achieved in this study were higher than the OLRs

reported in most available literature, whilst still achieving COD removal efficiencies of above 80 %. The calculated oxygen transfer efficiencies of both reactors was 5.4 %. The higher specific air requirement of the BFBR using GAC as support matrix in comparison to the BFBR using sand as support matrix may be attributed to the higher biomass levels (TS) associated with the GAC support matrix. The results obtained in this study compare favourably to the activated sludge systems currently used at SASOL SynFuels, Secunda for the treatment of Fischer-Tropsch reaction water (7 fold increase in OLR and 55 % decrease in specific air requirement). However, when compared to results obtained by SASOL Technology Research and Development in independent studies using the high-rate compact reactor (HRCR) and the biological aerated filter (BAF) reactor the results obtained using the BFBRs are less favourable. Specific air requirements of 18 m^3 air/kg COD_{rem} and 11 m^3 air/kg COD_{rem} were obtained for the HRCR and BAF reactors, respectively. The maximum OLR achieved for both aerobic BFBRs was approximately 25 kg COD/m^3.d. The HRCR and the BAF reactor both achieved OLRs of 35 kg COD/m^3.d, with average COD removal efficiencies of 70 % and 80 %, respectively.

2.2. Anaerobic Biological Fluidised-Bed Reactors

Despite several attempts at reinoculation and start-up, substantial problems were encountered with the establishment of the biofilm in the anaerobic BFBR using sand as a support matrix. Removal efficiencies remained low (< 30 %) and very low levels of biogas was formed. As a result further studies on this reactor were terminated. In contrast the anaerobic BFBR using GAC as support matrix initially had very high COD removal efficiencies (approximately 90 %) which decreased steadily to approximately 60 % as the reactor stabilised. This initial high COD removal efficiency is suspected to be as a result of the reactors being run in batch mode for 10 days prior to the start-up of the study, allowing biomass to build up on the support matrices and enabling bacteria to adjust to the environment. The decrease in the COD removal efficiency is thought to be caused by the adjustment of the organic acid concentration through the study. A COD removal efficiency in excess of 60 % could be obtained using the anaerobic BFBR up to an OLR of approximately 10 kg COD/m^3.d. When the OLR was increased to 15 kg COD/m^3.d the removal efficiency, however, decreased to approximately 50 % but

recovered slowly. At an OLR of approximately 20 kg COD/m^3.d the COD removal efficiency dropped below 40 % and the reactor did not recover. These results indicate that the anaerobic reactor functioned better at lower OLR. Although COD removal efficiency was highly erratic throughout the study a clear trend could be observed and the average COD removal efficiency obtained during this study was 44 %. This is thought to have occurred primarily due to acidification (as illustrated by the increase in VFA/alkalinity ratio) possibly due to the washout of biomass at the low HRTs. The VFA/alkalinity ratio was determined to obtain a measure of the reactor stability (Borja *et al.*, 2001). The results obtained in the anaerobic BFBR using GAC as support matrix indicated that the reactor was initially stable at low OLRs (VFA/alkalinity ratios < 0.3 – 0.4). However, as the OLR increased (> 12 kg/m^3.d) the VFA/alkalinity ratio increased to approximately 5. This ratio is indicative of the increased instability and acidification of the reactor. Borja *et al.*, 2001, using an anaerobic fluidised-bed reactor to treat wastewater derived from the production of proteins from extracted sunflower flour obtained a VFA/alkalinity ratio below the failure limit values (< 0.3 - 0.4) throughout the study. However the VFA/alkalinity ratio increased to 3.01 towards the end of the study when the OLR increased to 12.10 g COD/L.d, indicative of decreased stability in the reactor. Results obtained during this study indicated that the biomass was extremely sensitive to pH. If the pH decreased to values below the pKa value of the organic acids in the feed, then the removal efficiencies decreased to approximately 50 %. However, once the pH was returned to between 6.5 and 7 the anaerobic reactor recovered from the pH shock loadings and COD removal efficiencies increased.

In contrast to the aerobic BFBRs, the anaerobic BFBR did not require aeration making the process more economically viable. Furthermore the anaerobic process also produces methane, which may be used as an alternative energy source. Results obtained during this study indicated that the biogas yield increased with the increase of the OLR. When an OLR of 10 kg COD/m^3.d was achieved the biogas yield was 0.3 m^3 biogas/$m^3_{reactor\ vol}$.d. However, when the OLR was increased to 20 kg COD/m^3.d the biogas yield increased to 0.6 m^3 biogas/$m^3_{reactor\ vol}$.d. At an OLR of 10 kg COD/m^3.d the methane yield was determined to be 0.1 m^3 CH_4/$m^3_{reactor\ vol}$.d. When the OLR was further

increased to 20 kg COD/m^3.d the methane yield increased to 0.23 m^3 $CH_4/m^3_{reactor\ vol}$.d. The methane yield obtained during this study was similar to the methane yield reported by Joubert and Britz, (1987), who achieved a methane yield of 0.254 m^3 $CH_4/m^3_{reactor\ vol}$.d at a OLR of 15 kg COD/m^3.d using an anaerobic hybrid reactor treating a synthetic fatty acid substrate analogous to the Fischer-Tropsch reaction water. The maximum theoretical methane yield is generally accepted to be 3.51 m^3 CH_4/kg COD_{rem}. The maximum theoretical methane yield assumes that all the carbon has been used by the biofilm for anaerobic respiration, growth and maintenance (Michaud *et al.*, 2002). The methane yield obtained during the study increased as the OLR increased and reached 100 % of the maximum theoretical methane yield at around an OLR of 6 kg/m^3.d. However, at an OLR of approximately 8 kg/m^3.d the methane yield obtained during the study leveled off and remained constant, even though the OLR was increased. It is hypothesised that this may be due to the biomass limitation in the reactor due to biomass washout. This was concluded on the basis of the significant reduction in TS on the support matrix. Loss of biomass has been reported to reduce the ability of the methanogens to reduce the acetate to methane, resulting in decreased methane yields.

Results obtained during this study indicated that pH had a significant effect on the percentage methane produced. When the pH was stable at around 6.5 – 7 the percentage methane was in excess of 80 %, however when the pH decreased below 5 the percentage methane decreased below 20 %, due to inhibition. This may also be attributed to the decreased solubility of CO_2 at these pH levels. Methanogens have been reported to be particularly sensitive to environmental changes and as a result the methane production is affected. It is essential that pH levels of the BFBRs be regularly monitored in order to maintain higher COD reduction levels and methane yields.

The anaerobic BFBR using GAC as support matrix obtained TS values (sessile phase) of approximately 1200 mg/g, and TSS values (planktonic phase) of approximately 0.5 mg/L. As was noticed in the aerobic BFBRs, the TS values decreased over time, while the TSS values increased. This may be as a result of biomass washout caused by the decrease in HRT. The VSS/TSS ratio of the anaerobic BFBR using GAC as support matrix was

initially very low (0.4). The ratio however, increased gradually during the study and stabilised just below 1.

The main conclusions that could be made from this study were as follows:

The COD removal efficiencies of the aerobic (80 – 85 % COD removal efficiencies at an OLR of 25 kg/m^3.d) and anaerobic (60 % COD removal efficiencies at an OLR of 10 kg/m^3.d) BFBRs compare favourably to the activated sludge systems currently in use at SASOL SynFuels, Secunda, South Africa. The aerobic BFBRs functioned at significantly lower specific air requirement rates (41 m^3 air/kg $COD_{removed}$ in the BFBR using GAC as support matrix and 35 m^3 air/kg $COD_{removed}$ in the BFBR using sand as support matrix) than the activated sludge systems (75 m^3 air/kg $COD_{removed}$) currently in use at SASOL SynFuels, Secunda, which would reduce the cost of the existing treatment process. In comparison to the activated sludge system, the BFBRs had a 55 % decrease in specific air requirements and a 7-fold increase in OLR. These results indicate that the application of aerobic and anaerobic BFBRs could serve as suitable alternative treatment technologies for the treatment of Fischer-Tropsch reaction water as generated during the Synthol process at SASOL SynFuels.

Excessive biofilm formation on the GAC support matrix necessitated frequent backwashing. Significant problems were experienced with plugging and channeling when GAC was used as support matrix.

In contrast, no biofilm could be established in the anaerobic BFBR treatment of the synthetic effluent using sand as support matrix and further studies were terminated. GAC served as a better support matrix than sand during this study for the anaerobic treatment of Fischer-Tropsch reaction water using a BFBR.

The aerobic BFBRs performed better than the anaerobic BFBR achieving higher OLRs and higher removal efficiencies. Therefore, the aerobic BFBRs are a preferred option to the anaerobic BFBR. The anaerobic reactors are considered to be the more economical

of the BFBRs in that these reactors do not require oxygen to operate and produce methane, which can be used as an alternative energy source.

However, when compared to other treatment processes investigated by SASOL Technology Research and Development, the BFBRs do not achieve favourable results. The high-rate compact reactor and the biological aerated filter reactor are both able to achieve higher OLRs than the BFBR while maintaining high COD removal efficiencies. The anaerobic digestion also achieves a higher average COD removal efficiency (92 %) at a higher OLR (15 $kg/m^3.d$) than the anaerobic BFBR is able to operate at.

3. Future Research

Based on the results obtained during this study, a number of opportunities for further research were identified:

- In order to obtain a basic understanding of the function and structure of the microbial communities involved in the various aspects of the process, as well as to determine how the microbial communities shift during operation, shock loadings, etc., it is important that the functional and structural diversity of the microbial communities associated with the different support matrices, such as sand and GAC are characterised. To achieve this, the application of molecular techniques such as denaturing gradient gel electrophoresis (DGGE) and signature lipid biomarker analysis are recommended. These studies could also include the determination of the effect of dO_2 on the functional and structural diversities of the aerobic microbial communities at varying concentrations.

- Quantification of the relative contribution of the planktonic as compared to the sessile microbial communities to the total aerobic and anaerobic COD removal efficiencies.

- Determination of the effect of varying COD shock loadings on the removal efficiencies of the aerobic and anaerobic BFBRs using sand and GAC as support matrices, respectively.

- Evaluation of the suitability of the BFBRs for the biological treatment of the authentic SASOL Synthol Fisher-Tropsch reaction water. Evaluation could include laboratory and pilot scale studies.

- Evaluation of the suitability of BFBRs for the treatment of primary column bottoms acid water, a low-strength COD petrochemical effluent, obtained from the Gas to liquid Fischer-Tropsch process using a cobalt catalyst.

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Appendix A

Schematic illustration of the volatile fatty acid removal in the aerobic BFBR using both sand and GAC as support matrices.

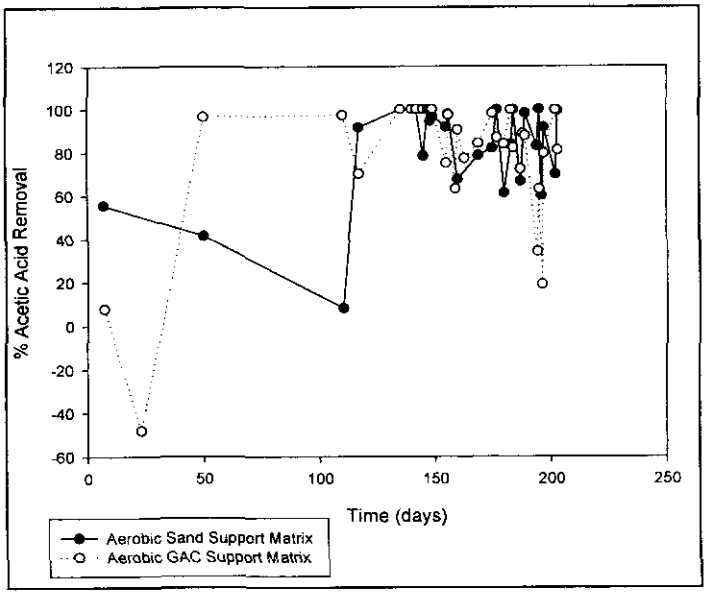

Figure 1. Percentage acetic acid removal.

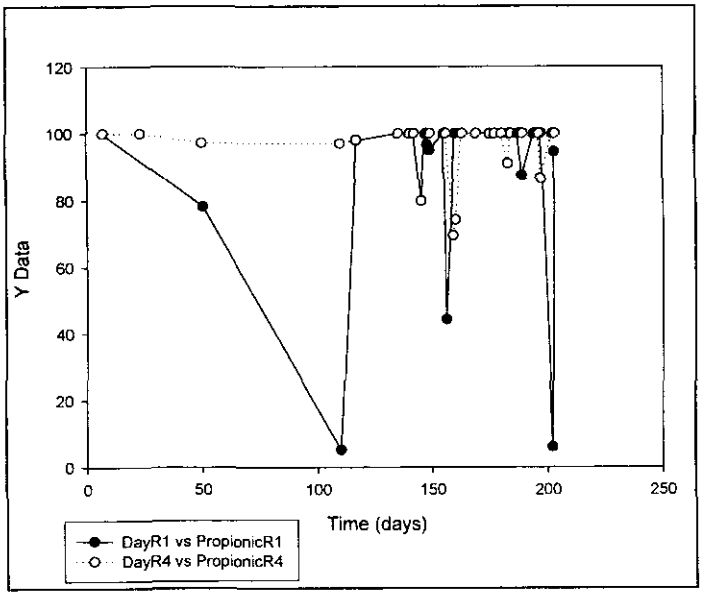

Figure 2. Percentage propionic acid removal.

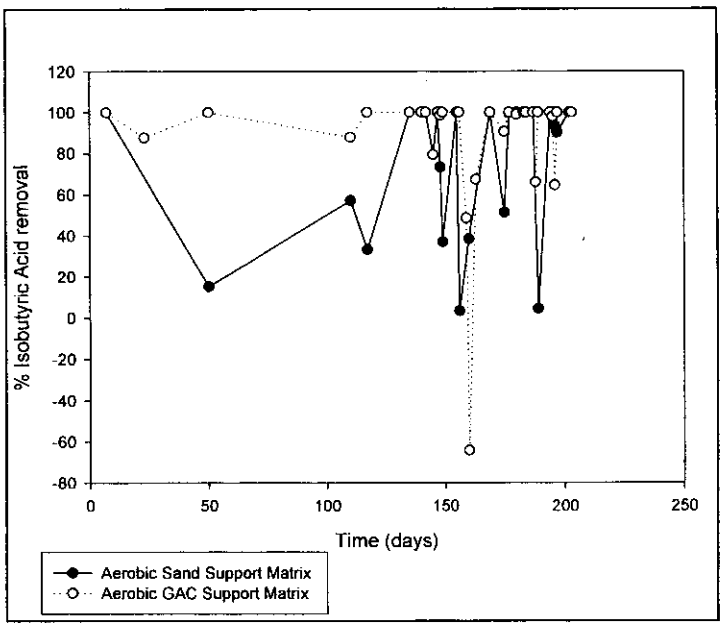

Figure 3. Percentage isobutyric acid removal.

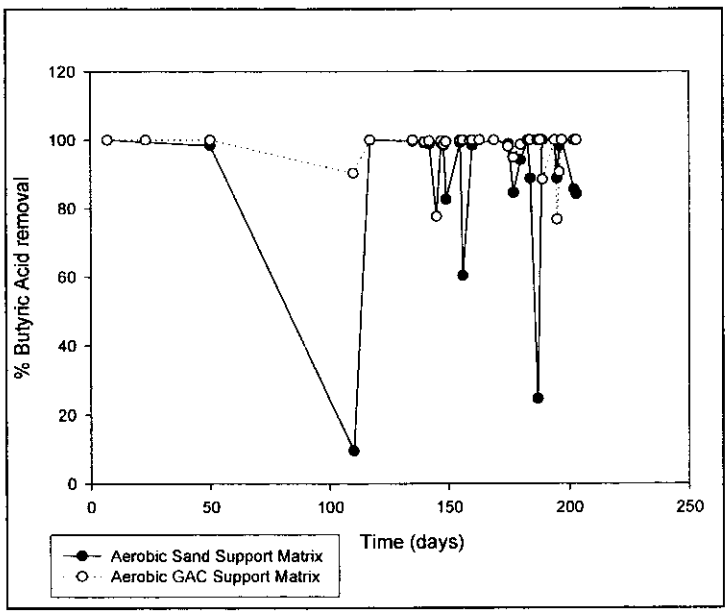

Figure 4. Percentage butyric acid removal.

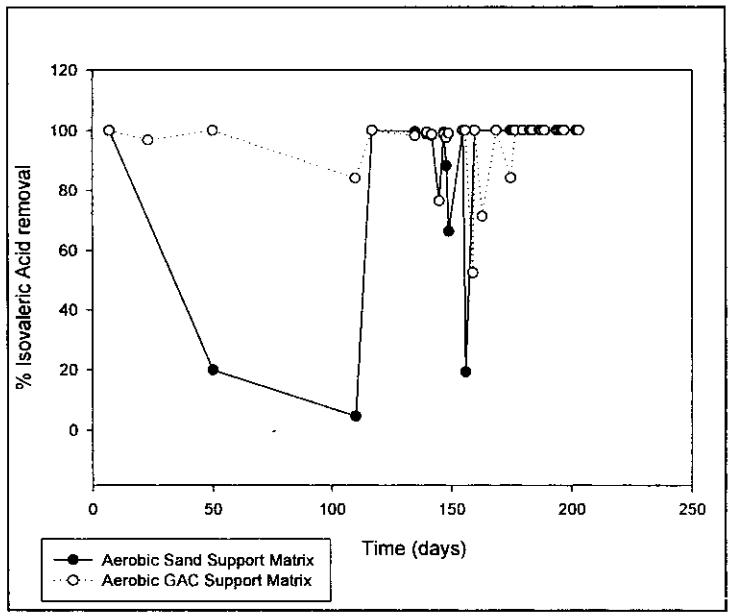

Figure 5. Percentage isovaleric acid removal.

Appendix B

Schematic illustration of the results obtained for the volatile fatty acid removal in the anaerobic BFBR using GAC as a support matrix.

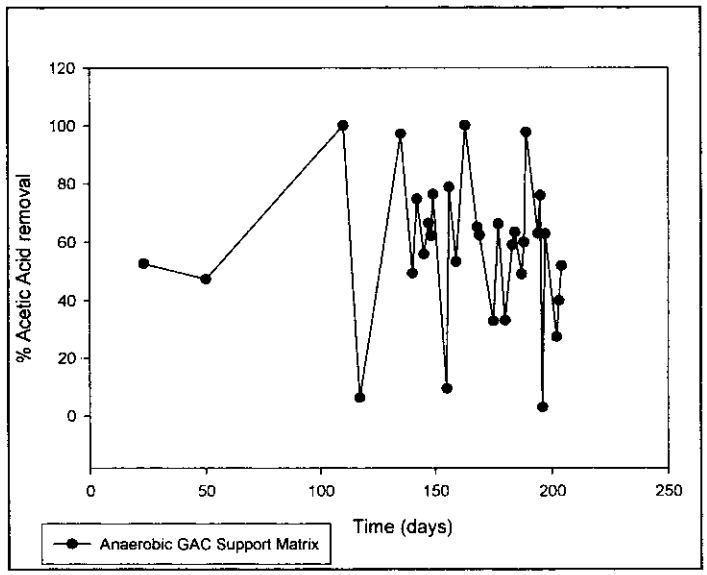

Figure 1. Percentage acetic acid removal.

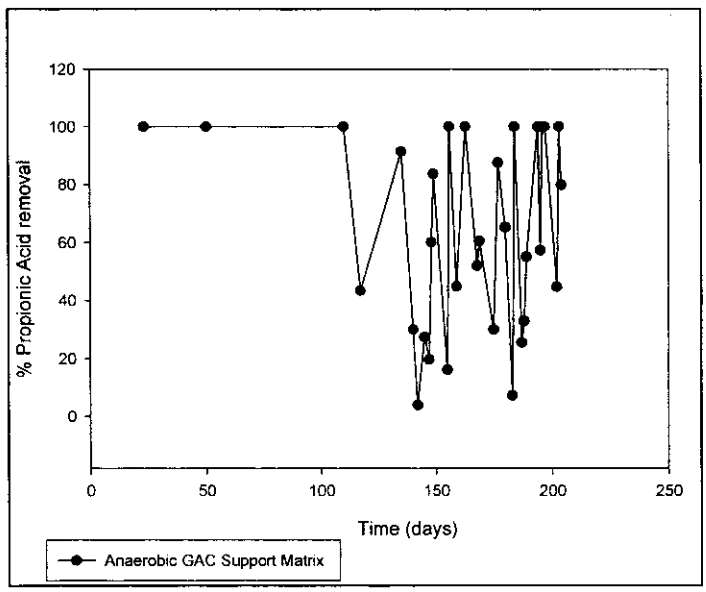

Figure 2. Percentage propionic acid removal.

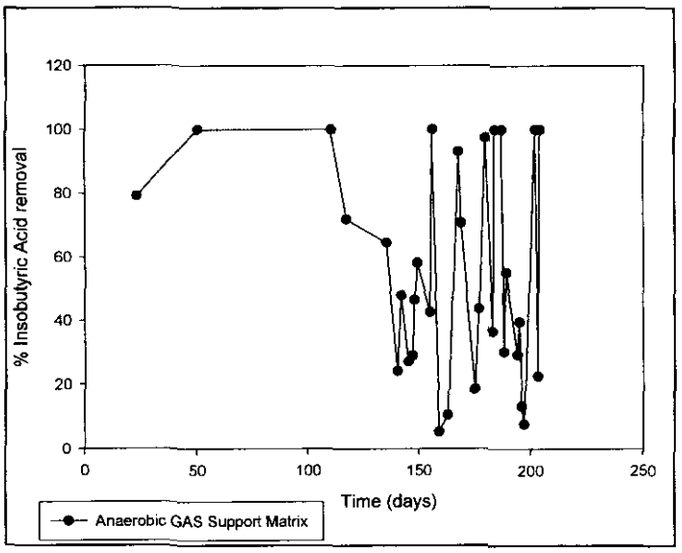

Figure 3. Percentage isobutyric acid removal.

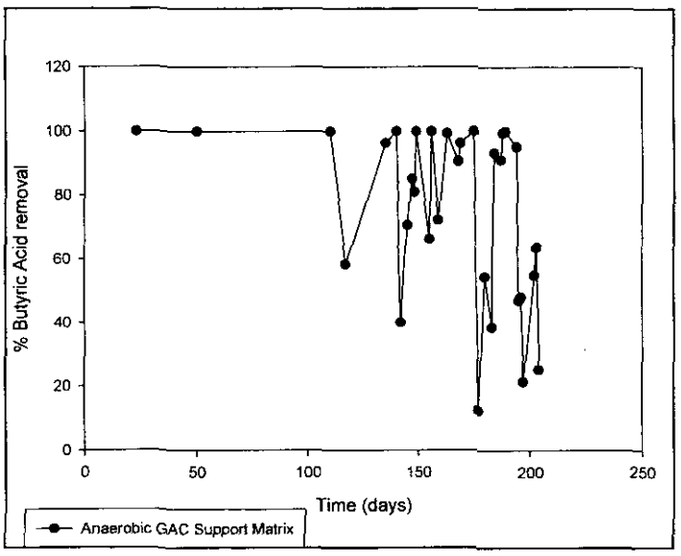

Figure 4. Percentage butyric acid removal.

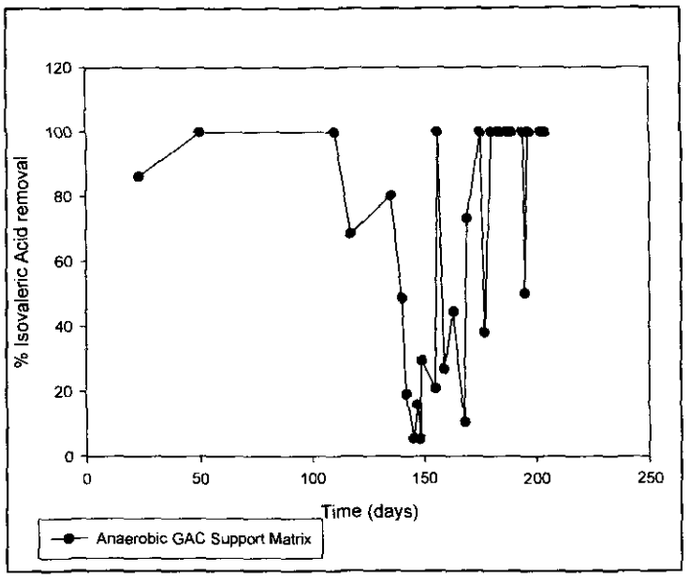

Figure 5. Percentage isovaleric acid removal.

Conferences

Poster Presentation

Riedel, K.J., Swabey, K.G.A., Edwards, W. and Jansen van Rensburg, P.J. (2003). Evaluation of Fluidised-bed Reactors for the Biological Treatment of Synthol Reaction Water, a High Strength COD Petrochemical Effluent. *International Water Association Conference held in Cape Town. 11-14 September 2003*