TREATMENT OF APPLE AND WINE PROCESSING WASTEWATERS USING COMBINED UASB TECHNOLOGY AND OZONATION SCENARIOS

GO Sigge • TJ Britz • T McLachlan •
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Water Research Commission

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EXECUTIVE SUMMARY

BACKGROUND AND MOTIVATION

Water pollution in South Africa is rapidly increasing, seriously affecting sustainable economic growth. Agro-processing industries are thus faced with two major problems. Firstly, maintaining a profitable level of production while reducing the intake of fresh, potable water, and secondly, disposing of the large volumes of wastewater in an environmentally-friendly manner.

Various methods of wastewater disposal exist, including aerobic treatment by activated sludge, oxidation ditches, biological trickling filters, aerobic and anaerobic ponds and lagoons, spray irrigation, anaerobic digestion and chemical treatment. Spray irrigation of agro-processing wastewaters is a commonly used form of disposal in South Africa, mainly due to the availability of cheap land. Anaerobic digestion of agro-processing wastewaters has been successfully evaluated and has several advantages over conventional disposal methods. The efficiency of anaerobic digestion can often be improved by including a pre- or post-treatment step, and advanced oxidation technologies such as ozonation have been shown to be effective and could offer potential as a combination treatment. The need, however, exists to specifically tailor these technologies for smaller agro-processors and also to the variety of unique and specific food and beverage processing wastewaters.

On-site waste treatment of effluents poses several advantages to industries. It offers prospects of water re-use, lower capital outlay for water, lower surcharges for waste disposal, recovery of processing chemicals and generation of useful substances. Thorough investigation and optimisation of wastewater treatment processes and the tailoring of these processes to South African scenarios will ultimately result in effective knowledge transfer to the agro-processing industries involved. By streamlining and minimising the generation of wastewaters and the effective treatment of these wastewaters industries will optimise production and profit in a environmentally sustainable manner.

OBJECTIVES

The main objective of this research programme was to investigate the efficiency of utilising combinations of ozone and UASB technologies to treat winery and apple juice processing wastewaters. This was done by:

1. Evaluating and optimising UASB reactors treating winery and apple juice processing wastewaters. The efficiency of the UASB process was monitored by determining the COD reduction efficiency, pH stability, loading rates, biogas production and reduction of wastewater specific components;
2. Evaluating and optimising the pre- and post-UASB ozonation treatments in terms of optimum ozone dose and reaction time. The efficiency of the combined process was also monitored by determining the COD reduction efficiency, pH stability, loading rates, biogas production and reduction of wastewater specific components;
3. Evaluating and optimising the results obtained in lab-scale trials on pre- and post-UASB ozonation on a 600 L pilot-scale UASB process. The efficiency of the UASB process was monitored by determining the COD reduction efficiency, pH stability, loading rates, biogas production and reduction of wastewater specific components. This pilot-scale study was done only using winery wastewater for logistical supply and consistency reasons;

4. Furthermore, based on the results obtained in the different studies, recommendations concerning the cost efficiency of the pre- and post-ozonation treatment processes were made.

METHODOLOGY

The research conducted in this study, using UASB digesters to anaerobically degrade apple and wine processing wastewaters, was initially done on laboratory-scale reactors. Ozonation as pre- and post-treatment was investigated concurrently with the laboratory-scale UASB trials. Once laboratory-scale studies were completed the process was scaled up to 600 L pilot-scale, to further verify the efficiency of the combination treatments.

RESULTS AND CONCLUSIONS

The research in this study focussed firstly on the use of anaerobic digestion as a treatment option for certain apple and wine processing wastewaters, secondly, the use of ozonation technology as an additional treatment step to anaerobic digestion (more specifically the UASB process) and thirdly, on scaling-up the combined treatment process to a pilot-scale (600 L) UASB system. The following conclusions were made from the results obtained:

1. It was shown that anaerobic digestion of winery wastewaters in an UASB process was feasible, even though it is known that cellar wastewaters are nutrient deficient substrates and are usually difficult to treat. The lowest efficient operational substrate pH was found to be 5.73 for a substrate with COD less than 5 000 $mg.L^{-1}$. Higher substrate loads at this pH led to drastic decreases in the effluent pH and alkalinity. At a substrate pH of 6.0, it was possible to successfully treat wastewaters (COD reduction = 84%) at a HRT of 19.7 h and a corresponding OLR of 9.75 kg $COD.m^{-3}d^{-1}$ producing an effluent with a COD of 1 200 $mg.L^{-1}$. Although legal limits of 75 $mg.L^{-1}$ and 400 $mg.L^{-1}$ for disposal in a natural resource and irrigation, respectively, were not met, these reductions could possibly have cost-saving implications for the wine producing industry.

2. From the results obtained during this study it is clear that the UASB design is feasible for the effective treatment of an apple juice processing wastewater. COD reductions were in the region of 85 to 90% throughout the study. The high organic loads fed during the increased OLR stage had no drastic effect on the system's efficiency. This study indicated that UASB systems can cope with the large increases in OLR during an apple processing season. Excessive sludge overflow did, however, occur at times, especially during the start of the study, due to the low sludge density and settling ability of the seed sludge. Lower sludge overflow, was however, experienced by the end of the study due to granulation having taken place. The effluent COD varied between 300 and 1 500 $mg.L^{-1}$ and further treatment will be required before the legal discharge limits of 75 and 400 $mg.L^{-1}$ are met.

3. The use of ozone as a pre- or post-treatment to anaerobic digestion of winery wastewater was shown to be successful in that total COD and colour reduction were increased. An ozone dose of *ca.* 350 mg $O_3.L^{-1}$ wastewater was applied in the less efficient bubble column during ozonation. Ozonation of the winery wastewaters alone was less effective in reducing the COD (20%) than anaerobic digestion by UASB (65%). Ozonation as a post-treatment to UASB (73%) seemed to be less

effective than using ozonation as a pre-treatment to UASB (89%). Ozone as a pre- and post-treatment to UASB, however, achieved the best results in reducing the COD (91%) and colour of the wastewaters. It was also shown that the long-term use of pre-ozonated winery wastewater as UASB substrate improved the total COD reduction efficiency of the UASB reactor (from 65 to 89%), while also increasing the methane production per COD load. Although legal limits for discarding into a natural resource (75 $mg.L^{-1}$) and irrigation (400 $mg.L^{-1}$) were not quite met, significant progress was made in reducing COD levels. The use of ozonation, not only as a post-treatment, but also as a pre-treatment to anaerobic digestion is a feasible option in the treatment of winery wastewaters. By using a combination of pre- and post-treatment, significant improvements in the wastewater treatment efficiency can be achieved, which could be beneficial financially and environmentally.

4. The combination of ozonation and UASB technology resulted in increased COD reductions and could be a viable treatment option for apple juice processing wastewaters. The higher reduction by a pre- and post-UASB ozonation process (97%) compared to ozonation (12%), UASB treatment (78%) and pre-ozonation + UASB treatment (92%) indicated that ozonation and the UASB process can complement each other. It was also shown that the long term use of a pre-ozonated apple juice processing wastewater as reactor substrate did not inhibit reactor performance but actually increased the COD reduction efficiency of the UASB system (78 to 93%). Post-ozonation of reactor effluents was effective in reducing the COD of the effluent to 180 $mg.L^{-1}$, well below the legal irrigation limit of 400 $mg.L^{-1}$. An ozone dose of *ca.* 350 mg $O_3.L^{-1}$ wastewater was applied in the less efficient bubble column during ozonation. COD concentrations of below the South African discharge limit (75 $mg.L^{-1}$) were, however, not achieved but these reductions could signify possible cost-savings in wastewater treatment penalties.

5. The use of ozone as a combined pre- and post-UASB treatment option for winery wastewaters was shown to be feasible on pilot-scale. The 600 L pilot-scale UASB was shown to be effective in that a COD reduction efficiency of between 77 and 81% was maintained. Post-ozonation of the UASB reactor effluent was found to be effective in further reducing the COD, with a reduction averaging 22%. It was shown that with the mobile test unit pre-ozonation increased the biodegradability of the wastewaters, as the COD reduction efficiency of the UASB reactor increased from 81 to 92%. It was found that the COD reduction efficiency of the mobile unit's UASB with pre- and post-ozonation was 93%. Making use of the purpose-built venturi, circulating contactor system significantly reduced the required ozone doses to between 25 and 45 mg $O_3.L^{-1}$ wastewater. Although the COD was not lowered to below the South African legal limit of 75 $mg.L^{-1}$ for discharge to a natural water resource, the reductions did lower the COD (377 $mg.L^{-1}$) to below the legal limit of 400 $mg.L^{-1}$ for irrigation. It has thus been shown that the use of ozone as a pre- and/or post-treatment to anaerobic digestion is a feasible option for use by wineries generating wastewaters from the production of a variety of red and white wines. Wastewater treatment efficiency can be improved, providing financial benefits to industries involved and contributes to the sustainability of our fresh water resources.

The research work summarised in this report has addressed and met all the objectives set out at the start of the study. This study has re-confirmed that anaerobic digestion, specifically UASB technology, is a feasible treatment option for seasonal wastewaters such as apple juice processing and winery wastewater, where excellent COD reduction efficiencies of up to 93%, were found.

This study has provided the fruit juice processing and winery industries with proof that anaerobic digestion and ozonation can be combined into effective and feasible wastewater treatment processes. The use of pre- and post-ozonation steps together with anaerobic digestion, in the form of an UASB reactor, is a technically feasible option to treat fruit juice processing and winery wastewaters. The combination of these technologies can improve the efficiency of the wastewater treatment process to such an extent that major financial savings could be achieved in the cost of wastewater discharges. On-site wastewater treatment could produce effluents much lower in COD, possibly below the legal limit of 75 $mg.L^{-1}$, and therefore reduce the cost of fines payable to municipal wastewater treatment plants. Alternatively, the wastewaters would then conform to levels allowing irrigation of the wastewaters. Capital costs and running costs will varying according to the volumes of wastewaters produced, organic load of the wastewaters and specific composition of the organic load. In general, capital costs would amount to *ca.* R1.00 per m^3 for 10 years, whereafter the cost would revert to a running cost of only R0.21 per m^3 (see Chapter 8).

The research chapters in this study have also provided these industries with indications of achievable wastewater treatment efficiencies under various production scenarios. This will enable industries to make better decisions as to the feasibility of wastewater treatment options for their own wastewater.

This study has also shown that the successful lab-scale treatment combinations could be scaled-up to pilot-scale – further confirming the feasibility of the combination treatments.

RECOMMENDATIONS FOR FUTURE RESEARCH

In this study several potential avenues of future investigation were identified, which if implemented could further enhance the efficiency of wastewater treatment in these industries.

1. It is recommended that the efficiency of the ozonation step be further investigated at laboratory-scale to better simulate the application of ozone to wastewaters in industrial-scale applications. More accurate indications of COD reductions and improvement in biodegradability would be obtained. More efficient contacting systems (such as static mixers) would permit higher flowrates and mixing efficiency of the ozone and wastewater, resulting in cost savings on ozone requirements. A more efficient contacting process could also reduce the time required for ozonation and thus increase the volume capacity of the treatment process. It is also recommended that intermittant ozonation of the wastewater and its effect on UASB efficiency be investigated as a possible cost-saving advantage;

2. A further recommendation is that a specific cost analysis of available ozonation systems, for full-scale applications, be done so as to determine the specific cost of ozonating particular volumes of wastewater. More precise predictions regarding the amount of ozone required to bring about specific reductions in wastewater components, which are of concern, will be able to be made;

3. It would also be of great value if more research was conducted into waste minimisation at specific industries. Firstly, by investigating the potential cost-saving implications on the waste treatment process itself and, secondly, the potentially

positive effect on the efficiency of the waste treatment process (due to a reduction in the concentration of certain wastewater components).

4. It would also be of great value if more research were conducted into waste minimisation at specific industries. Firstly, by investigating the potential cost-saving implications on the waste treatment process itself and, secondly, the potentially positive effect on the efficiency of the waste treatment process (due to a reduction in the concentration of certain wastewater components).

With the availability of South African made ozone generators (also a WRC project) incorporating new innovations, the cost of using ozonation in wastewater treatment has been considerably reduced. Commercialisation of this new South African technology will further reduce the cost. Implementation of these wastewater treatment technologies along with further efficiency improvements, as outlined above, will not only benefit these industries financially, but also enhance their image of being environmentally responsible and ensuring a sustainable and profitable business.

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The Steering Committee responsible for this project consisted of the following persons:

Dr. G. Offringa	Water Research Commission (Chairman)
Mr. O.C.E. Hempel	Water Research Commission (Secretary)
Dr. P.C. Fourie	SAPO
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GLOSSARY AND ABBREVIATIONS

GLOSSARY

Acidogens – bacteria that depolymerise organic polymers, carbohydrates, proteins and lipids and ferment these to organic acids, alcohols, hydrogen and carbon dioxide.

Aerobes – microorganisms whose growth requires the presence of air or free oxygen.

Anaerobes – microorganisms that grow in the absence of air or oxygen; organisms that do not use molecular oxygen in respiration;

Anaerobic digestion – a microbial fermentation of organic matter to methane and carbon dioxide that occurs in the near absence of air.

Biodegradable – a substance that can be broken down into smaller molecules by microorganisms or their enzymes.

Chemical oxygen demand – the amount of oxygen required to completely oxidise the organic matter in a wastewater sample.

Effluent – the liquid discharge from reactors.

Granules – a mass of microbes cemented together in a slime or extracellular matrix produced by certain bacteria, usually found in waste treatment plants or specifically in upflow sludge blanket reactors.

Methanogens – methane-producing prokaryotes; a group of archaebacteria capable of reducing carbon dioxide or low-molecular-weight fatty acids to produce methane.

Wastewater – the liquid discharge from industrial sites.

ABBREVIATIONS

AD	Anaerobic digestion
AJPWW	Apple juice processing wastewater
BK	Bergkelder, Distell
BOD	Biochemical oxygen demand
CE	Cellar Effluent
CH_4	Methane
CO_2	Carbon dioxide
COD	Chemical oxygen demand
DOC	Dissolved organic carbon
EGSB	Expanded granular sludge bed
FFAP	Free fatty acid phase
H_2	Hydrogen
HRT	Hydraulic retention time
O_3	Ozone
OLR	Organic loading rate
R-RF	Rupert and Rothschild, Fredericksburg
TDS	Total dissolved solids
TKN	Total Kjeldahl nitrogen
TSS	Total suspended solids
TVFA	Total volatile fatty acids
TVS	Total volatile solids
UASB	Upflow anaerobic sludge blanket
VFA	Volatile fatty acids
VSS	Volatile suspended solids

CHAPTER 1

INTRODUCTION

1.1 Specific industry wastewater problems

Water is South Africa's most valuable and also most threatened resource. It is a basic requirement of the legislation on pollution control that wastewater purification be an integral part of industrial processes and that the producer of wastewater should provide staff, capital and plant to purify his own effluent to prescribed standards before the purified wastewater is returned to its stream of origin or is re-used (Republic of South Africa, 1998).

Apple Processing Industry

The South African apple juice processing industry annually produces 6.8 million m^3 of wastewater (D. Murray, Elgin Fruit Juices (Pty) Ltd, Grabouw, South Africa, personal communication, 2002). Most of this is produced during the months of February to June when the apples are harvested and processed (Fig. 1.1). These high wastewater volumes and organic loads put considerable stress on water treatment systems (D. Murray, Elgin Fruit Juices (Pty)Ltd, Grabouw, South Africa, personal communication, 2002).

Apples contain between 5 000 and 16 000 $mg.L^{-1}$ pectin (Whitaker, 1990) and a large portion of this pectin ends up in the wastewater (Mannapperuma *et al.*, 1995). Previous studies have shown that anaerobic systems are incapable of effectively degrading pectin and that wastewaters with high pectin contents interfere with biological treatments (Shivakumer & Nand, 1995). Pectin also has the ability to form a gel when the hydroxyl group forms a link with calcium resulting in the formation of a pectin network, trapping water and thus producing a gel (Hoejgaard, 2003). Apple juice processing wastewater (AJPWW) has a pH of between 3.5 and 5.0 (Sam-Soon *et al.*, 1986) and a pH adjustment is required before the wastewater can enter a biological treatment system. The use of calcium hydroxide or calcium oxide, in the form of lime, are the most popular pH adjusters due to their cost effectiveness (D. Murray, Elgin Fruit Juices (Pty)Ltd, Grabouw, South Africa, personal communication, 2002). The combination of the pectin in the apple juice processing wastewater and the Ca^{2+} from the lime often leads to the formation of a pectin-calcium gel. The increase in viscosity within the UASB reactor due to gel formation may then lead to biomass retention and washout problems (Battimelli *et al.*, 2003), which subsequently reduces reactor efficiency and even causes reactor failure.

Wine Industry

The wine industry contributes to "water demand" and the increased wine production over the last decade has led to even more pressure being placed on South Africa's limited water resources (Van Schoor, 2000). Between 700 and 3 800 L of water per ton grapes processed or 0.8 to 4.4 L per litre of wine produced, are generally used (Water Research Commission, 1993). Bottling operations lead to further water requirements and subsequent increased volumes of polluted wastewater.

In the cellars *ca.* 50% of the water is used for cooling of fermentation cellars and/or vessels to around 15°C (Water Research Commission, 1993). The other 50% is used for the washing of vessels, equipment and floors. On average, 70% of the water taken in becomes a source of polluted wastewater. As batch processing is practised and cellar activities differ during the vintage and non-vintage seasons, the wastewater quality shows significant daily and seasonal variation in pollution load. However, due to on-going cellar

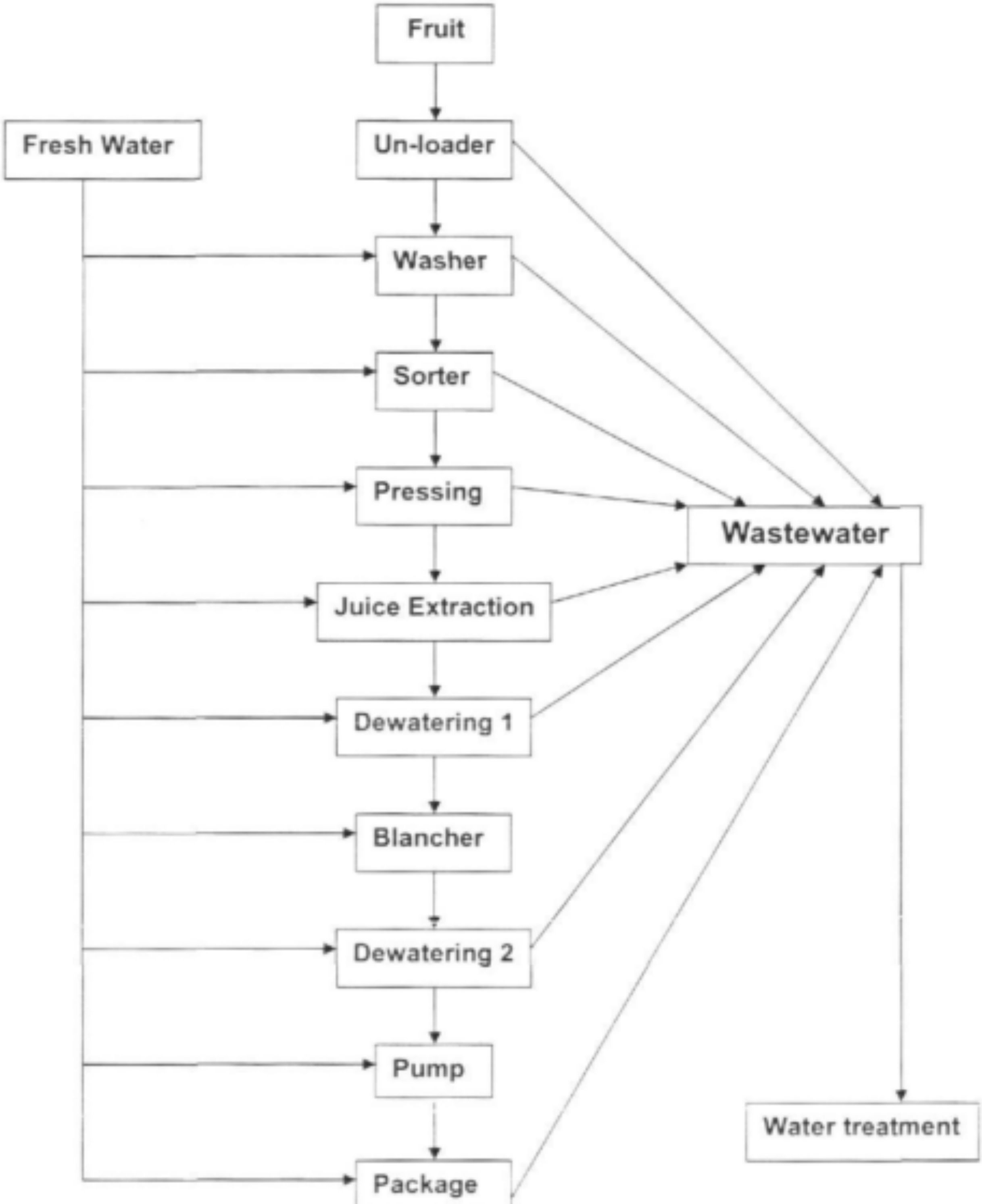

Figure 1.1. Flow diagram of an apple juice concentrate processing plant (Mannapperuma *et al.*, 1994).

activities (Fig 1.2 and 1.3), wastewater with a chemical oxygen demand (COD) of 800 to 12 800 $mg.L^{-1}$ (Petruccioli *et al.*, 2002), is produced throughout the year (Bezuidenhout *et al.*, 2002).

Currently, irrigation is the preferred method for cellar wastewater disposal (Bezuidenhout *et al.*, 2002). To irrigate less than 500 $m^3.d^{-1}$, the wastewater should have a COD of less than 400 $mg.L^{-1}$. To dispose of the wastewater to a natural resource, the COD must be lower than 75 $mg.L^{-1}$ (Anon., 1999). Treatment prior to disposal is thus a necessity. Furthermore, public concern for the environment, which has led to stricter legislation and higher penalties for non-compliance, and the wish to stay competitive in an increasingly globalised market place (Hayward *et al.*, 2000), has forced cellars to consider and implement on-site wastewater treatment options.

1.2 Rationale for Project

The treatment of polluted wastewater was greatly stimulated by the development of the upflow anaerobic sludge blanket (UASB) process and its successful full-scale application (Lettinga *et al.*, 1997). The UASB design permits high space loading rates (30 $kgCOD.m^{-3}$ at low hydraulic retention times (24h). However, one of the main problems in the application, is the fact that this technology alone is not a total solution to a problem.

Due to the nature of the food and beverage processing, large volumes of water are used in product transportation, washing, rinsing, blanching, retorting and cooling operations (Wayman, 1996). This industry is thus faced with firstly, maintaining a profitable level of production while reducing the intake of fresh, potable water, and secondly, disposing of the large volumes of effluent in an environmentally responsible manner. The COD levels of the UASB treated food and beverage processing effluents (Britz *et al.*, 2000) are often still well above the South African legal limit permitted for wastewaters (75 $mg.l^{-1}$) to be discharged to a water system (Republic of South Africa, 1999) and a further treatment is thus necessary.

Ozonation is an old water treatment technology, already used by some European countries since the beginning of the twentieth century (Yu & Yu, 2001). Since ozone does not leave any residual compounds in the wastewater (Graham, 1997), it may be an excellent option as a "pre- and post-treatment" addition to the UASB process.

It is known that some organic compounds react more slowly with ozone and in some cases are only partially oxidized, leading to the formation of low molecular weight compounds which would be better adsorbed onto activated carbon. It has also been reported that smaller organic solutes are sometimes more susceptible to biological oxidation (Gulyas *et al.*, 1995). As a pre-treatment to the UASB, ozone makes recalcitrant compounds more biodegradable (Gottschalk *et al.*, 2000). Andreozzi *et al.* (1998) found that phenols and unsaturated lipids, both inhibitory to anaerobic digestion (AD), could be reduced by 50% using an ozone treatment. Ozone has also been shown to increase the methane yield during the AD process (Benitez *et al.*, 1999; Martin *et al.*, 2002). However, oxidation processes such as ozonation could also lead to the formation of reaction intermediates of greater toxicity than the starting substances (Andreozzi *et al.*, 1997; Martin *et al.*, 2002). Ozonation only improves biodegradability until a specific maximum is reached. Upon further ozonation, biodegradability decreases (Gottschalk *et al.*, 2000).

As a post-treatment, ozone has been shown to reduce colour and COD levels (Athanasopoulos & Athanasopoulos, 1998; Gottschalk *et al.*, 2000). Athanasopoulos & Athanasopoulos (1998) used a post-ozonation treatment to reduce the COD and colour of the effluent from an UASB reactor treating "currant" wastewater by 73 and 74%, respectively.

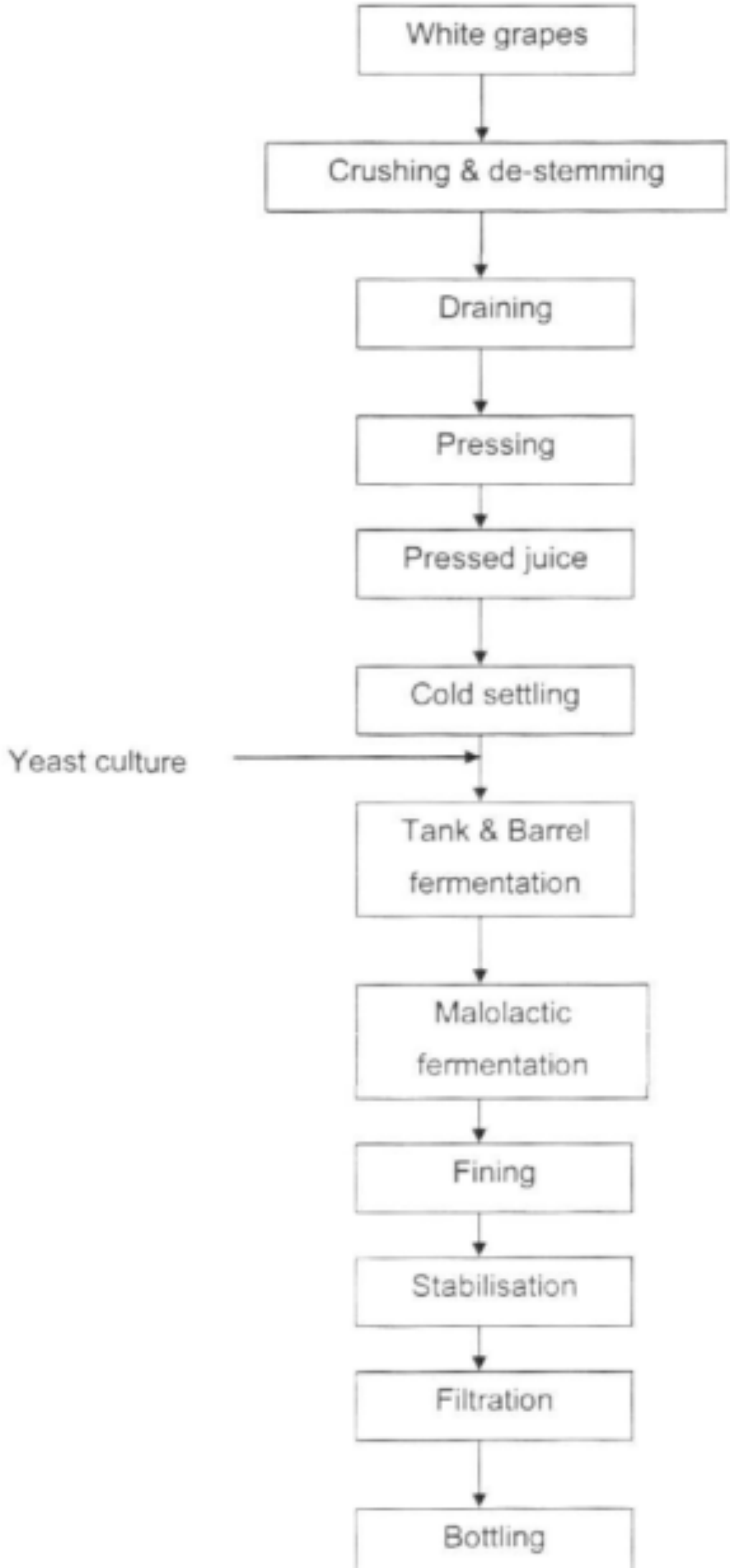

Figure 1.2. Flow diagram of white wine production (Marais, 2001).

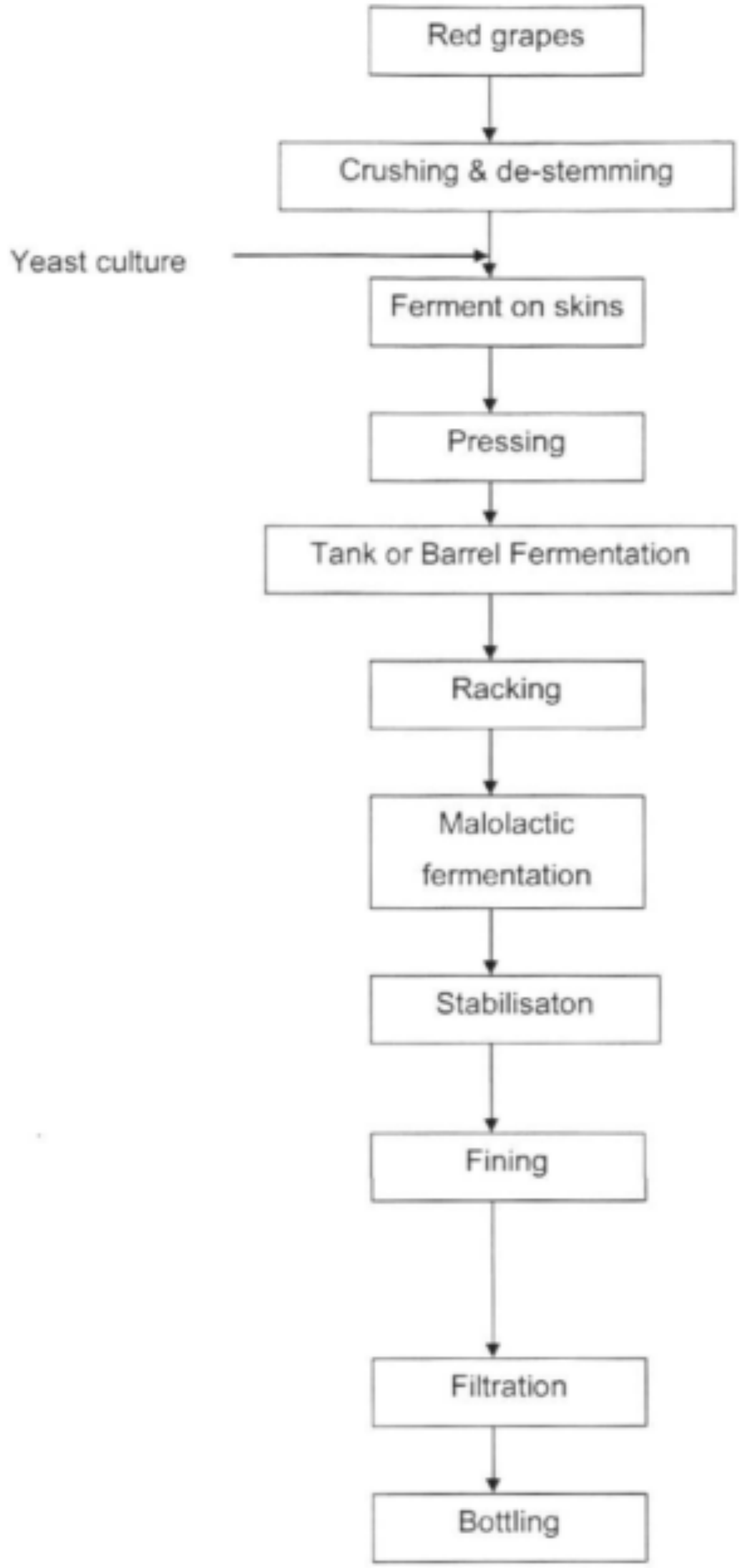

Figure 1.3. Flow diagram of red wine production (Marais, 2001).

The successful integration of ozonation with anaerobic digestion in a mobile test unit has important economic implications for the identification of feasible treatment options for the food and beverage processing industry.

1.3 Research aims

The main objective of this research programme is to investigate the efficiency of utilising combinations of ozone and UASB technology to treat winery and apple juice processing* wastewaters. This will be done by:

1. Evaluation and optimisation of an UASB reactor treating winery wastewater;
2. Evaluation and optimisation of an UASB reactor treating apple juice processing wastewater;
3. Evaluation of ozonation as a pre- and post-treatment to anaerobic digestion of winery wastewater;
4. Evaluation of ozonation as a pre- and post-treatment to anaerobic digestion of apple juice processing wastewater;
5. Evaluation and optimisation of a mobile unit incorporating a scaled-up 600 L UASB reactor and pre- and post-ozonation;

* Originally winery and dairy processing wastewaters would have been used, but a decision was made in consultation with the Steering Committee to change to an apple juice processing wastewater. This was done for logistical reasons as well as the apple juice processing industries expressing an interest in the project as they had wastewater treatment facilities with problems of their own.

1.4 Description of wastewater sources

Cellar wastewaters used during this study were obtained from the Rupert and Rothschild Fredericksburg (R-RF) (Simondium, South Africa) and the Bergkelder, Distell (BK) (Stellenbosch, South Africa) cellars. The apple juice processing wastewater used in this study was obtained from Elgin Fruit Juices (Pty) Ltd, Elgin, South Africa.

Rupert and Rothschild Fredericksburg is situated between Paarl and Franschoek and is a predominantly red wine (85%) producing estate. The main cultivars grown and harvested are: Cabernet Sauvignon, Cabernet Franc, Merlot, and Chardonnay.

Bergkelder, Distell is situated in Stellenbosch and produces a wide variety of red wines, white wines and sparkling wines. Some brandy and liquors are also mixed and bottled at Bergkelder. The main grape varieties used for wine making are Cabernet Sauvignon, Merlot, Pinotage, Shiraz, Sauvignon Blanc, Chenin Blanc, Chardonnay, Gewürztraminer, Semillon and Weisser Riesling.

1.5 Legal requirements

The legal requirements for irrigation of wastewater on land or the discharge of wastewater to a natural water source are defined by the Department of Water Affairs and Forestry in the South African Government Gazette No. 26187, Government Notice 399 (26 March 2004) in amendments to the General Authorisations No. 1191. A summary of these regulations are given in Tables 1.1 and 1.2.

Table 1.1. Wastewater limit values for the irrigation of wastewater according to the South African Government Gazette of 26 March 2004 (Republic of South Africa, 2004).

Parameter	**Limit**
Less than 2 000 m ^{3} of biodegradable industrial wastewater per day	
Fecal coliforms	1 000 per 100 mL
Chemical Oxygen Demand (COD)	75 mg.L^{-1}
pH	5.5 – 9.5
Ammonia (ionised and un-ionised) as Nitrogen	3 mg.L-1
Nitrate/Nitrite as Nitrogen	15 mg.L^{-1}
Chlorine as Free Chlorine	0.25 mg.L^{-1}
Suspended solids (TSS)	25 mg.L^{-1}
Electric conductivity	70 - 150 mS.m^{-2}
Orthophosphate	10 mg.L^{-1}
Fluoride	1 mg.L^{-1}
Soap, oil or grease	2.5 mg.L^{-1}

Parameter	**Limit**
Less than 500 m ^{3} of biodegradable industrial wastewater per day	
Fecal coliforms	100 000 per 100 mL
Chemical Oxygen Demand (COD)	400 mg.L^{-1}
pH	6 - 9
Electric conductivity	200 mS.m^{-2}
Sodium Absorption Ratio (SAR)	< 5

Parameter	**Limit**
Less than 50 m ^{3} of biodegradable industrial wastewater per day	
Fecal coliforms	1 000 000 per 100 mL
Chemical Oxygen Demand (COD)	5 000 mg.L^{-1}
pH	6 - 9
Electric conductivity	200 mS.m^{-2}
Sodium Absorption Ratio (SAR)	< 5

Table 1.2. Wastewater limit values for the disposal of wastewater in a natural water source according to the South African Government Gazette of 26 March 2004 (Republic of South Africa, 2004).

Parameter	General Limit	Special Limit
Less than 2 000 m ^{3} of biodegradable industrial wastewater per day		
Faecal Coliforms (per 100 mL)	1 000	0
Chemical Oxygen Demand ($mg.L^{-1}$)	75 (i)	30(i)
pH	5,5-9,5	5,5-7,5
Ammonia (ionised and un-ionised) as Nitrogen ($mg.L^{-1}$)	6	2
Nitrate/Nitrite as Nitrogen ($mg.L^{-1}$)	15	1,5
Chlorine as Free Chlorine ($mg.L^{-1}$)	0,25	0
Suspended Solids ($mg.L^{-1}$)	25	10
Electrical Conductivity ($mg.L^{-1}$)	70 mS/m above intake to a maximum of 150 mS/m	50 mS/m above background receiving water, to a maximum of 100 mS/m
Ortho-Phosphate as phosphorous ($mg.L^{-1}$)	10	1 (median) and 2,5 (maximum)
Fluoride ($mg.L^{-1}$)	1	1
Soap, oil or grease ($mg.L^{-1}$)	2,5	0
Dissolved Arsenic ($mg.L^{-1}$)	0,02	0,01
Dissolved Cadmium ($mg.L^{-1}$)	0,005	0,001
Dissolved Chromium (VI) ($mg.L^{-1}$)	0,05	0,02
Dissolved Copper ($mg.L^{-1}$)	0,01	0,002
Dissolved Cyanide ($mg.L^{-1}$)	0,02	0,01
Dissolved Iron ($mg.L^{-1}$)	0,3	0,3
Dissolved Lead ($mg.L^{-1}$)	0,01	0,006
Dissolved Manganese ($mg.L^{-1}$)	0,1	0,1
Mercury and its compounds ($mg.L^{-1}$)	0,005	0,001
Dissolved Selenium ($mg.L^{-1}$)	0,02	0,02
Dissolved Zinc ($mg.L^{-1}$)	0,1	0,04
Boron ($mg.L^{-1}$)	1	0,5

(i) after removal of algae

CHAPTER 2
LITERATURE REVIEW

2.1 Background

South Africa is a semi-arid country with limited water reserves and an average annual rainfall well below the world average (Pybus, 1999). Pollution of rivers, waterways and other water resources is prohibited by the National Water Act, Act 36 of 1998 (Republic of South Africa, 1998). By the year 2020 South Africa's water demand will overtake the water supply, but shortages already exist on a regional basis (Pybus, 1999) and, therefore, proposals have been made to encourage re-use of factory effluents (Republic of South Africa, 1991). It has also been reported that water pollution is rapidly increasing in South Africa, seriously affecting sustainable economic growth. Current disposal practices at fruit processors and wineries include the disposal of effluents by irrigation onto lands, evaporation in basins or treatment in lagoons or ponds before irrigation onto lands. Some of the larger fruit processors and wineries, however, dispose of their effluents to municipal sewers. Irrigation of effluents normally leads to ground water pollution problems, odour problems, fly-breeding and an accumulation of toxic contaminants in the soil (J. Visser, 1997, Ashton Canning Company, Ashton, South Africa, personal communication).

Due to the nature of the fruit processing, large volumes of water are used in the transportation of the product, washing and rinsing, peeling, blanching, retorting and cooling operations (Wayman, 1996). The South African wine industry is no different, producing large volumes of wastewater throughout the year. Most of the water originates from cellar cooling and floor and equipment washdown (Ronquest & Britz, 1999). Both these industries are thus faced with two major problems. Firstly, maintaining a profitable level of production while reducing the intake of fresh, potable water, and secondly, disposing of the large volumes of effluent in an environmentally friendly manner. Disposal of fruit processing effluent is often complicated by the presence of suspended solids and particulate organics (Harada *et al.*, 1994), cleaning solutions (most commonly sodium hydroxide), often in formulations with various chelating, softening or surface-active additives, and nitric and phosphoric acids (Mawson, 1997) and sodium hydroxide in the effluent. Wastewater from the wine and spirits industry usually has a high organic content, contains both suspended and dissolved solids and is acidic (Bezuidenhout *et al.*, 2002). Winery wastewater may also contain caustic soda, various soaps, detergents and surfactants used during cleaning of tanks and process equipment. Sulphide compounds, which can lead to odour problems, and salts originating from anti-corrosion and anti-scaling agents in cooling waters may also be present in the wastewater (Water Research Commission, 1993; Bezuidenhout *et al.*, 2002).

2.2 The UASB process

Anaerobic digestion (AD) is a biological process in which organic matter is converted to methane and carbon dioxide. The process involves a bacterial community with complex nutritional requirements and specialized ecological roles (Ianotti *et al.*, 1987 Barnett *et al.*, 1994). In contrast to aerobic waste processing, anaerobic digestion results in much smaller amounts of biomass (Forday & Greenfield, 1983; Barnett *et al.*, 1994).

The AD process is ascribed to the synergistic relationship of four trophic groups of bacteria, namely: hydrolytic, fermentative acidogenic, acetogenic and methanogenic bacteria (Forday & Greenfield, 1983; Ditchfield, 1986; Bitton, 1999).

Hydrolytic Bacteria - Anaerobic bacteria break down complex organic molecules, like proteins, cellulose, lignin, lipids and carbohydrates, by a process of hydrolysis into soluble monomer molecules such as amino acids, glucose, fatty acids and glycerol. The monomers are directly available to the next group of bacteria. Hydrolysis of the complex molecules is catalyzed by extracellular enzymes such as cellulases, proteases and lipases (Forday & Greenfield, 1983; Bitton, 1999; Batstone *et al.*, 2002; Mata-Alvarez, 2003).

Fermentative/Acidogenic Bacteria - Acidogenic bacteria convert sugars, amino acids and fatty acids to organic acids (e.g., acetic, propionic, formic, lactic, butyric or succinic acids), alcohols and ketones (e.g., ethanol, methanol, glycerol and acetone), acetate, CO_2, and H_2. Acetate is the main product of carbohydrate fermentation. The products formed vary with the type of bacteria as well as with culture conditions (temperature, pH, redox potential) (Forday & Greenfield, 1983; Ditchfield, 1986; Ianotti *et al.*, 1987; Bitton, 1999; Batstone *et al.*, 2002; Mata-Alvarez, 2003).

Acetogenic Bacteria - Acetogenic bacteria (acetate and H_2 - producing bacteria) convert fatty acids (e.g., propionic acid, butyric acid and valeric acid) and alcohols into acetate, hydrogen, and carbon dioxide (Ianotti *et al.*, 1987). This group requires low hydrogen tensions for fatty acid conversions. A close monitoring of hydrogen concentration is thus necessary. Under relatively high H_2 partial pressure, acetate formation is reduced and the substrate is converted to propionic acid, butyric acid, and ethanol (Bitton, 1999). There is a symbiotic relationship between acetogenic bacteria and methanogens. Methanogens help achieve the low hydrogen tension required by acetogenic bacteria (Ianotti *et al.*, 1987). Ethanol, propionate, and butyrate are converted to acetate by acetogenic bacteria according to the following reactions (Forday & Greenfield, 1983; Bitton, 1999; Batstone *et al.*, 2002; Mata-Alvarez, 2003). The conversion of these higher volatile fatty acids, caproate, butyrate and propionate to methanogenic substrates, hydrogen and acetate, is an important step in the digestion process as the unionized forms of these acids are particularly toxic to the methanogenic bacteria (Wang *et al.*, 1997; Dhaked *et al.*, 2003).

Methanogens - This group is composed of both Gram-positive and negative bacteria with a large variation in morphology (Bitton, 1999). They are obligatory anaerobes, requiring a lower oxidation reduction potential (-300 mV) for growth than most anaerobic bacteria (Forday & Greenfield, 1983; Ianotti *et al.*, 1987). Methanogens can be subdivided into two sub-categories, namely those utilizing hydrogen and those that split acetate (Ditchfield, 1986; Bitton, 1999). The hydrogenotrophic methanogens convert hydrogen and carbon dioxide to methane (Ianotti *et al.*, 1987; Tchobanoglous & Burton, 1991). The hydrogen-utilizing methanogens help maintain the very low-level hydrogen partial pressure necessary for the conversion of volatile fatty acids and alcohols to acetate (Speece, 1983). The acetotrophic methanogens, also known as acetoclastic bacteria, convert acetate into methane and carbon dioxide (Tchobanoglous & Burton, 1991; Bitton, 1999). About two thirds of methane is derived from acetate conversion by acetotrophic methanogens. The other third is the result of carbon dioxide reduction by hydrogen (Ditchfield, 1986; Mackie & Bryant, 1981). Wastewater must be nutritionally balanced (nitrogen, phosphorous, sulphur) to maintain an adequate anaerobic digestion. The C : N : P ratio for anaerobic bacteria is 700 - 1000 : 5 : 1 (Sam-Soon *et al.*, 1986).

Application of Anaerobic Digestion to Food and Beverage Processing Wastes Hemming (1981) reported on a full-scale anaerobic digestion plant treating potato processing effluent. The effluent had a BOD of 5 000 $mg.L^{-1}$ which was reduced by 60%, had an HRT of seven days and produced 1 800 $m^3.d^{-1}$ of gas containing 70% methane. The feasibility of the upflow anaerobic sludge bed process for the treatment of crude potato-maize wastewater of a chip processing industry was also investigated (Kalyuzhnyi *et al.*, 1997). The wastewater had a high concentration of suspended solids (up to

7 000 $mg.L^{-1}$), a high content of insoluble fraction of COD (up to 60% of total COD) and significant quantities of potentially foaming substances like proteins and fats. Organic loading rates of up to 14 000 mg $COD.L^{-1}.d^{-1}$ were employed and treatment efficiencies higher than 73 and 63% were achieved for dissolved and total COD, respectively (Kalyuzhnyi *et al.*, 1997). Potato processing wastewaters generally have COD levels between 4 500 and 7 500 $mg.L^{-1}$ and relatively high suspended solids concentrations (800 – 1 500 $mg.L^{-1}$) and thus, different anaerobic configurations have been applied as treatment options (i.e. UASB and expanded granular sludge bed (EGSB)). The advantage of EGSB's is that their smaller footprint and greater height allows COD loads of up to 30 $kgCOD.m^{-3}.d^{-1}$, compared to the 10 kg $COD.m^{-3}.d^{-1}$ of conventional UASBs treating potato processing wastewater. In both cases COD removal efficiencies of *ca.* 80% were obtained, with excellent stability and all-year efficiency and reliability (Zoutberg & Eker, 1999). An UASB reactor was also adapted to incorporate a denitrification step during the treatment of parboiled rice industry wastewater (Lopes *et al.*, 2001). The top of the UASB reactor (an anoxic zone) was used to facilitate denitrification. Nitrification was then performed in an aerated mixed reactor. A fraction of the nitrification reactor effluent was recycled into the top of the UASB reactor above the sludge blanket for denitrification in the anoxic zone. The maximum removal efficiency of TKN was 80% when using the recycle loop (Lopes *et al.*, 2001).

Nadais *et al.* (2001) investigated the application of shock loadings (organic, hydraulic and fat shocks) on the performance of an UASB reactor treating dairy wastewater. Total influent COD ranged from 5.6 to 11.9 $g.L^{-1}$ and fat concentration between 2.7 and 6.1 $g.L^{-1}$. Total COD removals of 74 – 93% and fat reductions of 78 – 91% were achieved at HRT's of 6 – 12 h and OLR's of 12 g $COD.L^{-1}.d^{-1}$. The use of an EGSB reactor with internal circulation was used to treat a low strength dairy industry wastewater, a medium strength food industry wastewater (potato based salads and various vegetables) and a high strength brewery wastewater (Driessen & Yspeert, 1999). The dairy wastewater influent COD averaged 1 550 $mg.L^{-1}$ and a total COD removal of 51% was achieved. The food industry wastewater had an influent COD in the range of 995 to 7 450 $mg.L^{-1}$ (average = 4 550 $mg.L^{-1}$). Volumetric loading rates of up to 42 kg $COD.m^{-3}.d^{-1}$ at HRT's of 3.6 to 9.1 h were attained with a total COD removal efficiency of 80%. When treating the high strength brewery wastewater with an average COD load of 13 000 $mg.L^{-1}$ (max. 23 000 $mg.L^{-1}$), a total COD removal of 70 – 90% was achieved. Soluble COD removal amounted to 80 – 98%, while the reactor was stable at volumetric loading rates of up to 36 kg $COD.m^{-3}.d^{-1}$ at HRT's of 8 – 24 h (Driessen & Yspeert, 1999).

The performance of UASB and EGSB reactors have also been compared using ethanol, brewery wastewater and coffee processing wastewater as substrates. During the operation of an EGSB reactor treating ethanol at 500 $mg.L^{-1}$ and a sludge loading rate of 0.8 g COD.g $VSS^{-1}.d^{-1}$, COD removal efficiencies of up to 80% were obtained. The UASB's performance was similar at 75%. Operating both reactors at ethanol concentrations of 10 $g.L^{-1}$, removal efficiencies of 98% were achieved. Biogas production was 0.4 L.g COD^{-1} removed. Operation of the same reactors with diluted beer as substrate, with organic loadings of 0.8 g COD.g $VSS^{-1}.d^{-1}$, resulted in removal efficiencies of 85% for the EGSB and 70% for the UASB reactor. With coffee industry wastewater, the COD removal efficiencies were somewhat lower, probably as a result of the complex nature of the wastewater, at around 60%. The EGSB reactor gave a slightly better removal efficiency (ca. 5%) than the UASB reactor at sludge loading rates of 0.7 g COD.g $VSS^{-1}.d^{-1}$ (Jeison & Chamy, 1999).

Olive mill effluents (OME) are known to contain biorecalcitrant and/or inhibiting substances (essentially phenols and lipids) which hinder the methanogenic process (Andreozzi *et al.*, 1998; Beccari *et al.*, 1998 and 2001). A two reactor system, consisting of an acidogenic phase followed by a methanogenic phase, was used to treat the OME. A maximum of 5% of the total COD was converted to methane in the acidogenic reactor. Complete methanogenic activity was established in the second reactor. Polyphenols were not degraded at all in the acidogenic reactor, while 20 – 30% was removed in the methanogenic reactor. Lipids removal in the acidogenic phase was low (13.6%) but the total two reactor system gave a 77.2% removal. An overall COD removal of 76.5% was achieved (Beccari *et al.*, 1998). Chemical and physical treatments have been employed to remove the biorecalcitrant compounds from OME before anaerobic treatment (Beccari *et al.*, 2001). The addition of $Ca(OH)_2$ to a pH value of 6.5 and bentonite addition at 15 $g.L^{-1}$, followed by centrifugation, resulted in lipid and phenol removals of 99.5 and 45.0%, respectively. A laboratory-scale continuous methanogenic reactor was also fed with the substrate mixture (OME, $Ca(OH)_2$ and bentonite) to evaluate the anaerobic treatability enhancement (Beccari *et al.*, 2001). At the most demanding conditions tested (organic load = 8.2 kg $COD.m^{-3}.d^{-1}$; dilution ratio = 1:1.5) the reactor performance was excellent (total COD removal = 91%; methane yield = 0.80 g CH_4 (as COD).g^{-1} total COD; lipid removal = 98%; phenol removal = 63%) (Beccari *et al.*, 2001).

Research has also been conducted on the anaerobic treatment of winery and distillery wastewaters (Garcia-Bernet *et al.*, 1998; Ronquest & Britz, 1999; O'Kennedy, 2000; Ruiz *et al.*, 2002). Garcia-Bernet *et al.* (1998) applied a down-flow fluidized bed reactor to treat a wine distillery wastewater anaerobically. The system attained TOC removal efficiency rates between 75 and 95% at an OLR of 17 kg $TOC.m^{-3}.d^{-1}$ and HRT of 0.35 d. The wastewater had a TOC content between 5.2 and 6 $kg.m^{-3}$. Similarly, COD reductions of 93% at an OLR of 11.05 kg $COD.m^{-3}.d^{-1}$ and a HRT of 14 h were achieved treating a winery wastewater in an UASB (Ronquest & Britz, 1999). Ruiz *et al.* (2002), using an anaerobic sequencing batch reactor (ASBR), treated a winery wastewater. The reactor was operated at an OLR around 8.6 g $COD.L^{-1}.d^{-1}$ with a soluble COD removal efficiency greater than 98%, HRT of 2.2 d and a specific organic loading rate of 0.96 g COD.g $VSS^{-1}.d^{-1}$. The influence of a high strength distillery effluent on the anaerobic digestion process was investigated using a mesophilic lab-scale UASB reactor (O'Kennedy, 2000). It was found that at an OLR of 30 kg $COD.m^{-3}.d^{-1}$, the pH, alkalinity and biogas production stabilized to values of 7.8, 6 000 $mg.L^{-1}$ and 18.5 $L.d^{-1}$, respectively. An average COD removal > 90% was achieved indicating excellent bioreactor stability (O'Kennedy, 2000).

Anaerobic digestion has been applied to the treatment of cannery effluents for some time. Hills & Roberts (1982) suggested the use of anaerobic digestion to treat peach and tomato cannery effluents. COD removals of 70 - 88% were achieved at organic loading rates of 1 - 2 kg of volatile solids per digester per day. The gas produced had a methane content of 60%, and a CO_2 content of 40%. Total solids were reduced by 71 - 86%. Trnovec & Britz (1998) applied anaerobic digestion to the treatment of fruit canning effluents. The mesophylic laboratory-scale UASB reactor achieved COD removals of 90 - 93% at an OLR of 10.95 kg $COD.m^{-3}.d^{-1}$, at a HRT of 10 h.

Austermann-Haun *et al.* (1994) employed an UASB reactor for treating fruit juice factory effluent. COD removal efficiency of 80 - 90% was achieved with a space loading rate of 3.6 kg $COD.m^{-3}.d^{-1}$, a COD influent of 2 337 $mg.L^{-1}$. The two main problems encountered were washout of granules and decreasing sludge activity. Similar results were obtained in a later study (Austermann-Haun *et al.*, 1997) with COD removal efficiencies still between 82 - 88% at a volumetric loading rate of about 3.5 kg $COD.m^{-3}.d^{-1}$. Sam-Soon *et al.* (1986) achieved COD removal efficiencies ranging from 49 - 98% for hydraulic retention times ranging from 3.9 – 20.0 h, respectively. These results were obtained using apple processing wastewater with an influent COD level of 2 500 $mg.L^{-1}$ and an OLR of 7.5 - 12.5 kg $COD.m^{-3}.d^{-1}$. More recently, Britz *et al.* (2000) used an UASB reactor to treat a fruit cannery effluent devoid of lye. Organic loading rates of 9.2 kg $COD.m^{-3}.d^{-1}$ were achieved at HRT of 10 h, with an average COD removal of 81 – 84%.

Influent COD levels ranged between 3 800 and 4 300 $mg.L^{-1}$, and influent pH levels of 5.0 could be successfully treated in the system.

Anaerobic digestion in conjunction with ultrafiltration (ADUF) has been employed to treat fruit processing waste in Ceres, South Africa (Strohwald, 1993). COD reduction of more than 95% was obtained, with final treated effluent COD values as low as 50 $mg.L^{-1}$ at loading rates of not more than 1.5 kg $COD.m^{-3}.d^{-1}$. Operation at higher loading rates resulted in the deterioration of the COD reduction potential with a sharp increase in COD levels of the ultrafiltration permeate and volatile acid/alkalinity ratio, both of which are indicative of imminent digester failure. Operation at loading rates up to 3 kg $COD.m^{-3}.d^{-1}$ was possible, albeit at lower COD reduction rates of 70 - 85%.

2.3 Ozone technology

Ozone is a pale blue gas with a pungent odour and due to its molecular structure it is highly unstable making it one of the most powerful oxidizing agents (Murray, 1999). It is toxic, but can be detected by smell at levels far below that at which it becomes dangerous. Due to its instability, it breaks down into oxygen very quickly. Commercially, ozone is produced by the passage of a high voltage, alternating electric discharge through a gas stream containing oxygen (Essop, 1998). This discharge results in the breakdown of diatomic oxygen molecules and the reformation of some into triatomic oxygen (Gottschalk *et al.*, 2000). Ozone is the most powerful chemical oxidant available for water treatment. Once dissolved in water ozone can react with many organic compounds either by direct reaction as molecular ozone or by indirect reaction through the formation of secondary oxidants like free radicals (Sigge *et al.*, 2002).

Ozonation is usually utilised as a method of water disinfection but it also has potential as pre-treatment method before biological degradation processes (Essop, 1998; Gottschalk *et al.*, 2000). Ozonation is a promising technology, as it has many of the oxidizing properties desirable for an efficient wastewater treatment option (Benitez *et al.*, 1999; Gottschalk *et al.*, 2000).

It is well known that ozone can hydrolyze organic polymers into smaller units (Gottschalk *et al.*, 2000; Sigge *et al.*, 2002). Ozonation enhances the biodegradability of organic matter by increasing molecule polarity and by forming smaller molecular weight substances (Volk *et al.*, 1993). The increase in biodegradability after ozonation has already been shown for 28 substituted aromatic compounds under aerobic conditions and for some phenolic compounds under anaerobic conditions (Gottschalk *et al.*, 2000).

Combined treatment strategies are used when a biological or chemical treatment alone are not efficient enough to achieve the required result (Gottschalk *et al.*, 2000). A chemical oxidation process, such as ozonation, may be used to improve biodegradability of compounds in wastewater as a pre-treatment to a biological process.

Fernando *et al.* (2001) reported that ozonation was successfully combined with activated sludge treatment for the treatment of cherry stillage. In this case, ozonation played an important role in the oxidation of the polyphenols that are present in high concentrations in the cherry wastewater.

Martin *et al.* (2002) also investigated ozonation as a pre-treatment combined with anaerobic digestion, of vinasse. The function of the ozonation process was to convert refractory and toxic compounds, such as phenol, into simpler molecules with lower molecular weights that could then be used as substrate by the anaerobic populations. In this case, ozonation for two hours did decrease the COD of the vinasse from 109 200 to 82 100 $mg.L^{-1}$. However, it did not show improved kinetic behavioural results during the anaerobic digestion step. In contrast, it was found that when vinasse was treated with ozone in the presence of UV-light and titanium oxide, the specific rate of CH_4 production (mL $CH_4/g^{-1}VSS.h^{-1}$) did increase by a factor of 1.25 (from 3.56 to 4.50) when compared to the untreated wastewater.

Benitez *et al.* (1999) investigated the purification kinetics of winery wastes in separate ozonation and anaerobic digestion studies and in a combined ozonation pre-treatment anaerobic digestion process in a magnetically stirred batch digestion unit. It was found that the winery waste COD could be reduced by 20% using just ozonation. When ozonation was combined with oxidants, UV radiation and hydrogen peroxide, the COD reduction increased to 30%. A methane yield coefficient of 187 mL $CH_4.g^{-1}$ COD degraded and COD removal efficiencies of more than 98%, could be attained in the separate anaerobic treatment set-up. The combined ozonation pre-treatment and anaerobic digestion further increased the methane yield coefficient to 215 mL $CH_4.g^{-1}$ COD degraded.

A study in Greece showed that anaerobic digestion in an UASB reactor can decrease the organic load of "currant"-wastewater by 95.5% yielding an effluent with a COD of only 185 $mg.L^{-1}$ (Athanasopoulos & Athanasopoulos, 1998). This value was still well above the Greek legal limit of 50 $mg.L^{-1}$ for underground discharge. A post treatment with ozone for three hours at a concentration of 300 $mg.h^{-1}$ reduced the COD to the legal limit.

2.4 Ozone contacting systems

As ozone is generated as a gas, the gas and liquid (wastewater) have to be brought into contact. This is usually done in an ozone contacting system and employing a specific ozone diffuser (Gottschalk *et al.*, 2000). Each contacting system has its own characteristic hydrodynamic behaviour. Knowledge of the hydrodynamic behaviour as well as its mass transfer characteristics is important for evaluating the experimental results. Mass transfer in gas-liquid contacting systems is affected by various design parameters, which must be considered (Marais, 2001):

Bubble size – except when bubbles are formed at an opening or sparger, it can be stated that the balance between bubble break-up and coalescence determines the bubble size distribution.

Interfacial area – gas-liquid interfacial area plays an important role in the mass transfer rate, and thus the volumetric mass transfer coefficient.

Gas hold-up – is characterised by the hydrodynamics of the contacting system and is mainly determined by the gas velocity, power input and physical properties of the liquid.

Mass transfer coefficient – most contacting systems are characterised by the fact that mass transfer rates are limited by the transport of gas to the liquid and extensive literature is available.

Volumetric mass transfer coefficient – correlations for the volumetric mass transfer coefficient are obtained from the product of the interfacial area and the mass transfer coefficients.

Bubble columns and stirred tank reactors are the most frequently used types of reactors in laboratory-scale ozonation experiments. Bubble columns can be roughly assumed to behave like perfectly mixed reactors with respect to the liquid phase, provided the height to diameter ratio is small (≤ 10).

In small laboratory-scale stirred tank reactors almost complete mixing of the gas-phase can also be assumed whereas plug-flow or mixed behaviour can be generally assumed for the gas phase in bubble columns (Gottschalk *et al.*, 2000; Marais, 2001).

Bubble columns – Bubble columns and various modifications such as airlift reactors, impinging jet reactors and downflow bubble columns are often used in laboratory-scale ozonation trials. Due to their ease of operation they are usually operated in a cocurrent mode. Laboratory-scale bubble columns preferably have a reactor liquid phase volume of 2 – 10 L, with a height-to-diameter ratio of 5 – 10. The gas mixture is supplied through a ceramic or stainless steel porous plate diffuser. Since mixing is only due to the power produced by the gas flow, very small gas flow rates might cause incomplete mixing in the contacting system (Bitton, 1999; Gottschalk *et al.*, 2000, Marais, 2001).

Stirred Tank reactors – Stirred tank reactors are the most frequently used contacting systems for laboratory-scale trials. There are various modifications with regard to the types of gas diffusers used. Normally laboratory-scale experimental contacting systems will make use of ring pipes with holes of 0.1 – 1.0 mm i.d., venturi's or membrane diffusers. Efficiency is considerably higher than in bubble columns and the main advantage is that in stirred tank reactors, the stirring speed can be varied, and thus the ozone mass transfer coefficient, independently of the gas flow rate.

Tube reactors – One trick to achieve plug-flow and it's higher reaction rates compared to completely mixed stirred tank reactors, is to use an indirectly gassed system. The practicality of this application depends on the amount of ozone required. In long tube reactors with relatively high ozone consumption, additional ozone can be dosed, as gas or ozonated water, along the length of the tube reactor. The ozone gas is absorbed in a highly efficient ozone absorber, consisting of an injector nozzle and absorber chamber. Micro-bubbles of ozone are produced, increasing the mass transfer efficiency. The length and width of these systems is comparable to a conventional water pipe. Such systems are thus of practical relevance in industrial applications where pipelines of considerable length exist for wastewater transportation (Bitton, 1999; Gottschalk *et al.*, 2000).

Static mixers – static mixers can also be used for gas-liquid mixing. The mixer consists of several mixing elements arranged in series within a pipe. Such systems are small and easy to handle. Important advantages are:

- in-line setting up in a pipe;
- compact dimensioning;
- no mobile parts; and
- very little maintenance.

The main operating characteristics are plug-flow for both phases and radially intensive mixing. The hydrodynamic conditions provide a uniform distribution of dissolved ozone in the wastewater and of small bubbles over the whole flow cross-section. The interfacial area is thus also increased, resulting in a high mass transfer rate.

To achieve the high mass transfer rate, the specific power consumption, required to push the liquid through the mixer, is quite high. A high pressure drop also develops within the system and large liquid flow rates are usually required for efficient operation (Gottschalk *et al.*, 2000).

2.5 Wastewater characterisation

Cellar wastewaters, a nutrient deficient substrate, are difficult to treat, even more so than sewage (Toffelmire, 1972). Cellar wastes include pomace (dewatered grape skins, seeds and pulp), lees, stillage, bottle washings, spillage waters, cooling waters and salt waters from ion-exchange processes. The final wastewater has a fairly high COD varying between 800 to 12 800 $mg.L^{-1}$ (Petruccioli *et al.*, 2002). It also has the tendency to become acid and odorous when left standing (Toffelmire, 1972).

During the vintage period, which lasts between 6 and 20 weeks, grapes are harvested and pressed while the juice is fermented to wine (Van Schoor, 2000). This forms the bulk, generally more than 50%, of the wastewater produced (Bezuidenhout *et al.*, 2002). Due to the nature of vinification, the wastewater frequently exhibits large daily and seasonal variations. Stabilisation, filtration, maturation, blending and the bottling of wine are the major activities during the non-vintage period (Van Schoor, 2000).

Bezuidenhout *et al.* (2002) audited 14 South African wineries during the 2000 and 2001 vintage seasons. An additional 9 cellars were included in the 2001 audit. A summary of the results is given in Table 1 and the typical composition of wastewater produced during bottling processes is shown in Table 2 (Storm, 1997).

Monitoring, inspection, auditing and policing structures, including the determination of the amount of water consumed, the amount of wastewater generated and the pollution load, should be followed in wine cellars to ensure continuing compliance to legislation (Bezuidenhout, 2002). Legislation also requires the analysis of electrical conductivity, pH, sodium adsorption ratio and chemical oxygen demand by an accredited laboratory (Van Schoor, 2001). All these analyses are not only required for environmental purposes but are also necessary to remain competitive in an increasingly globalised market place (Hayward *et al.*, 2000).

The apple processing industry in South Africa is a large and expanding industry. South Africa has 24 000 hectares of commercially planted apple trees and this figure is growing by 500 hectares per year (Mabiletsa, 2002). An estimated 22 million trees are harvested each year and produce on average 710 000 metric tons of apples. 515 000 metric tons are used for fresh consumption, locally and abroad. The remaining 195 000 metric tons are processed into mainly fresh and concentrated apple juice (Mabiletsa, 2002). Approximately 9.5 m^3 of wastewater is produced for every ton of apples processed (Mannapperuma, 1995) giving approximately 6.8 million m^3 of undiluted high oxygen demanding wastewater every year (Wayman, 1996).

Table 2.1. Summary of data obtained in an audit of South African cellar wastewater during the vintage periods 2000 and 2001 (Bezuidenhout *et al.*, 2002).

	2000			2001		
Constituent	**Min**	**Max**	**Average**	**Min**	**Max**	**Average**
Chemical Oxygen Demand ($mg.L^{-1}$)	2 796	33 180	12 972	1 401	19 754	8 664
Total Dissolved Solids ($mg.L^{-1}$)	1 186	11 424	3 381	618	4 275	2 537
Suspended Solids ($mg.L^{-1}$)	223	18 806	2 406	232	7 478	1 511
pH	305	5.6	4.2	3.5	8.8	4.6
Conductivity ($mS.m^{-1}$)	4	230	93	19	253	105

Table 2.2. Composition of the waste stream generated by a large operating winery during bottling operations (Storm, 1997).

Constituent	Concentration (mg.L^{-1})
Chemical Oxygen Demand (COD)	9 330
Biochemical Oxygen Demand (BOD)	5 845
Total Suspended Solids (TSS)	1 251
Ammonia Nitrogen (NH_3)	14.6
Volatile Suspended Solids (VSS)	722
Total Nitrogen (N)	81
Total Dissolved Solids (TDS)	178
Total Phosphorous (P)	8.8
Settleable Solids	2.1
pH	5.1

Apple juice production consists of several stages: Sorting; washing; grinding to produce a mash; enzyme treatment; pressing; juice treatment; and pomace disposal (Mannapperuma, 1995). A yield of between 70 and 80% would normally be obtained from the pressing of good apples (Rutledge, 1996). In the food processing industry water is used in most of the processing operations (Brand & Martin, 1994; Mannapperuma, 1995), including: transportation; cleaning; blanching; retorting; cooling; cooking; peeling; washing; and sanitizing operations. Wastewater is produced during the washing, pressing, juice extraction and dewatering stages. During the pressing a solid waste (pomace) is produced, which is usually resold as animal feed (Wayman, 1996). The dewatering operation is responsible for the largest volume of wastewater produced, and the washing and pressing operations are responsible for the highest organic load in the effluent (Grismer *et al.*, 2002).

The characteristics of wastewater from the apple processing industry are extremely variable (Dold *et al.*, 1987) since they are affected by numerous factors, like processing rate, plant capacity utilization, raw material quality, preparation equipment, water reuse and housekeeping practices (Shober, 1989; Ross *et al.*, 1999). Wastewater parameters of major pollutional significance are the biological oxygen demand (BOD), chemical oxygen demand (COD), total suspended solids (TSS), turbidity, temperature, nitrogen and phosphorus (Mannapperuma, 1995). Apple juice processing wastewater will usually contain varied COD concentrations (400 – 15 000 mg.L^{-1}), 92 – 116 mg.L^{-1} nitrogen (as total Kjeldal nitrogen) and 11 – 27 mg.L^{-1} phosphorus (in the phosphate form). The solid content of the wastewater will vary considerably depending on the process in the plant and the equipment used (Dold *et al.*, 1987). A variety of substances such as antioxidants, clarifying aids, preservatives, reducing agents, firming agents, sequesterants, pH controllers, anti-caking agents, thickening agents, acidulants and nutrients are also present in the wastewater (Somogyi & Kyle, 1978; Broomfield, 1996).

Complex solid and suspended organic polymers like pectin, cellulose and lignin are also present in apple juice processing wastewater with concentrations depending on various factors, like processing methods and type of raw materials used (Morris, 1985). The nature and functional abilities of the complex organic matter present, can interfere with wastewater treatment processes (Van Lier *et al.*, 2001). One of the major problems encountered during apple processing wastewater is the ability of pectin to increase the viscosity of the wastewater. The fact that pectin is not readily biodegradable may lead to serious problems in the treatment of pectin containing apple wastewaters (Tanabe *et al.*, 1987).

2.6 Conclusions

Anaerobic digestion of fruit processing and winery wastewaters has been successfully implemented (Austermann-Haun *et al.*, 1997; Ronquest & Britz, 1999; Trnovec & Britz, 1998) and has several advantages over conventional disposal methods. Large areas of land are not required (Wood, 1992); bulking of the biomass within the digester is appreciably less than with other treatment methods (Lin & Yang, 1991); bad odours do not occur; chemical oxygen demand (COD) is substantially lowered; nutrient requirements are low; and water (H_2O), methane (CH_4) and carbon dioxide (CO_2) are obtained as final metabolic products (Lettinga, 2001). Treatment of these effluents (seasonal fruit processing and winery) by upflow anaerobic sludge blanket (UASB) reactors has recently been shown to be a feasible option.

Ozonation in combination with anaerobic digestion could be useful in increasing the efficiency of biological wastewater treatment processes to such an extent that wastewaters can either be re-used or safely returned to the environment. The use of ozone in the treatment of wastewaters has been shown to be effective in reducing COD, removing colour and increasing the biodegradability of compounds in the wastewater (Gottschalk *et al.*, 2000). The efficiency of ozone in wastewater treatment is mainly due to it's strong oxidising capacity, resulting from the formation of highly reactive hydroxyl radicals. These hydroxyl radicals attack organic molecules by abstracting a hydrogen atom or by adding to the double bonds, thereby mineralising the compounds to non-toxic forms such as carbon dioxide and water (Gulyas *et al.*, 1995; Beltrán *et al.*, 1999). Ozonation as a post-treatment to reduce the COD content of treated food processing wastewaters has been successful and wastewaters treated include fruit cannery, distillery, poultry, tomato processing, yeast production and table olive debittering wastewaters (Chang & Sheldon, 1989; Filipović-Kovačević & Sipos, 1995; Beltrán *et al.*, 1997, 1999, 2001a and 2001b). Ozonation as a pre-treatment to anaerobic digestion is not as extensively documented as ozonation as a post-treatment. The ozonation process may thus possibly be used to improve the biodegradability of wastewaters and thus improve the overall efficiency of wastewater treatment processes, in an attempt to reach final COD levels below the "general" legal limit of 75 $mg.L^{-1}$ for discharge to a natural water resource or below the irrigation limit of 400 $mg.L^{-1}$ (Republic of South Africa, 1999).

CHAPTER 3

EVALUATION AND OPTIMISATION OF AN UASB REACTOR TREATING WINERY WASTEWATER

3.1 Summary

A mesophylic, laboratory-scale upflow anaerobic sludge bed (UASB) bioreactor was evaluated for the treatment of cellar wastewaters. The bioreactor was subjected to an acclimatisation period at a hydraulic retention time (HRT) of 24 h and the substrate pH poised at 8.0 to avoid rapid acidification. Extreme variations in effluent pH and chemical oxygen demand (COD) reduction efficiencies between 29 and 64% were experienced. An addition of strains of *Acinetobacter haemolyticus*, *Burkholderia cepacia* and *Cryseomonas luteola* isolated from raw cellar effluent, to the substrate, did not lead to greatly improved performance. Chemical oxygen demand reduction efficiencies with variations of 35 to 77% were experienced. An increase in organic loading rate (OLR) by increasing the substrate COD led to the COD reduction stabilising above 60%. The substrate pH was lowered from 8.00 to 5.73 while the HRT was kept at 24 h to find the lowest efficient operational pH. At substrate pH 7.5 stable-state in terms of COD reduction and effluent pH was reached. The lowest efficient operational pH was found to be 5.73 (substrate COD < 5 000 $mg.L^{-1}$). In a further study at pH 6.0 where the HRT was reduced from 24 to 17.4 h and subsequently the OLR increased from 8.39 to 10.95 kg $COD.m^{-3}d^{-1}$, the most efficient operational HRT was found to be at 19.7 h. The COD reduction efficiency was 84%. Lower HRT's led to severe reactor acidification and granule wash-out. The economic implication of the UASB functioning at low pH in terms of neutralisation costs and a relatively short HRT are considerable.

3.2 Introduction

The wine industry significantly contributes to South Africa's pollution problems. This also includes the increased salination and eutrofication of water resources and ultimately soil degradation (Van Schoor, 2000). Water usage for wine-making ranges from 700 to 3 800 L per ton of grapes processed and 70% of the water in-take is returned as wastewater. Typical, nutrient deficient, acidic cellar wastewaters show considerable compositional variation with average chemical oxygen demand (COD) values varying from 800 to 12 800 $mg.L^{-1}$ (Petruccioli *et al.*, 2002). This variation in COD values together with high penalties for not complying to set standards and the necessity to remain competitive in an increasingly globalised market place (Hayward *et al.*, 2000) has forced cellars to consider various wastewater treatment options.

The use of the UASB bioreactor design has been shown to be successful in the treatment of various food industry wastewaters (Ross, 1989; Strydom *et al.*, 1997; Puñal & Lema, 1999). Since wastewaters from the alcoholic fermentation industry, such as cellar and distillery wastewaters, are also highly polluted, the anaerobic digestion technology may be applied as a treatment option (Driessen *et al.*, 1994; O'Kennedy, 2000). UASB treatment has already been shown to be feasible for the treatment of cellar wastewaters (Andreottola *et al.*, 1998; Müller, 1998; Ronquest & Britz, 1999).

The aim of this research was to evaluate the use of a laboratory scale mesophylic UASB system as a treatment option of cellar wastewater. This will involve a comprehensive stabilisation study including nutrient additions, microbial enhancement, and the heat treatment of the raw substrate. In a second phase, the reactor will be optimised in terms of lowering the substrate pH so as to minimise neutralisation costs. A third phase will involve the determination of the organic loading rate (OLR) at which the best overall operational efficiency could be maintained.

3.3 Materials and methods

Bioreactor

A laboratory scale UASB bioreactor at 35°C (Meyer *et al.*, 1985) an operational volume of 2.3 L, was used. The substrate was pulse-fed from the bottom of the reactor using a peristaltic pump (Watson-Marlow 101U/R) controlled by an electronic timer and the biogas exited at the top via an open gas/solid separator. The volume of biogas produced was determined using a manometric unit. The upflow velocity was set at 2.8 $m.h^{-1}$ for re-circulation.

Bioreactor start-up

The bioreactor was seeded with a mixed anaerobic granule consortium, obtained from the Department of Food Science, University of Stellenbosch to a settled height of 300 mm (30% of the reactor height). The hydraulic retention time (HRT) was set at 24 h and a granule acclimatisation period was implemented with a diluted cellar wastewater as substrate (COD of 2 000 $mg.L^{-1}$).

Substrate

The cellar wastewater was obtained from the Rupert and Rothschild Fredericksburg cellar (R-RF) (Simondium, South Africa) during the period April 2002 to March 2003. The substrate batches, which included wastewater from the vintage (harvest) and non-vintage (non-harvest) seasons, were kept at -18°C. As cellar wastewater is a nutrient deficient substrate (Water Research Commission, 1993) it was supplemented with the following when used as bioreactor substrate: 500 $mg.L^{-1}$ urea and 200 $mg.L^{-1}$ K_2HPO_4 to prevent N and P limitations; and 500 $mg.L^{-1}$ sucrose, from day 83 onwards, to stimulate reactor performance. From day 30 onwards it was also supplemented with 500 $mg.L^{-1}$ $KHCO_3$ to increase alkalinity. Substrate pH was adjusted as required for each study (8.00 to 5.73) using 1 M KOH.

Analytical methods

The following operational parameters were monitored according to Standard Methods (Standard Methods, 1998): pH; alkalinity; total suspended solids (TSS); and total volatile suspended solids (VSS). Chemical oxygen demand (COD), orthophosphate phosphorous (PO_4), and total Kjeldahl nitrogen (TKN) were determined colorimetrically using a DR 2000 spectrophotometer (Hach Co. Loveland, CO) and standardised procedures (Standard Methods, 1998).

Dissolved organic carbon (DOC) was determined by Environmentek, CSIR, Stellenbosch, using an automated Persulphate-Ultraviolet oxidation method based on the colorimetric detection of CO_2 generated (Mike Louw, 2002, personal communication).

Polyphenols were determined using the Folin-Ciocalteau method (Singleton & Rossi, 1965). The volatile fatty acids (VFA) were determined on a Varian (Model 3700) gas chromatograph, equipped with a flame ionisation detector and a 30 m fused silica capillary column with free fatty acid phase (FFAP) bonded stationary phase (Quadrex Co. New Haven).

A Fisions 3 300 gas chromatograph equipped with a thermal conductivity detector and 2.0 m x 3.0 mm i.d. column packed with Hayesep Q (Supelco, Bellefonte, PA), 80/100 mesh, was used to determine biogas composition.

Microbial isolations
Cellar effluent media (CE-medium), consisting of 20% (v/v) cellar effluent, 80% water (v/v), 200 mg.L^{-1} each of urea and K_2HPO_4, was prepared and 14 g.L^{-1} agar (Merck) was added. Pour plate dilution series' were carried out on the R-RF cellar wastewater "batch 2" and a cellar wastewater obtained from the Bergkelder, Distell (Stellenbosch, South Africa). The plates were incubated aerobically and anaerobically at 35°C for 48 h.

Prevalent strains from the 10^{-5} dilution range for both wastewaters were inoculated into 10 mL sterile CE-medium and then incubated at 35°C for 48 h. One mL of this medium was then used to inoculate 9 mL sterile CE-medium, incubated at 35°C for 48 h. Every 48 h, 1 mL of the latest inoculated medium was used to inoculate a further 9 mL sterile CE-medium, which was again incubated at 35°C for 48 h. After 14 days, the best strains were streaked out onto CE-agar until pure colonies were obtained. The morphology of each of the isolates was determined by bright field microscopy of Gram preparations. The purified isolates were characterised using catalase and oxidase character tests and combinations of the API 20E and 20NE systems (bioMérieux sa, 69280 Marcy l'Etoile, France).

Experimental study I: General bioreactor stabilisation
In the first study the reactor performance was stabilised while feeding a substrate with the pH poised at 8.0. An increase in alkalinity facilitated by $KHCO_3$ additions from day 30 (500 mg.L^{-1}), sucrose supplementations (500 mg.L^{-1}) to the substrate from day 83, heat-treated (100 kPa at 121°C for 15 min) substrate from days 113 to 192 and microbial supplementation from days 120 to 170, were investigated as methods to enhance bioreactor stability. The microbial supplementation process used to enhance digestion of cellar wastewater prior to anaerobic digestion involved additions of mixtures of the isolated bacteria (>10^8 cfu.mL$^{-1)}$, grown for 24 h at 35°C in 10 mL CE-media.

Experimental study II: Lowering of substrate pH
In this study the substrate pH was reduced from 8.00 to 5.73 in seven steps. The HRT and substrate COD's were kept constant at 24 h and 3 440 mg.L^{-1} (min = 2 219 and max = 4 855 mg.L^{-1}), respectively.

Experimental study III: Increase in OLR
The third study was divided into two phases. In the first phase the OLR was increased by increasing the substrate COD from *ca.* 3 000 to 8 000 mg.L^{-1}. Substrate pH was kept at 5.73 from days 357 to 396 and adjusted to 6.00 on day 397 to prevent possible system failure. In the second phase, the OLR was further increased by shortening the HRT from 24 to 17.6 h in five steps. The substrate pH was kept constant at 6.00 throughout the second phase of this study.

3.4 Results and discussion

Wastewater Composition
The compositions of the cellar wastewater batches used in this study are shown in Table 3.1. It is evident that the wastewater showed considerable variation in organic content and pH value. This was, however, expected as cellar wastewater varies according to cellar operation during especially the harvest and post-harvest periods (Van Schoor, 2000). The data also showed low nitrogen and phosphorous content necessitating wastewater N and P supplementation before use as reactor substrate.

Study I: General bioreactor stabilisation
The performance of the UASB bioreactor over the first 278 days is shown in Fig. 3.1. During the first eight days of the study, a diluted cellar wastewater substrate with a pH poised at 8.00 and COD of 2 000 mg.L^{-1}, was fed to the UASB reactor. This led to a drop in reactor effluent pH from 7.60 to 5.25. Therefore, on day 9 the inlet feed was further diluted to a COD of 1 000 mg.L^{-1}. Reactor performance did not improve (COD reduction efficiency = 52 – 69%), and subsequently the HRT was lengthened from 24 to 41.7 h on day 21. In order to increase the reactor alkalinity to try and stabilise the reactor buffering capacity, $KHCO_3$ additions were made daily from day 30 onwards. The COD reduction efficiency during this period (days 30 – 82) varied considerably (28 – 64%).

Table 3.1. Composition of the raw wastewater batches, obtained from the Rupert and Rothschild Fredericksburg (R-RF) cellar.

Parameter		Batch			
		1	2	3	4
COD_{total} (mg.L^{-1})		4 896	3 500	3 492	10 206
$COD_{soluble}$ (mg.L^{-1})		3 852	2 690	2 376	9 936
DOC (mg.L^{-1})		1 010	n.d.	651	2 481
pH		6.2	6.3	3.6	3.6
Phosphorous (mg PO_4.L^{-1})		26	20	14	39
TSS (mg.L^{-1})		426	648	639	572
VSS (mg.L^{-1})		326	562	360	507
TKN (mg.L^{-1})		6.25	n.d.	0.00	5.83
Conductivity (μS.s^{-1})		818	n.d.	1 040	1 390
Polyphenols (mg gallic acid equivalents.L^{-1})		32	n.d.	15	50
VFA (mg.L^{-1}):	Acetic	62	n.d.	15	109
	Propionic	18	n.d.	17	59
	Butyric	0	n.d.	10	0
	Valeric	0	n.d.	6	0
	Total VFA's	80	n.d.	48	168

n.d. = not determined

Reactor instability displayed by the large variation in COD reduction efficiency during this phase led to other stimulation methods being considered. Since cellar wastewater is carbohydrate deficient as it results from a yeast fermentation process, sucrose additions of 500 mg.L^{-1} were made to the wastewater from day 83 onwards. The COD reduction efficiency improved from 20% on day 86 to 61% on day 92. However, COD reduction efficiency again decreased and the data showed the continuing varying of COD reduction efficiency pattern similar to that observed prior to sucrose additions. In a

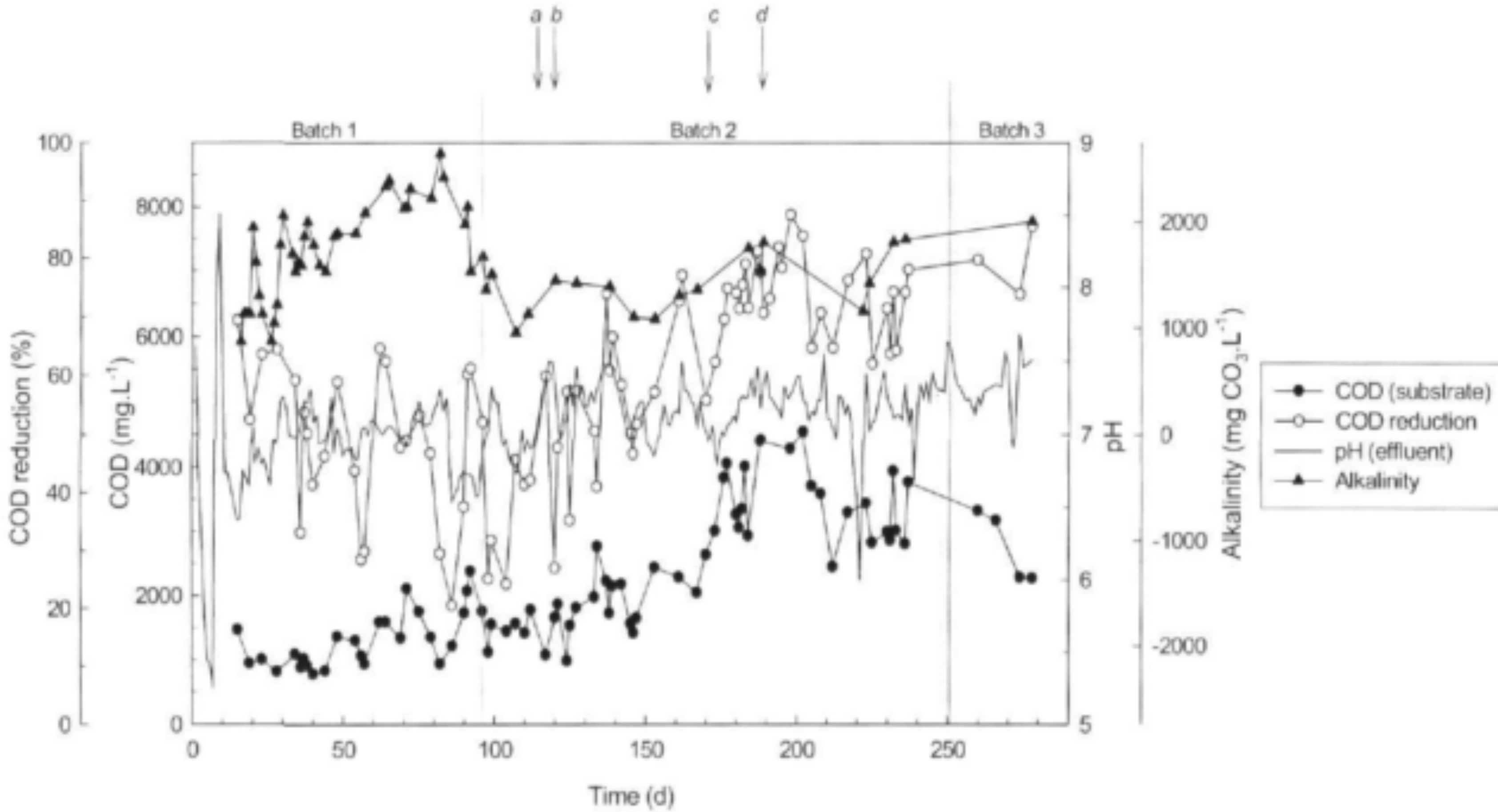

Figure 3.1. Reactor performance during the stabilisation study: a = start of substrate heat treatment; b = start of pre-degradation; c = end of pre-degradation; and d = end of substrate heat treatment.

second attempt to stimulate the COD reduction efficiency, the OLR was increased by the HRT being lowered to 24 h on day 113. The COD reduction continued to vary as before.
In order to try to improve the reactor biodegradability, the substrate was then subjected to a heat-treatment process from days 113 to 192. As can be seen from Fig. 3.1, COD reduction efficiency continued to be inconsistent, but in total, the COD reduction efficiency by day 191 had increased to 73%. It is not certain whether this increase can be attributed directly to the heat treatment process.

During the same period (days 120 – 170), pre-degradation and possible bioaugmentation of the reactor with bacteria isolated from cellar effluents were attempted. Additionally, the substrate COD was also gradually increased from 2 200 $mg.L^{-1}$ on day 142 to 4 400 $mg.L^{-1}$ by day 188. Once the heat-treatment was terminated, a slight decrease in COD reduction efficiency was observed. The termination was, however, coupled to a decrease in substrate COD, which also could have led to the slight decrease in COD reduction efficiency.

In the past it has been shown that the inoculation of the reactor substrate with bacteria naturally occurring and actively degrading the organic compounds in the original wastewater, could improve the anaerobic digestion process (Keyser *et al.*, 2003). Based on the above, three different dominant bacterial strains were obtained from the cellar wastewater and identified as *Acinetobacer haemolyticus* (ID =89%), *Burkholderia cepacia* (ID = 99%) and *Cryseomonas luteola* (ID = 98%). All three isolates grew well on CE-agar.

Cellar effluent medium containing mixtures of the three isolates (>10^8 $cfu.mL^{-1}$) were added to the reactor substrate from day 120. Since COD reduction efficiency remained variable during the complete microbial supplementation study (35 – 77%), the additions were terminated on day 170.

The increase in substrate COD from 2 635 $mg.L^{-1}$ on day 170 to 4 055 $mg.L^{-1}$ by day 177 (Fig. 3.2) most probably led to the increase in COD reduction efficiency. The average COD reduction prior to the increase was 55% (days 120 – 170) compared to 77% (days 180 – 202) after the increase. The possibility of the higher substrate load stimulating COD reduction efficiency should be considered as it was found that lower substrate COD's generally led to lower COD reduction efficiencies (days 170 – 208).

From day 170 the bioreactor was regarded as stable. The COD reduction efficiency and alkalinity remained above 70% and 1 000 mg $CaCO_3.L^{-1}$, respectively. The reactor continued with this performance after the introduction of substrate batch 3 on day 251. It was found that the effluent pH varied between 7.2 and 7.6 and COD reduction was above 74%.

Study II: Lowering of substrate pH

Wastewaters discharged from cellars often have a pH as low as 3.6 (Table 3.1). To prevent stressing the microbial population of the bioreactor, especially the methanogenic population that functions optimally at pH 6.7 to 7.4 (Bitton, 1999), the pH should be neutralised before introducing the wastewater to the reactor. However, neutralisation contributes greatly to the operational costs of the UASB treatment process. For economic reasons it was thus decided to find the lowest operational pH and subsequently acclimatise the microbes present in the bioreactor to lower substrate pH's.

Substrate pH reduction was implemented on the UASB reactor after it showed good performance in terms of COD reduction efficiency (> 70%) and effluent pH stability (Fig. 3.1). The substrate pH was lowered from 8.0 to 7.5 on day 279 (Fig. 2) and kept at 7.5 for 9 days and, as can be seen (Fig. 3.2), the COD reduction increased to 88%. On day 288 the substrate pH was further lowered to 7.0 and COD reduction decreased to 80%, but rapidly recovered to 89%.

Since the reactor effluent pH remained above 7.10, the substrate pH was further decreased to 6.5 on day 294. The effluent pH was found to increase and remained above

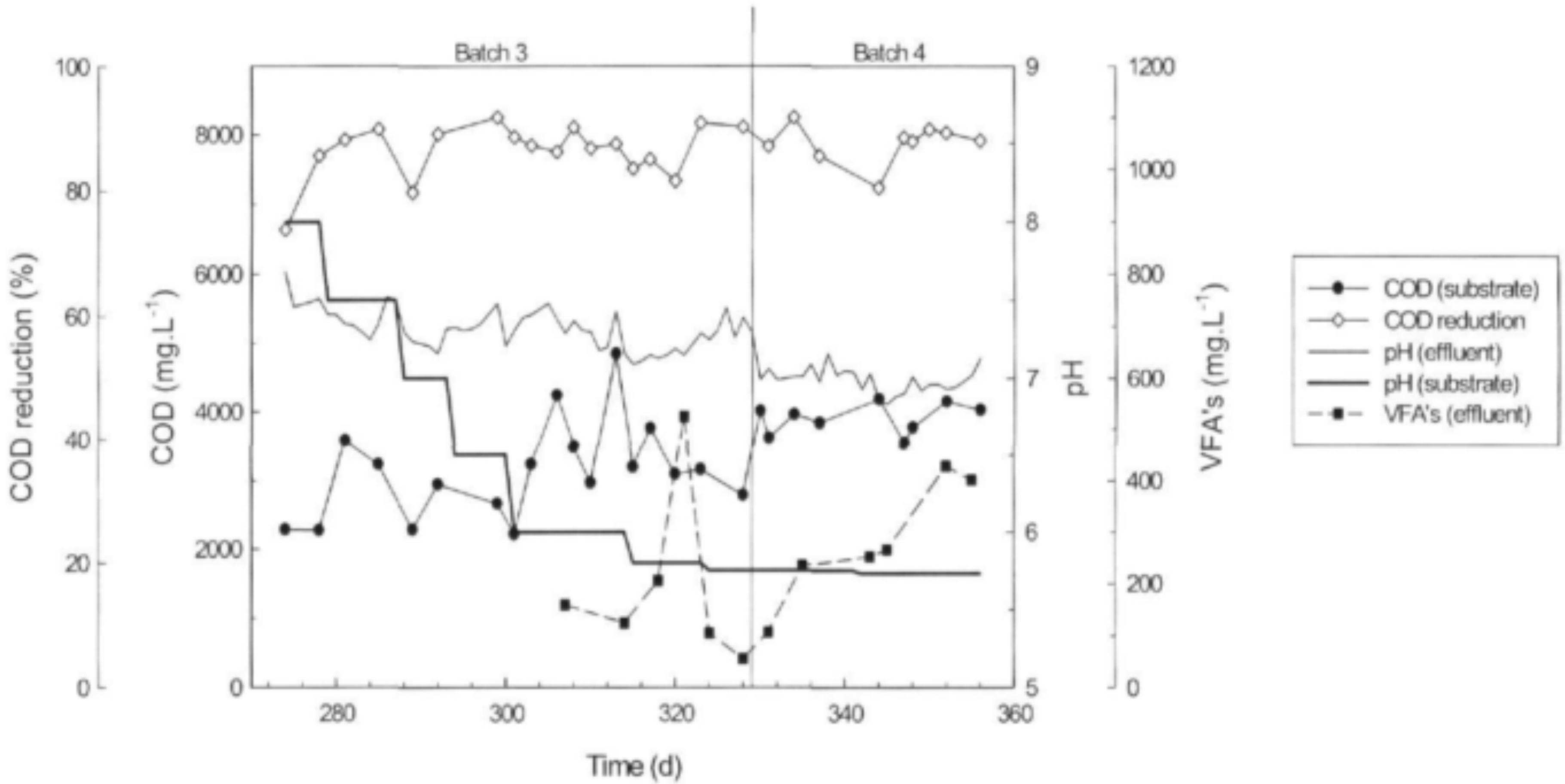

Figure 3.2. Reactor performance during the pH reduction study from days 274 to 356.

7.20, and COD reduction efficiency increased to 91%. After a further 7 days the substrate pH was reduced to 6.00. The reactor effluent still showed a good average pH of 7.32 and the COD reduction efficiency was stable between 86 and 90%. The effectiveness of the bioreactor could further be illustrated by the low VFA's of 159 and 124 mg.L^{-1} in the effluent on days 307 and 310, respectively. The setting of the substrate pH to 5.75 did not initially affect the effluent pH. The excellent reactor performance at this stage was highlighted by VFA's of 106 mg.L^{-1} on day 331. At the same time a COD reduction efficiency of 91% was achieved.

On day 329 a new batch (4) of wastewater (COD = 3 800 mg.L^{-1}) was introduced to the reactor. The reactor effluent pH decreased to about 7.03 and the VFA's to 234 mg.L^{-1}. The COD reduction efficiency remained above 85% and a further reduction of the substrate pH to 5.73 on day 342 led to the COD reduction efficiency being reduced to 80%. The reactor once again stabilised in terms of COD reduction efficiency within 3 days and the average COD reduction was 88%. However, the low substrate pH led to a high VFA concentration of 415 mg.L^{-1}. Since the effluent pH now remained below 7.0 and the VFA concentration was above 400 mg.L^{-1}, it was decided to stop this study and accept 5.73 as the lowest efficient operational substrate pH. The economic implications regarding savings in neutralisation costs as a result of the use of a lower substrate pH should be significant.

Study III - Increase in organic loading rate

(a) Increasing substrate COD: During the original wastewater collection period (Table 3.1) it was found that cellar wastewater can have a COD of > 10 000 mg.L^{-1}, which could lead to drastic overloading and reactor failure. It was thus decided to increase the substrate organic load by decreasing the dilution factor of the reactor substrate (days 357 – 450) (Fig. 3.3) and to optimise the reactor in terms of OLR. The substrate pH and HRT were kept at 5.73 and 24 h, respectively.

From days 357 to 364 (Fig. 3.3), the substrate COD was increased stepwise to 5 087 mg.L^{-1}. During this period the alkalinity remained constant at 1 631 mg $CaCO_3$.L^{-1} and the average VFA concentration was 228 mg.L^{-1}. Chemical oxygen demand reduction efficiencies of more than 87% were maintained. When the substrate COD was increased to 5 500 mg.L^{-1}, the COD reduction efficiency and effluent pH dropped to 80% and 6.85, respectively. Although COD reduction efficiency later improved to 86%, the reactor effluent pH was still relatively low at 6.63. By keeping the substrate COD above 5 000 mg.L^{-1}, a decrease in the average COD reduction efficiency to 82% and VFA-concentration to 536 mg.L^{-1}, respectively was found. A drop in alkalinity over the same period, indicated reactor instability and 30 days after the final COD substrate load increase, the bioreactor had not regained previous reduction efficiencies and the VFA concentration increased to 615 mg.L^{-1}. As further increases in substrate COD at an input substrate pH of 5.73 would probably have led to system failure, the substrate pH was reset to 6.0 and retained at this pH for the remainder of the study.

The increased substrate pH led to an almost immediate recovery of reactor performance as the VFA concentration decreased to 281 mg.L^{-1} and an average COD reduction efficiency of 85% was maintained. The substrate COD was then increased to 7 100 mg.L^{-1}. The effluent pH remained above 7.0 and the average COD reduction for this period was 88%. When the substrate COD was however, increased to 8 300 mg.L^{-1} on day 446, the pH of the effluent dropped to 6.78 (Fig. 3.3) and VFA concentration increased to 580 mg.L^{-1}. The pH recovered to 6.92 by day 447, VFA's decreased to 473 mg.L^{-1} by day 450 and COD reduction stabilised at an average of 86%. As the pH of the effluent was now considerably lower than when substrates with lower COD's (<8 000 mg.L^{-1}) were fed, it was decided that for the remainder of the studies only to increase the OLR by reducing the HRT.

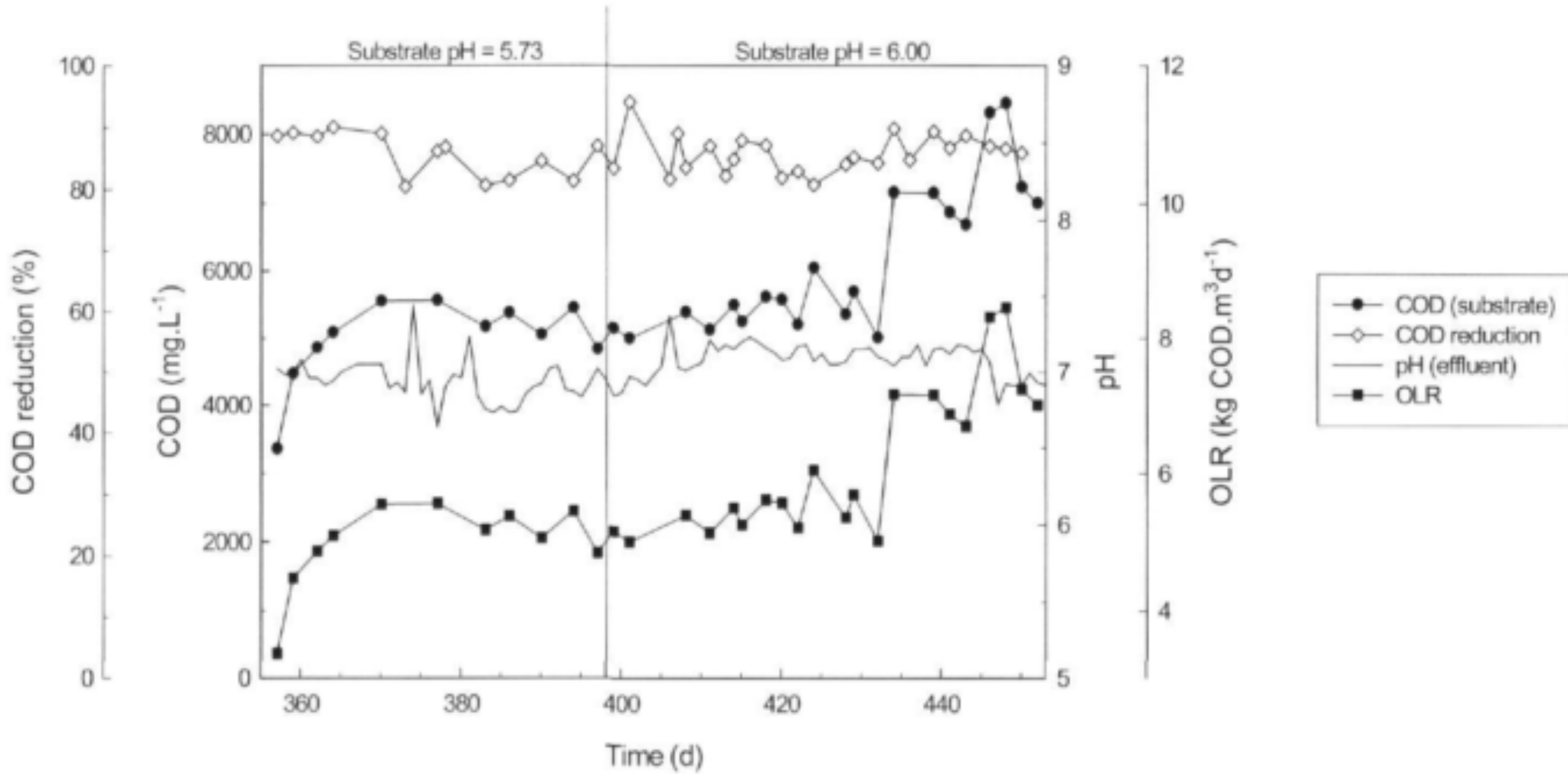

Figure 3.3. Reactor performance during the increase in substrate COD from days 357 to 452.

(b) Reducing the HRT: For economic reasons, it is important to treat wastewater as quickly and effectively as possible. It was thus necessary to find the shortest possible HRT where efficient degradation by the reactor microbial consortium was still possible. In this study the HRT thus was shortened from 24 to 17.4 h in five steps (Table 3.2) with a subsequent increase in OLR from 8.39 to 10.95 kg $COD.m^{-3}d^{-1}$. During the first four steps the pH (6.9 – 7.2) and alkalinity (1 650 – 1 750 $mg.L^{-1}$) of the bioreactor effluent remained fairly constant. Sufficient alkalinity (>1 000 mg $CaCO_3.L^{-1}$) was most probably the key to satisfactory digestion with COD reduction efficiencies of 84 to 89% (Tchobanoglous & Burton, 1991). However, re-setting the HRT at 19.7, led to some granule wash-out.

The reduction of the HRT from 19.7 to 17.4 led to a considerable decrease in pH and alkalinity. The effluent pH dropped to 6.7 on the first day and to 5.5 by the second day of feeding at an HRT of 17.4 h. The alkalinity level was greatly reduced to 675 $mg.L^{-1}$ $CaCO_3$ and the COD reduction efficiency dropped to 79%. Granule wash-out now also became more severe and led to blockages and substantial over-flow and subsequent granule loss. All attempts to stabilise the reactor at a HRT of 17.4 h failed.

The lowest efficient operational HRT was thus found to be around 19 h. This HRT was not as short as the HRT of 2.3 h achieved by Torkian & Hashemian (2003) who treated a slaughterhouse. This study was, however, better than that achieved by Strydom *et al.* (1997) of 1.7 d while treating a dairy wastewater using a hybrid reactor.

The optimum corresponding OLR was thus 9.75 kg $COD.m^{-3}d^{-1}$ (Table 3.2) which compared well to results found by Trnovec & Britz (1998) where the optimum OLR was found to be 8.68 kg $COD.m^{-3}d^{-1}$ using a similar laboratory-scale reactor treating cannery wastewater.

Table 3.2. Operational conditions and reactor efficiency during the study on the shortening of the HRT.

Parameter	1	2	3	4	5
HRT (h)	24.0	23.0	21.0	19.7	17.4
Substrate COD ($mg.L^{-1}$)	8 386	9 077	7 630	8 003	7 938
Substrate pH	6.0	6.0	6.0	6.0	6.0
Bioreactor effluent pH	6.9	7.0	7.2	7.0	6.4
COD reduction (%)	86	89	86	84	79
OLR (kg $COD.m^{-3}.d^{-1}$)	8.39	9.47	8.72	9.75	10.95
Alkalinity ($mg.L^{-1}$ $CaCO_3$)	1 738	1 750	1 650	1 600	675
Biogas ($L.d^{-1}$)[#]	7.55	8.16	8.55	9.29	-[*]
Y_{biogas} ($m^3.kg^{-1}.COD_{removed}$)	0.455	0.421	0.496	0.493	-[*]

[*] malfunctioning of biogas measuring unit as a result of excess granules being washed out
[#] methane content of the biogas was on average of 35% CH_4 throughout the study

3.5 Conclusions

It is well known that cellar wastewaters are nutrient deficient substrates and thus are difficult to treat (Toffelmire, 1972). In this study it was shown that an UASB bioreactor could efficiently be used to degrade this type of wastewater. The stabilisation process was, however, lengthy and was probably influenced by nutrient deficient substrate and a too high substrate pH.

The lowest efficient operational substrate pH was found to be 5.73 for a substrate with COD less than 5 000 $mg.L^{-1}$. Higher substrate loads at this pH led to drastic decreases in the effluent pH and alkalinity. At a substrate pH of 6.0, it was possible to successfully treat wastewaters (COD reduction = 84%) at a HRT of 19.7 h and a corresponding OLR of 9.75 kg $COD.m^{-3}d^{-1}$ producing an effluent with COD of 1 200 $mg.L^{-1}$. Although legal limits of 75 $mg.L^{-1}$ and 400 $mg.L^{-1}$ for disposal in a natural resource and irrigation, respectively (Republic of South Africa, 2004), were not met, this might have great implication for the wine producing industry. It is, however, recommended that the use of anaerobic digestion in combination with a pre- and/or post-treatment should be investigated.

CHAPTER 4

EVALUATION AND OPTIMISATION OF AN UASB REACTOR TREATING APPLE JUICE PROCESSING WASTEWATER

4.1 Summary

A mesophylic laboratory-scale upflow anaerobic sludge bed bioreactor seeded with 600 mL of anaerobic sludge obtained at an apple juice wastewater treatment plant was evaluated for the anaerobic digestion of an apple juice processing wastewater. During the experimental study, a start-up period of 50 days was followed by a reactor optimisation period of 256 days, both at a hydraulic retention time of 27.6 h. During the start-up period an average chemical oxygen demand (COD) reduction of 80% was accomplished while the organic loading rate (OLR) was increased to 2.78 kg $COD.m^{-3}.d^{-1}$. Average COD reductions of 87% at an OLR of 4.5 kg $COD.m^{-3}.d^{-1}$ were achieved throughout the reactor optimisation period. COD reduction efficiencies of 92% at an OLR of 14 kg $COD.m^{-3}.d^{-1}$ and HRT of 14.6 h were achieved during this phase of the study. The reactor effluent COD content during the entire study varied between 300 and 1500 $mg.L^{-1}$ and further treatment will thus be required before the legal limits of 75 $mg.L^{-1}$, for discharge into a natural water system, are achieved.

4.2 Introduction

The South African apple industry is growing by 2.1%, in terms of hectares harvested, annually. Even so, a large part of the apple harvest (28.5%) cannot be used for fresh consumption because of the strict quality criteria set by the consumer, and this portion has to be processed (Mostert, Elgin Fruit Juices (Pty) Ltd, Grabouw, South Africa, personal communication, 2003). Large volumes of heavily polluted wastewater (9.5 m^3 per ton of apples processed) are subsequently produced, which has a significant environmental impact when discharged (Mannapperuma, 1995).

The nature and strength of apple juice processing wastewater (AJPWW) provides an ideal substrate for anaerobic digestion (Dold *et al.*, 1987) as 10 to 16% of the total chemical oxygen demand (COD) consists of organic acids that originate from the fruit itself (Austermann-Haun *et al.*, 1997). The successful use of anaerobic digestion in the treatment of food processing wastes has made this option very attractive to food industries since this technology has many advantages over the traditional aerobic treatment process (Anderson & Saw, 1994), including the ability to degrade wastewaters at high organic loading rates (OLR) of more than 10 kg $COD.m^{-3}.d^{-1}$.

Many different anaerobic reactor designs are available today (Bitton, 1999), but the up-flow anaerobic sludge blanket (UASB) system has been the most successful in the treatment of a wide variety of wastewaters from many different sectors in the food industry (Lettinga & Hulshoff Pol, 1991). The main advantage of anaerobic digestion is that a significant COD reduction is achieved without the production of excess biomass. Another advantage is energy recovery in the form of biogas, as up to 95% of the organic matter can be converted into biogas (Weber *et al.*, 1984; Bitton, 1999). The advantage of the UASB system lies in the high biomass retainment in the form of granules, despite relatively high upflow velocities due to short hydraulic retention times (HRT) (Trovnec & Britz, 1998). Anaerobic systems have the advantage that active anaerobic biomass can be preserved unfed for several months where after rapid reactivation is possible (Anderson & Saw, 1994).

Austermann-Haun *et al.* (1997) found that the UASB reactor is well suited for the fruit juice industry where high organic loads have to be treated during two to three months of the year while an average wastewater COD of less than 1 000 mg.L^{-1} is produced during the remaining months. Austermann-Haun *et al.* (1997) also evaluated different anaerobic reactor designs in the treatment of fruit juice wastewater and found that the UASB reactor design could reach a maximum OLR of 17.6 kg COD.m^{-1}.d^{-1} compared to that of a fixed-film reactor that only managed effective digestion at an OLR of up to 9.5 kg COD.m^{-1}.d^{-1}.

During the South African apple juice processing season (February to June) large volumes of wastewater with a high organic content are produced. Daily and seasonal variations in wastewater volume, composition and concentration make treatment extremely difficult. The aim of this study was firstly, to evaluate the use of a mesophylic UASB bioreactor as a treatment option for apple juice processing wastewater, and secondly, to optimise the efficiency of the bioreactor in terms of COD reduction, organic loading rate and hydraulic retention time.

4.3 Materials and methods

Bioreactor

A laboratory-scale UASB bioreactor set at 35°C (Meyer *et al.*, 1985) with an operational volume of 2.3 L and an up-flow velocity of 4 m.h^{-1} was used. Substrate was semi-automatically introduced at the bottom of the bioreactor while the gas exited at the top via an open gas/solids separator. The overflow of the bioreactor drained through a U-shaped tube to prevent any atmospheric oxygen from entering the system. The volume of the biogas was determined using a manometric unit equipped with an electronically controlled counter and gas tight valve.

Wastewater composition

Apple juice processing wastewater was obtained from Elgin Fruit Juices (Pty) Ltd, Elgin, South Africa. Substrate batches were kept at -18°C until required. The wastewater was supplemented with urea and K_2HPO_4 (100 mg.L^{-1}) to prevent N and P deficiencies and the pH adjusted with 1 M sodium hydroxide (NaOH). The substrate was enriched with trace elements (1 mL.L^{-1} substrate) once a week (Nel et al., 1985) and Potassium hydrogen carbonate ($KHCO_3$) was added at times to increase the buffering capacity of the substrate.

Bioreactor start-up

The bioreactor was inoculated with 600 mL of water drained sludge from the industrial scale UASB reactor at Elgin Fruit Juices (Pty) Ltd. (Elgin, South Africa). The HRT was set at 27.6 h and a diluted apple juice processing wastewater (COD = 3 000 mg.L^{-1}) was then fed for 50 days until stable state (Cobb & Hill, 1990) was achieved.

Bioreactor operation

The bioreactor was run for 444 days to determine the overall long term stability of the system. During this period various changes that reflect the seasonal variations that occur in a full-scale apple juice processing plant, occurred in the wastewater used as reactor substrate. The reactor performance was divided into three periods:

1. Start-up (days 1 to 50);
2. Optimisation (days 51 to 305 during the non-processing season); and
3. Increased OLR period (days 306 to 444 during the processing season).

The start-up period occurred during the apple pressing season of 2002 and the wastewater was diluted from a COD of 8 000 mg.L^{-1} to suit reactor start-up conditions. The stabilization period occurred over the winter and spring of 2002 at an OLR of *ca.* 4 kgCOD.m^{-3}.d^{-1}.

Analytical methods
The following parameters were monitored according to APHA (Standard Methods, 1998): pH; alkalinity; total suspended solids (TSS); total volatile solids (TVS); chemical oxygen demand (COD); orthophosphate phosphorus; total Kjeldahl nitrogen (TKN) and sludge settling ability. Mineral analyses were done colometrically using a DR2000 spectrophotometer (Hach Co. Loveland, CO). The total volatile fatty acids (TVFA) and biogas composition were determined according to Sigge (2005). Pectin extraction was done according to the method developed by De Giorgi *et al.* (1985). Colometric determinations and calculations were done according to the carbazole method developed by Dische (1947) and modified by Bitter & Muir (1962).

To test the granular activity, the method developed by O'Kennedy (2000), was used. Three grams of granules and 12 mL basic test medium were used. Incubation was done for 10 h at 35 °C and the volume of biogas and the percentage methane were measured after the 10 hours.

4.4 Results and discussion

Substrate
The average composition of the raw apple juice processing wastewater is given in Table 4.1. It was found that the wastewater had higher COD, TKN, phosphate and TSS contents and a lower pH than the apple juice processing wastewaters described by Dold *et al.* (1987), Mannapperuma (1995) and Austermann-Haun *et al.* (1997).

Reactor granular sludge
The characteristics of the granular sludge as obtained from the full-scale UASB (1 ML) reactor treating apple juice processing wastewater, are summarized in Table 4.2. Settling ability and sludge density are two of the most important factors that influence the success of an UASB system as denser granules settle out quickly and this is directly related to sludge retention times. UASB granules should have a TSS content of at least 40 $g.L^{-1}$. Granules with a TSS of up to 100 $g.L^{-1}$ have been recorded in the past (Lin & Yang, 1991). The low solids content (11.9 $g.L^{-1}$) and long settling time of the apple juice reactor sludge as compared to that of the UASB granules (Table 4.2) from a brewery UASB suggest a serious settling problem with the apple sludge and its general unsuitability for use in an UASB reactor (Table 4.2). This apple juice sludge did, however, have better methane and biogas producing activity compared to the brewery granules (Table 4.2). The pectin content (150 $mg.L^{-1}$) of the apple juice processing wastewater sludge was found to be 12 times higher than that found in the brewery granules. This suggests the possibility of pectin build-up in the full-scale apple juice processing reactor at the Elgin plant.

In Fig. 4.1 the changes that occurred in granular density and particle size before and after lab-scale UASB treatment can be seen. Throughout the entire period of operation of the UASB there appeared to be a gradual change in sludge consistency from a very fine (Fig. 4.1A) to a more grainy flocculated form. During the last treatment period, a more rapid change occurred in sludge morphology and the presence of granules was observed (Fig. 4.1B). It was also found that sludge overflow gradually decreased as the size of the sludge granular particles in the reactor increased leading to washout of some granules.

It was also found that the TSS and VSS contents of the reactor sludge increased from 11.9 to 65.3 $g.L^{-1}$ and 7.3 to 56.2 $g.L^{-1}$, respectively. The large subsequent increase in TSS and VSS content of the reactor sludge was ascribed to successful granulation and filling of the reactor with granular biomass. This is in accordance with the report of Sam-Soon *et al.* (1986) who found that slow but long term granulation occurred while treating an apple processing wastewater with final TSS and VSS of 47 and 36 $g.L^{-1}$, respectively.

Table 4.1. Composition (mg.L^{-1}) of apple juice processing wastewater obtained during the period of March 2002 to June 2003.

Parameters	Concentration (mg.L^{-1})	According to Austermann-Haun *et al.* (1997)
pH	3.6 - 5.4	4.3 - 8.7
COD	1 125 - 9 620	939 - 3 767
BOD_5	n/d	1 000 - 1 661
TSS	1 250 - 2 640	n/d
VSS	770 - 1 550	n/d
Alkalinity	0 - 850	n/d
Kjeldahl Nitrogen	27.3 - 37.5	2.9 - 11.7
Total P	8.5 - 50.8	3.1 - 11.8
Pectin	130 - 450	n/d
Conductivity	1 239 - 850	n/d
Ca	13.1	nd
Na	416.9	n/d
Fe	0.6	n/d
K	84.1	nd
Mg	3.3	n/d
VFA	72 - 1 802	187 - 611

n/d Not determined

Table 4.2. Characteristics of granular sludge from the full-scale UASB reactor treating apple juice processing wastewater compared to UASB granules from a full-scale brewery UASB reactor.

Characteristics	Elgin sludge	Brewery granules
TSS (g.L^{-1})	11.9	60
VSS (g.L^{-1})	7.3	48
Settling ability (mL) *	925	150
Biogas production (mL)	4.37	3.6
Methane (%)	24.9	19.1
Pectin content (mg.L^{-1})	150	12.5

* Level of 150 mL of sludge after 45 min in a 1 000 mL Imhoff cone.

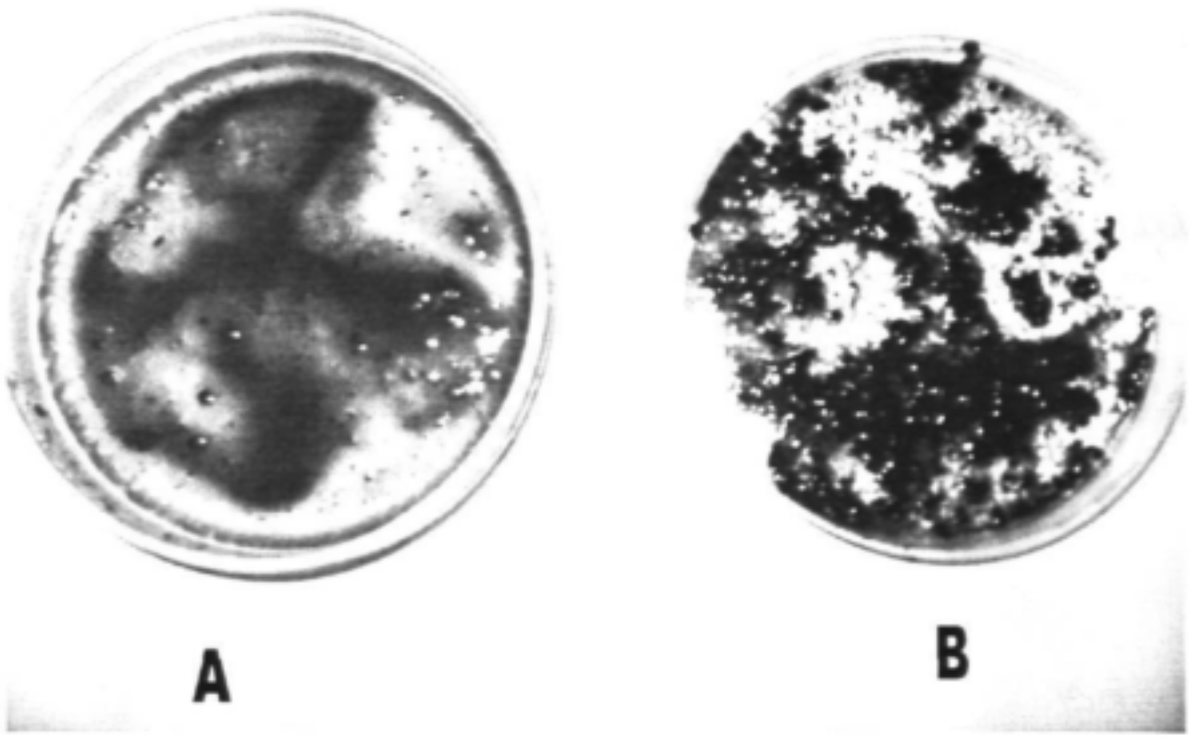

Figure 4.1. Lab-scale reactor sludge from day 1 (A) and from day 444 (B).

Overall reactor performance
The reactor performance in terms of OLR, COD reduction and HRT for the entire 444 d period is shown in Fig. 4.2. The COD reduction remained relatively constant at between 85 and 90% for most of the study. The HRT of 27.6 h was maintained during the first 2 phases of the study whereafter a stepwise HRT decrease to 14.6 h, which subsequently led to an increased OLR to over 14 kg COD.m^{-3}.d^{-1} (Fig. 4.2)

Optimisation period
The influent COD concentration during the first 92 days (day 50 to 142) of this period varied between 3 200 and 8 800 mg.L^{-1}. The COD reduction during this period averaged 90%, except for a short period when organic overloading occurred.

After day 142, a new batch apple juice processing wastewater was used as substrate. Due to the variability (off season) in the COD of this batch, supplementation with an apple juice concentrate had to be made to stabilise the influent COD concentration so as to not have a too wide variation in COD concentration. Even so, large variations in influent COD, and thus OLR (3.7 - 7.8 kg COD.m^{-3}.d^{-1}), occurred during this period. Higher COD reduction rates were experienced during this time and increases in OLR did not appear to negatively influence the reactor performance efficiency. COD reductions of between 83 and 95% were maintained in spite of the variations in influent COD and OLR.

In this study the reactor effluent pH remained stable at around 7.4 for the entire treatment phase with the exception of day 91 when the pH decreased to 4.6 due to a reactor overload. However, the pH stabilised and increased within a few days to 7.5. Constant COD reductions of around 90% were experienced after this incident despite

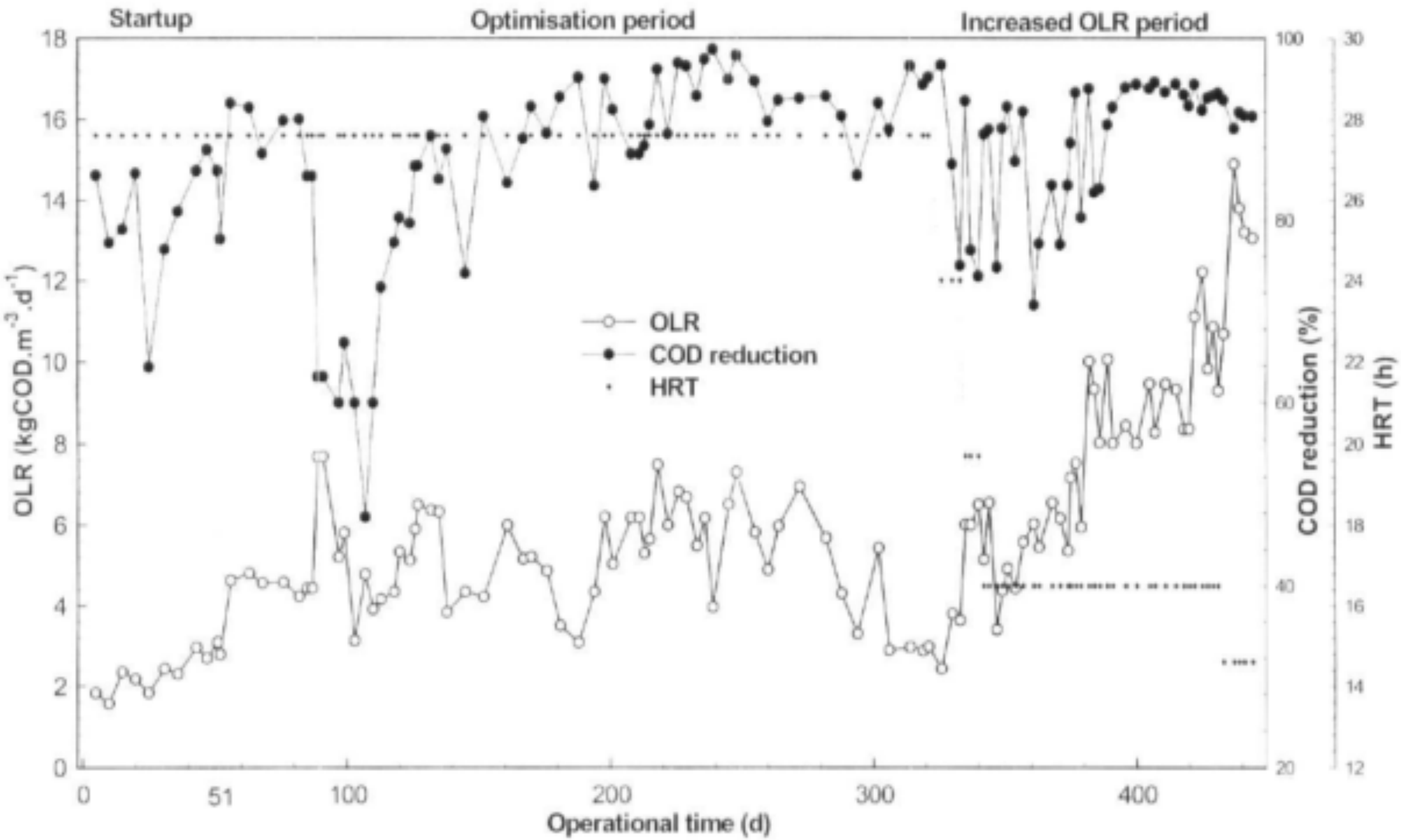

Figure 4.2. Reactor efficiency parameters for the 444 d treatment period in terms of OLR and COD reduction efficiencies and HRT changes.

higher OLR of over 7 kg.COD.$m^{-3}.d^{-1}$ that occurred at times. System stabilisation had thus occurred, but some sludge overflow was still experienced at times, causing occasional high effluent COD's.

OLR Increases

A summary of the reactor parameters during seven different stages of the "increased OLR period" are given in Table 4.3. A continuous shortening of the HRT from 27.6 to 14.6 was applied throughout this treatment phase. During the first four stages, the substrate COD was kept relatively constant between 2 958 and 4 777 mg.L^{-1} (Table 4.3). The increase in OLR during the first 3 stages, from 2.93 to 5.64 kg COD.$m^{-3}.d^{-1}$, is ascribed to the HRT decrease from 27.6 to 16.5 h (Table 4.3). During the last three stages, a combination of higher substrate CODs (3 878 mg.L^{-1} during stage 4 compared to 8 728 mg.L^{-1} at stage 7) and a shorter HRT (16.5 vs 14.6 h) resulted in an even sharper OLR increase from 5.64 at the end of stage 4 to 13.76 kg COD.$m^{-3}.d^{-1}$ at stage 7 (Table 4.3). The pH and alkalinity profiles during this stage are shown in Fig 4.3

The lower reactor stability during the first part of the OLR increase stages is similar to the results reported by Austermann-Haun *et al.* (1997). They also observed lower COD reductions of 70 to 85% during the first 25 days of reactor treatment whereafter constant reductions of over 90% were experienced during an OLR increase from 3 to 17 kg COD.$m^{-3}.d^{-1}$ in a commercial UASB reactor treating a fruit juice wastewater. These authors postulated that the stable reactor performance, experienced during later stages of this large OLR increase, was due to the time taken for the microbial community to adapt to the higher substrate concentrations in the reactor. Other authors have reported similar results while treating fruit juice processing, or other related wastewaters. Trnovec & Britz (1998) achieved a 93% COD reduction at an OLR of 10.95 kg COD.$m^{-3}.d^{-1}$ and HRT of 12 h in a lab-scale UASB reactor treating a fruit canning wastewater, while Ronquest & Britz (1999) achieved 93% COD reductions at an OLR of 11.05 COD.$m^{-3}.d^{-1}$ and a HRT of 14 h in the UASB treatment of a winery wastewater. Sam-Soon *et al.* (1986) found COD reductions of between 89 and 95% at OLR's between 5 and 14 kg COD.$m^{-3}.d^{-1}$ in the treatment of an apple juice processing wastewater but found that COD reduction started to decrease at an OLR of more than 14 kg COD.$m^{-3}.d^{-1}$ and only 49% reduction occurred at an OLR of 16 kg COD.$m^{-3}.d^{-1}$. From the literature it appears that the maximum OLR of apple juice processing wastewater is only about 14 kg COD.$m^{-3}.d^{-1}$ (Sam-Soon *et al.*, 1986), compared to 17 kg COD.$m^{-3}.d^{-1}$ for fruit juice wastewater (Austermann-Haun *et al.*, 1997). The reason why apple processing wastewater has a lower maximum OLR (14 kg COD.$m^{-3}.d^{-1}$) compared to a fruit juice processing wastewater (17 kg COD.$m^{-3}.d^{-1}$) might be due to the presence of more complex compounds, like pectin in the wastewater. Apples have a high pectin content of between 5 000 and 16 000 mg.L^{-1} compared to other fruits that contain less than 3 000 mg.L^{-1} pectin on average (Taylor, 1996). Based on this information no further OLR increases were made after a HRT of 14.6 h was achieved, as it was noticed earlier that drastic changes in influent COD and OLR caused reactor instability.

An increase in biogas was observed as the ORR increased, which is expected in anaerobic systems since most of the organic matter is converted to biogas and less biomass, as compared to aerobic systems (Weber *et al.*, 1984). The percentage methane in the biogas varied between 22 and 43% and slight decreases occurred after each OLR increase probably because of the higher growth rate of carbon dioxide producing bacteria compared to methane producing bacteria (Bitton, 1999). $CH_4\gamma$ was found to vary between 1.36 and 1.63 $m^3.kg^{-1}.COD_{removed}$ during this phase of the study. The maximum possible $CH_4\gamma$ in anaerobic systems is 0.355 $m^3.kg^{-1}.COD_{removed}$ (Lin & Yang, 1991). A relatively small portion (*ca.* 1.5 $m^3.kg^{-1}.COD_{removed}$ or 42%) of the potential methane (0.355 $m^3.kg^{-1}.COD_{removed}$) was thus utilised, possibly due to a lack of methanogenic activity.

Table 4.3: UASB bioreactor operating conditions and efficiency during the period where the OLR was increased.

	Treatment Stage						
Parameters	**1**	**2**	**3**	**4**	**5**	**6**	**7**
Operational time (d)	306 - 321	322 - 333	334 – 340	341 - 379	380 - 420	421 - 431	432 - 444
HRT (h)	27.6	24	19.7	16.5	16.5	16.5	14.6
OLR (kgCOD.m^{3}.d^{-1})	2.93	3.28	6.17	5.64	8.85	10.65	13.76
Substrate COD (mg.L^{-1})	3 369	2 958	4 777	3 878	6 078	7 328	8 728
Effluent COD (mg.L^{-1})	506	437	886	580	483	571	715
COD reduction (%)	84.9	86	81	85	92	92	92
Substrate pH	6.71	6.9	7.81	7.23	6.66	6.52	6.64
Effluent pH	7.37	7.39	7.21	7.26	7.35	7.25	7.38
Substrate alkalinity *	850	733	1 200	2 040	2 219	1 720	2 120
Effluent alkalinity *	2 037	1 866	2 116	2 680	2 889	2 240	2 340
Biogas (L.d^{-1})	2.76	3.14	4.08	5.10	9.19	10.36	13.36
ORR (kgCOD.m^{3}.d^{-1})	2.48	2.78	5.00	4.79	8.28	9.82	12.53
% methane in biogas	33.8	31.3	40.3	33.9	28.2	34.0	33.4
CH_4 γ (m^{3}.kg^{-1}.COD$_{removed}$)	0.163	0.153	0.142	0.156	0.136	0.155	0.154

* (as mg.L^{-1} $CaCO_3$)

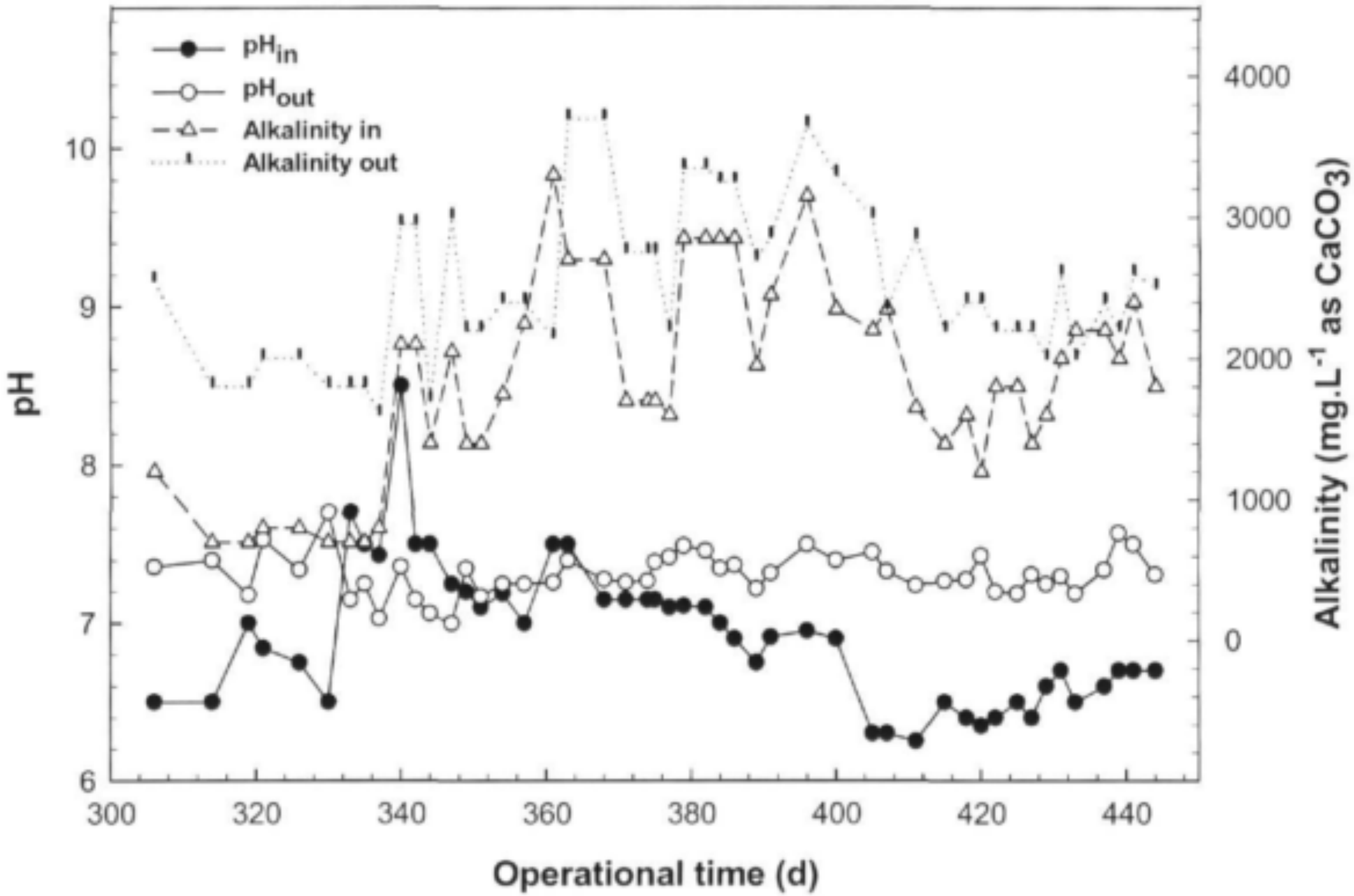

Figure 4.3. Reactor efficiency in terms of pH and alkalinity as obtained during the increased OLR period (days 306 to 444).

A relatively high substrate alkalinity (> 2 000 $mg.L^{-1}$) probably helped prevent drastic decreases in reactor pH during the OLR increases (Fig. 4.3). It has been observed that VFA content serves as an indicator of instability or stress for anaerobic systems (Ditchfield, 1986). The effluent VFA content during the period from day 306 to 44 remained between 68 and 149 $mg.L^{-1}$. The fact that the effluent pH remained in the region of 7.4, combined with the low effluent VFA content indicates that sufficient methanogenesis occurred throughout this period despite the large increases in OLR (Bitton, 1999). Lower granular sludge overflow also occurred during this period compared to the start-up and optimisation periods and the particle size of the sludge that washed out, increased. Biomass retention problems were thus reduced due to more effective granulation. This is in accordance with numerous UASB studies where it was found that biomass retention problems seldom occurred after granulation has taken place (Lettinga & Hulshoff Pol, 1991).

4.5 Conclusions

From the results obtained during this study it is clear that the UASB design is feasible for the effective treatment of an apple juice processing wastewater. COD reductions were in the region of 85 to 90% throughout the 444 day study period. The high organic loads fed during the increased OLR stage had no drastic effect on the system's efficiency. The study period reflected a typical processing season of an apple juice processing plant where large volumes of wastewater containing a high organic content are produced over a short period of the year. Treatment plants are thus forced to reduce HRTs, which combined with the higher wastewater COD values, puts considerable stress on the treatment system. This study indicated that UASB systems can cope with the large increase in OLR produced during an apple processing season. Excessive sludge overflow did, however, occur at times, especially during the start of the study, due to the low sludge density and settling ability of the seed sludge. Less sludge overflow, was however, experienced at the end of the study due to granulation having taken place. The effluent COD varied between 300 and 1 500 $mg.L^{-1}$ and further treatment will be required before the legal discharge limits of 75 $mg.L^{-1}$ are met (Water Research Commission, 1987).

CHAPTER 5

INFLUENCE OF PRE- AND POST-OZONATION ON THE EFFICIENCY OF AN UASB REACTOR TREATING WINERY WASTEWATER

5.1 Summary

The efficiency of ozonation as a pre-, post- and combined pre- and post-treatment to upflow anaerobic sludge blanket (UASB) treatment was investigated. A 5 min ozonation treatment process at a concentration of 73 $mg.L^{-1}$ was found to be optimal for both a pre- and post-treatment. Ozonation of cellar wastewater led to a 20% reduction in chemical oxygen demand (COD). The total suspended solids (TSS) and the volatile suspended solids (VSS) were both reduced by 73%. Polyphenol concentration was reduced by more than 73%. The UASB treatment alone led to a COD reduction of 67 to 85%, depending on the specific cellar wastewater. The TSS and VSS concentrations were reduced by 80 and 81%, respectively. The COD, TSS and VSS reduction could be increased to 88, 97 and 98%, respectively, when UASB treatment was followed by a post-ozonation treatment. Ozonation also led to an 80% reduction in colour of the UASB reactor effluent. Pre-ozonation of the cellar wastewater led to a substantial increase in COD reduction to 86% for an UASB reactor with a previous maximum COD reduction efficiency of 67%. Biogas production also increased from 1.4 $L.d^{-1}$ to 3.8 $L.d^{-1}$. Both the TSS and VSS reduction for a pre-ozonation UASB combined process, were 95%. Further post-ozonation led to the COD reduction efficiency being increased to 89% and a total reduction of 99% for both TSS and VSS.

5.2 Introduction

The wine industry contributes greatly to pollution of a limited natural resource, water. The wastewaters, which originate during cellar cooling operations and the washing of floors, vessels and equipment (Water Research Commission, 1993; Bezuidenhout *et al.*, 2002), are nutrient deficient and have a tendency of becoming acidic and odorous when left standing. Cellar wastewater has a chemical oxygen demand (COD) of 800 to 12 800 $mg.L^{-1}$ (Petruccioli *et al.*, 2002) depending on the season and precise cellar activities.

As wine production has increased during the last decade, the pressure on natural resources, specifically water, has also increased. Public concern for the environment, high levies charged for municipal treatment of wastewater and the aspiration to stay competitive in an increasingly globalised market place, have compelled cellars to consider on-site wastewater treatment options.

Anaerobic digestion (AD), specifically the upflow anaerobic sludge blanket (UASB) technology, has been shown to be feasible for the treatment of various food and beverage processing wastewaters, including wastewaters from wine cellars (Ross, 1989; Strydom *et al.*, 1997; Puñal & Lema, 1999; Ronquest & Britz, 1999; Sigge *et al.*, 2002). Müller (1998) found reduction efficiencies for COD and BOD of over 90% when treating a cellar wastewater in a 50 m^3 UASB reactor at influent COD levels of 941 to 13 600 $mg.L^{-1}$. In another study a COD reduction of more than 93% at an organic loading rate (OLR) of 10.1 kg $COD.m^{-3}d^{-1}$, a hydraulic retention time (HRT) of 14 h and an influent pH of 5.1, was achieved with a laboratory UASB system (Ronquest & Britz, 1999). Under these conditions the final reactor effluent COD was 182 $mg.L^{-1}$. The effluent COD was still above the legal limit of 75 $mg.L^{-1}$ for discharge in a natural water system (Republic of South Africa, 2004). To reduce the effluent COD to below legal limits, a further polishing step would thus be necessary.

Post-ozonation has been shown to be efficient as a polishing step. Athanasopoulos & Athanasopoulos (1998) used an UASB reactor to reduce the COD of "currant" wastewater by 95.5%, yielding an effluent with a COD of only 185 $mg.L^{-1}$. Ozonation of the effluent for three hours at a concentration of 300 $mg.h^{-1}$ led to the COD being further reduced to below 50 $mg.L^{-1}$. Similarly, Sigge *et al.* (2002) found UASB treatment to lower the COD of cannery and cellar wastewaters by 93 and 96%, respectively. In this case, post-ozonation for 30 min using a granular activated carbon column led to further COD reductions of the effluents. The lowest COD achieved was 247 $mg.L^{-1}$ for the cannery wastewater and 67 $mg.L^{-1}$ for the cellar wastewater, representing total COD reductions of more than 98% for both wastewaters.

The AD process is often limited by compounds in the wastewater not being biodegradable (Gottschalk *et al.*, 2000). It is known that chemical oxidation methods, such as ozonation as a pre-treatment may convert refractory and toxic compounds into simpler molecules with lower molecular weights that could then be used as substrate by the anaerobic populations. Andreozzi *et al.* (1998) showed that total phenols and unsaturated lipids in an olive mill wastewater could be reduced by 50% after a 3 h ozonation process. Martin *et al.* (2002) reported that the COD of vinasse could be decreased from 109 200 $mg.L^{-1}$ to 82 100 $mg.L^{-1}$ (25% decrease) using a two hour ozonation process. Benitez *et al.* (1999) also found that the COD of a wine distillery wastewater could be lowered by 20% by ozonation alone.

The aim of this study was firstly to investigate the feasibility of the following ozone combined UASB treatments for cellar wastewater degradation: ozone pre-treatment; ozone post-treatment; and an ozone pre- and post-treatment. As part of the study, the performance of an UASB reactor treating pre-ozonated cellar wastewater will be monitored.

5.3 Materials and methods

Wastewater

Cellar wastewaters were obtained from the Rupert and Rothschild Fredericksburg (R-RF) (Simondium, South Africa) (March 2003) and the Bergkelder, Distell (BK) (Stellenbosch, South Africa) (August 2003) cellars. The substrate batches were kept at -18°C in 25 L containers.

Anaerobic treatment set-up

A laboratory-scale UASB bioreactor with an operational volume of 2.3 L (Trnovec & Britz, 1998) was used and operated at 35°C (Meyer *et al.*, 1985). The upflow recirculation velocity was set at 2.8 $m.h^{-1}$. The volume of biogas, which exited at the top via an open gas/solid separator, was determined using a manometric unit fitted with a gas tight valve and an electronic counter.

Ozonation set-up

Ozonation proceeded in a batch glass bubbling column connected to an ozone generator (Oz Purification, Ifafi). The bubbling column (l = 90 cm; ϕ = 6 cm) had a sintered glass disc at one end for bubble generation. This column contained 1.70 L of wastewater for both the pre- and post-ozonation studies and the treatments were done at room temperature. The flow rate was kept at 4 $L.min^{-1}$.

Analytical methods

The ozone concentrations were determined using an iodiometric titration (Standard Methods, 1998) and the polyphenol concentration in the untreated wastewater was determined using the Folin-Ciocalteau method (Singleton & Rossi, 1965). The COD, orthophosphate phosphorous (PO_4); and total Kjeldahl nitrogen (TKN) were determined colorimetrically using a DR 2000 spectrophotometer (Hach Co. Loveland, CO) and standardised procedures (Standard Methods, 1998). Total suspended solids (TSS), volatile suspended solids (VSS) and pH were measured according to standardised procedures (Standard Methods, 1998). Colour reduction in the UASB effluent was determined by monitoring the absorbance of the effluent at 288 nm using a spectrophotometer (Spectronic Instruments, USA).

The volatile fatty acid (VFA) concentration of the UASB effluent was determined using a Varian (Model 3700) gas chromatograph, equipped with a flame ionisation detector and a 30 m fused silica capillary column with FFAP bonded stationary phase (Quadrex Co. New Haven).

A Varian 3300 gas chromatograph equipped with a thermal conductivity detector and 2.0 m x 3.0 mm i.d. column packed with Hayesep Q (Supelco, Bellefonte, PA), 80/100 mesh, was used to determine biogas composition.

Experimental studies

Various combinations of pre- and post-ozonation and UASB treatment were investigated Table 5.1). The reduction of COD, TSS, VSS, colour and polyphenols at a range (1 to 10 min) of ozonation times and ozone concentrations, were determined.

Table 5.1. Pre- and post-treatment combinations of cellar wastewaters.

Treatment	Description	Source	[Ozone] $mg.L^{-1}$	Ozonation (min)
A	Ozonation of cellar wastewater	BK, R-RF	47 & 73	1,2,5 & 10
B	UASB treatment of cellar wastewater	R-RF	-	-
C	UASB treatment + post-ozonation	R-RF	73	1,2,5 & 10
D	Pre-ozonation + UASB treatment	BK	73	1,2,5 & 10
E	Pre-ozonation + UASB treatment + post-ozonation	BK	73	1,2,5 & 10

Treatment A involved an investigation into the effect of different ozone concentrations and ozonation times on cellar wastewater in an attempt to reach the best possible COD reduction. The effect of ozonation on the polyphenol content of cellar wastewater was also determined in triplicate. Polyphenol degradation was monitored in both the R-RF and BK wastewater batches.

Treatment B, which only focused on the biological treatment step, namely the UASB activity, and Treatment C (UASB + O_3) were performed on the R-RF wastewater. During these treatment studies the HRT and OLR of the UASB reactor was set at 24 h and 5.4 kg $COD.m^{-3}d^{-1}$, respectively. Substrate pH was adjusted to 6.0 using 1 M KOH and additions of sucrose (500 $mg.L^{-1}$), urea (500 $mg.L^{-1}$) and K_2HPO_4 (200 $mg.L^{-1}$) were made to prevent nutrient limitations. $KHCO_3$ (500 $mg.L^{-1}$) was added to sustain alkalinity.

The treatments involving ozonated wastewaters for use as UASB substrates (treatments D and E) were performed on the BK wastewater. During these treatment studies, the HRT and OLR of the UASB reactor were set at 24 h and 4 kg $COD.m^{-3}d^{-1}$, respectively. In a previous study, when the UASB reactor was treating cellar wastewater at a HRT of 17.4 h, OLR of 10.95 kg $COD.m^{-3}d^{-1}$ and substrate pH of 6.0, severe granule wash-out and reactor acidification were experienced. Accordingly the HRT was re-adjusted to 24 h and the substrate pH was adjusted to 7.0 at the start of this part of the study and kept constant for the duration of the study. The reactor was acclimatised to a "raw diluted cellar wastewater substrate" with a COD of 4 000 $mg.L^{-1}$ and supplemented with nutrients as in Treatment B. Once the reactor had stabilised, "ozonated substrate" replaced the "raw diluted cellar wastewater substrate".

The ozone pre-treated cellar wastewater substrate was prepared using the bubble column system. An ozonation time of 5 min was used to treat the undiluted cellar wastewater at an ozone concentration of 73 $mg.L^{-1}$. The pre-ozonated wastewater was also diluted to a COD of 4 000 $mg.L^{-1}$. Treatment E involved a post-ozonation treatment process of the reactor effluent from Treatment D at a concentration of 73 $mg.L^{-1}$ (4 $L.min^{-1}$) for various times (1, 2, 5, 10 min).

5.4 Results and discussion

Wastewater

The composition of the wastewater used in the studies are given in Table 5.2. Both batches were high in organic content with COD's above 8 000 $mg.L^{-1}$ and had a low nitrogen and phosphorous contents necessitating N and P supplementation before use as reactor substrate.

Table 5.2. Composition of the wastewater batches obtained from the Rupert and Rothschild Fredericksburg (R-RF) and Bergkelder (BK) cellars.

Parameter	Batch	
	R-RF	BK
COD ($mg.L^{-1}$)	10 206	8 000
pH	3.6	4.5
Phosphorous (mg $PO_4.L^{-1}$)	39	39
TKN ($mg.L^{-1}$)	6	35
Polyphenols as gallic acid equivalents ($mg.L^{-1}$)	50	74
TSS ($mg.L^{-1}$)	572	1 180
VSS ($mg.L^{-1}$)	507	1 123
C:N:P ratio	1701:1:6.5	228.6:1:1.1

Treatment A: Ozonation of cellar wastewater

Initial pre-ozonation trials on the BK cellar wastewater (COD = 8 000 $mg.L^{-1}$, pH = 4.5) resulted in COD reductions of up to 20% after a 5 min ozonation at O_3 concentrations of 47 and 73 $mg.L^{-1}$. No further COD reductions were observed upon extending the ozone treatment time to 10 min. The 5 min ozone treatment time was found to be optimal for maximum COD degradation. The COD reductions at the ozone concentrations of 47 and 73 $mg.L^{-1}$ were similar. These results for the COD reduction were contradictory to those reported by Marais (2001) who did not find any reduction after ozonation in the COD of a cellar wastewater when the cellar wastewater had a pH lower than 7.5. However, the results from this study correlated well with those obtained by Benitez *et al.* (1999) who also achieved a COD reduction of 20% for a distillery wastewater (initial COD = 18 400 $mg.L^{-1}$) at a pH of *ca.* 4.0. Similarly, Sigge *et al.* (2002) found the COD of cellar wastewater (pH = 4.8; COD = 3 700 $mg.L^{-1}$) could be reduced by 30% after a 5 min ozone treatment.

The data also showed that ozonation led to a reduction in the polyphenol concentration of both the R-RF and BK wastewaters. For the R-RF wastewater the polyphenol concentration was reduced by 80% from 49.8 to 10.2 mg gallic acid equivalents ($mg.L^{-1}$) during the first 2.5 min of the ozonation treatment. For the same treatment time the polyphenol concentration in the BK wastewater was reduced by 73% from 74.3 to 19.8 mg gallic acid equivalents ($mg.L^{-1}$). A further 2.5 min ozonation period resulted in only a slight improvement in polyphenol reduction from 10.2 to 9.8 and 19.8 to 19.3 gallic acid equivalents ($mg.L^{-1}$) for the R-RF and BK wastewaters, respectively. The polyphenol reduction was deemed necessary, as phenolic compounds are known to lead to inhibitory and antibacterial activity in wastewaters during biological treatment. Polyphenols are specifically toxic to methanogenic bacteria and inhibit the production of methane and consequently, the efficiency of the anaerobic digestion process is decreased (Hamdi, 1993).

Treatments B and C: UASB treatment of cellar wastewater and post-ozonation of the UASB effluent

Treatment B involved the treatment of a diluted R-RF wastewater (COD = 5 400 $mg.L^{-1}$, TSS = 303 $mg.L^{-1}$, VSS = 268 $mg.L^{-1}$) using the UASB reactor. During the study the HRT and OLR were kept constant at 24 h and 5.4 kg $COD.m^{-3}.d^{-1}$, respectively. The UASB reactor effluent had a pH > 6.9 and the average reactor COD reduction efficiency was 85%. The TSS and VSS were reduced by 80 and 81%, respectively.

Post-ozonation (5 min) of the R-RF wastewater from the UASB reactor led to a 22.7% COD reduction (Fig. 5.1). An increase in the ozonation time to 10 min only resulted in a slight increase in COD reduction to 23.3%. The COD reduction after 5 min ozonation was lower than the 30% reduction reported by Sigge *et al.* (2002) while ozonating the effluent from an UASB treating a similar cellar wastewater. This difference in COD reduction, reported by Sigge *et al.*, (2002), may be explained by their use of a granular activated carbon contacting column in combination with the ozonation process by these authors.

Post-ozonation of the UASB reactor effluent also led to a reduction in both the TSS and VSS (Fig. 5.1). As was found with the COD reduction, the best degradation was achieved within the first five minutes of ozonation. After the 5 min treatment, the TSS was reduced from an average of 60.5 to 9.0 $mg.L^{-1}$ (85.1%). In the same period the VSS was reduced from an average of 50.5 to 5.6 $mg.L^{-1}$ (88.9%). With the 10 min ozonation treatment, the TSS and VSS were reduced only by 86.6 and 89.5%, respectively. For economical reasons, a 5 min post-ozonation treatment thus appears to be the most feasible option.

Ozonation of the UASB reactor effluent led to an increase in the effluent pH with the highest increase after only a 1 min treatment. The pH increase was expected as ozone decomposes in water to produce oxygen and free hydroxyl radicals (Hammer & Hammer, 1996). Increased ozonation was also found to give a decrease in colour. After 5 and 10 min ozone treatments the colour (absorption) of the effluent was reduced by 71 and 74%, respectively. In comparison, Athanasopoulos & Athanasopoulos (1998) only achieved a colour reduction of 74% after two hours ozonation in the treatment of an UASB treated "currant" effluent. The large difference in treatment time could be explained by the ozone production of only 300 $mg.h^{-1}$, compared to 17 500 $mg.h^{-1}$ as used in this study. The results obtained are, however, in accordance with the colour reductions of 68% and 80% for a 5 and 10 min ozonation treatment, respectively, reported by Sigge *et al.* (2002) while treating a similar cellar wastewater.

Treatment D: Pre-ozonation follwed by UASB treatment

The pre-treatment of cellar wastewater followed by an UASB treatment over a period of ± 80 days (Treatment D: O_3 + UASB) led to a total COD reduction of 84 – 89%. The UASB reactor with the BK wastewater at a substrate COD of 4 000 $mg.L^{-1}$ (minimum of 3 461 and maximum of 4 331 $mg.L^{-1}$), HRT of 24 h and pH poised at 7.00 (Fig. 5.2). After an acclimitisation period of 24 days the UASB reactor stabilised at COD reductions between 61 and 67%, average VFA-concentration of 760 $mg.L^{-1}$ and biogas production of 1.4 $L.d^{-1}$ (methane percentage = 26 – 30%).

On day 24, pre-ozonated cellar wastewater was introduced to the reactor. Pre-ozonation led to a 20% reduction in the COD of the cellar wastewater, which had an initial

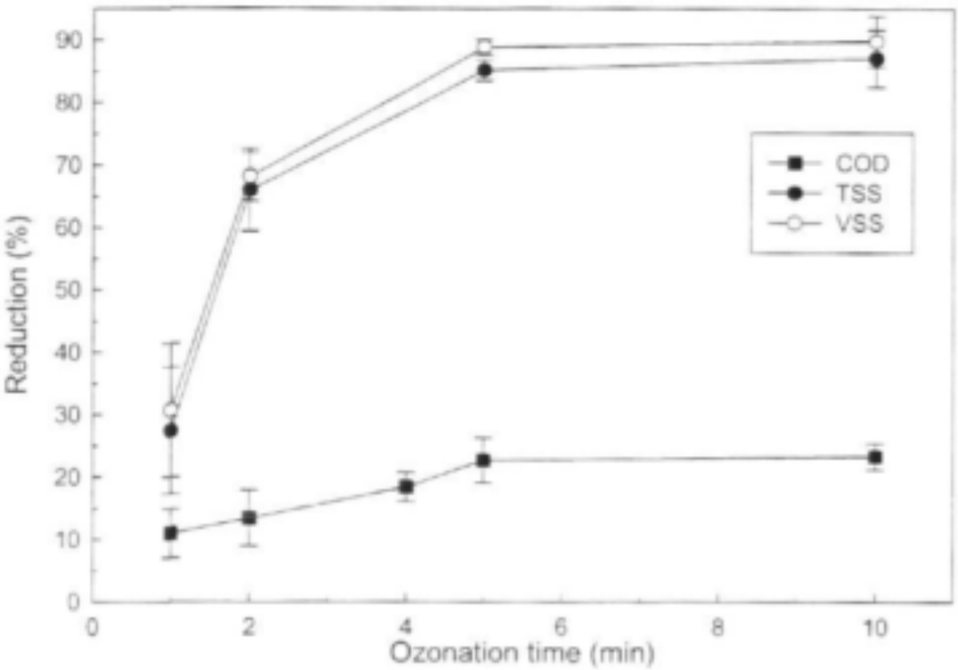

Figure 5.1. The influence of ozone treatments on the COD, TSS and VSS of UASB treated R-RF cellar effluent (COD = 810 $mg.L^{-1}$; TSS = 61 $mg.L^{-1}$; VSS = 51 $mg.L^{-1}$) (COD n = 6; TSS n = 4; VSS n = 4) (the standard deviation was used as the error-bar length).

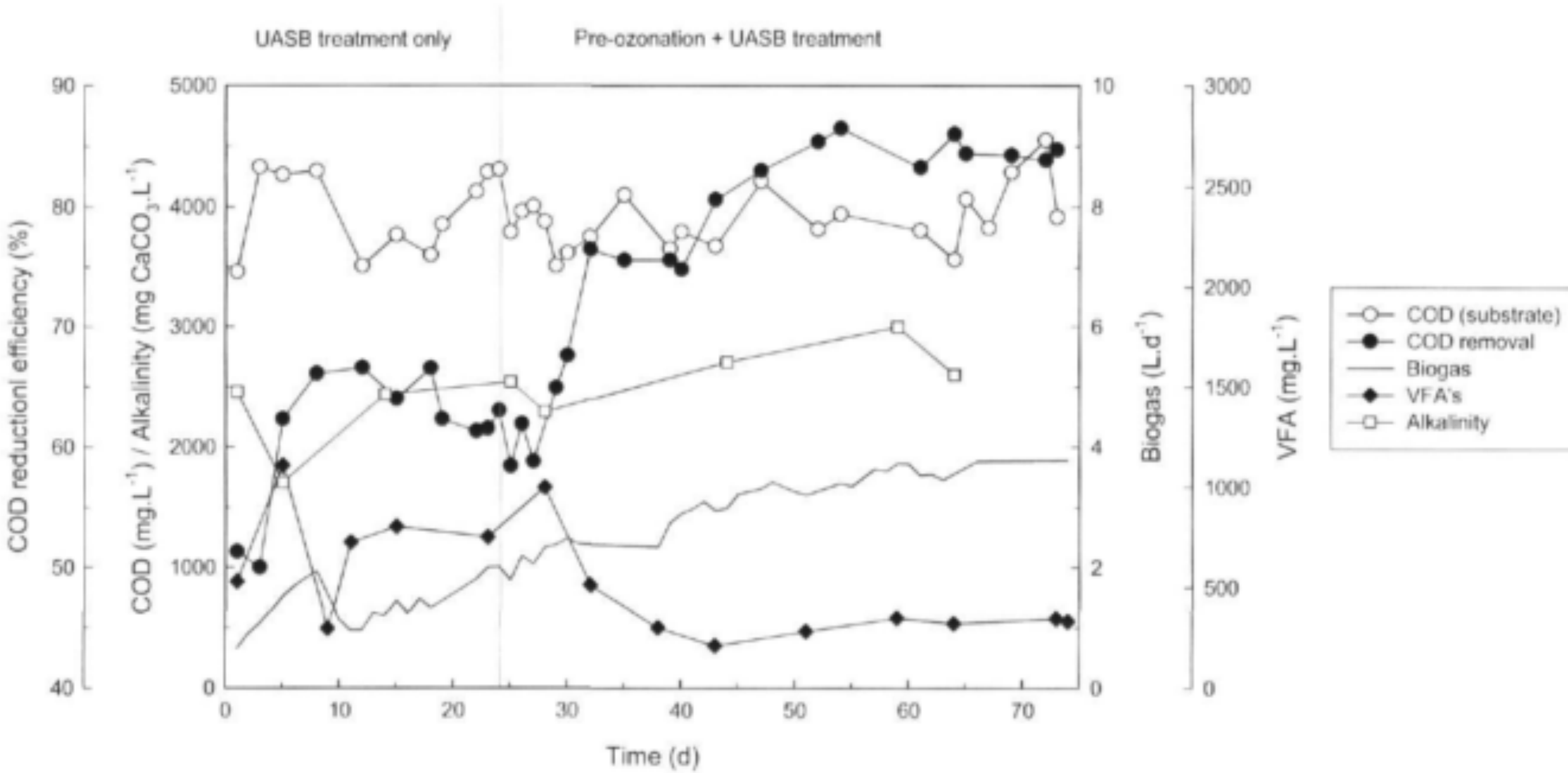

Figure 5.2. COD reduction efficiency parameters of the UASB bioreactor treating a raw diluted BK cellar wastewater and a pre-ozonated diluted BK cellar wastewater.

COD of *ca.* 8 000 $mg.L^{-1}$. The ozonated wastewater was subsequently diluted to the substrate COD of *ca.* 4 000 $mg.L^{-1}$ to which the reactor was acclimatised.

Initially the change in substrate led to the COD reduction efficiency being lowered to 58% (days 25 – 27) (Fig. 5.2). The decrease was coupled to an increase in the VFA-concentration to 998 $mg.L^{-1}$. By day 29 the reactor recovered to its best performance in terms of COD reduction efficiency (65%) prior to the substrate change. The biogas production by this stage had increased to 2.3 $L.d^{-1}$. By day 47 the COD reduction efficiency had improved to 83%. The reactor was now considered stabilised in terms of COD reduction efficiency, which varied between 83 and 86% for the remainder of the study.

The VFA concentration varied between 221 and 348 $mg.L^{-1}$ and alkalinity remained above 1 375 mg $CaCO_3.L^{-1}$ for the remainder of the study, highlighting the increased performance of the UASB reactor. By day 74 the biogas production had also increased to 3.8 $L.d^{-1}$ (Fig. 5.2) and the methane content of the biogas was 36%. The average methane production yield coefficient was now calculated as 402 mL $CH_4.g^{-1}$ COD. Other authors also found the yield coefficient for methane to improve when using ozonation prior to AD (Benitez *et al.*, 1999; Weemaes *et al.*, 2000; Martin *et al.*, 2002).

Treatment E

Ozonation of the effluent from the UASB reactor while treating pre-ozonated BK wastewater (Treatment E: O_3 + UASB + O_3) led to reduction in COD, TSS and VSS being reduced. These reductions for the UASB effluent (COD = 634 $mg.L^{-1}$; TSS = 40.3 $mg.L^{-1}$; VSS = 35.0 $mg.L^{-1}$) after a 5 min ozonation period were 16, 75 and 78%, respectively. The 5 min post-ozonated effluent gave final COD, TSS and VSS concentrations of 531, 10.1 and 7.6 $mg.L^{-1}$, respectively. Extending the post-ozonation treatment to 10 min, only led to slight improvements in reduction of COD, TSS and VSS.

As was found the case in Treatment C, the pH of the post-ozonated UASB bioreactor effluent rose after extending the ozonation time. The colour value (absorbance at 288 nm) was also lowered with a lengthening in ozonation time, from 1.10 to a final absorbance of 0.30 after 10 min ozonation. This was lower than the absorption of 0.40 achieved in treatment C. The colour reduction of 73% for the UASB treatment and post-ozonation step of Treatment E, did however, compare well to the results found in Treatment C (UASB + O_3) of 74%.

5.5 Conclusions

From the data obtained in this study it was concluded that 5 min is the optimal time in terms of efficiency for the pre- and post-ozonation treatments combined with UASB treatment. Ozonation of untreated wastewater (COD = 8 000 $mg.L^{-1}$; TSS = 1 180 $mg.L^{-1}$; VSS = 1 123 $mg.L^{-1}$) alone for 5 min (Treatment A: 5 min O_3) led to reductions in COD, TSS and VSS (Fig. 5.3).

The UASB treatment alone (Treatment B) was more effective in reducing COD, TSS and VSS. The reduction was, however, improved by a 5 min. post-ozonation treatment, resulting in a complete COD reduction for Treatment C (UASB + 5 min O_3) of 88%, compared to 85% for UASB treatment alone and 20% for a 5 min ozone treatment (Fig. 5.3). The total reduction of TSS for Treatment C (UASB + 5 min O_3) was 97% compared to 80% for UASB alone and 73% for a 5 min ozone treatment alone. The reduction for VSS was 98% (Fig. 5.3) compared to 81% for UASB alone and 73% for ozone treatment alone.

The total reduction when using the pre-ozonation UASB combination treatment (Treatment D: 5 min O_3 + UASB) was slightly less effective than Treatment C (UASB + 5 min O_3). The COD was reduced by an average 86% and TSS and VSS were both reduced by 95%, compared to the 88, 97 and 98% for COD, TSS and VSS reduction, respectively, for treatment C. It was however, still more effective than using UASB treatment alone.

The best reduction was obtained when using Treatment E (5 min O_3 + UASB + 5 min O_3). The total TSS and VSS reduction was 99% for both and the COD reduction for this treatment process was 89% (Fig. 5.3). Although legal limits for discarding into a natural resource were not met, significant progress was made in reducing COD levels. A summary of COD concentrations at various stages of treatment is given in Table 5.3.

Table 5.3. The COD concentrations at the different stages of the treatment.

	Treatment stage	**COD ($mg.L^{-1}$) before**	**COD ($mg.L^{-1}$) after**	**COD reduction (%)**
A	Pre-ozonation of raw winery wastewater	8 000 (5 000)	6 400 (4 000)	20
B	UASB treatment	4 000	1 400	65
B	Post-ozonation of UASB effluent	1 400	1 080	23
C	UASB + post-ozonation	4 000	1 080	73
D	UASB treatment of pre-ozonated winery wastewater	4 000	560	86
D	Pre-ozonation + UASB treatment	5 000	560	89
E	Post-ozonation of effluent from UASB treating pre-ozonated winery wastewater	560	470	16
E	Pre-ozonation + UASB + post-ozonation	5 000	470	91

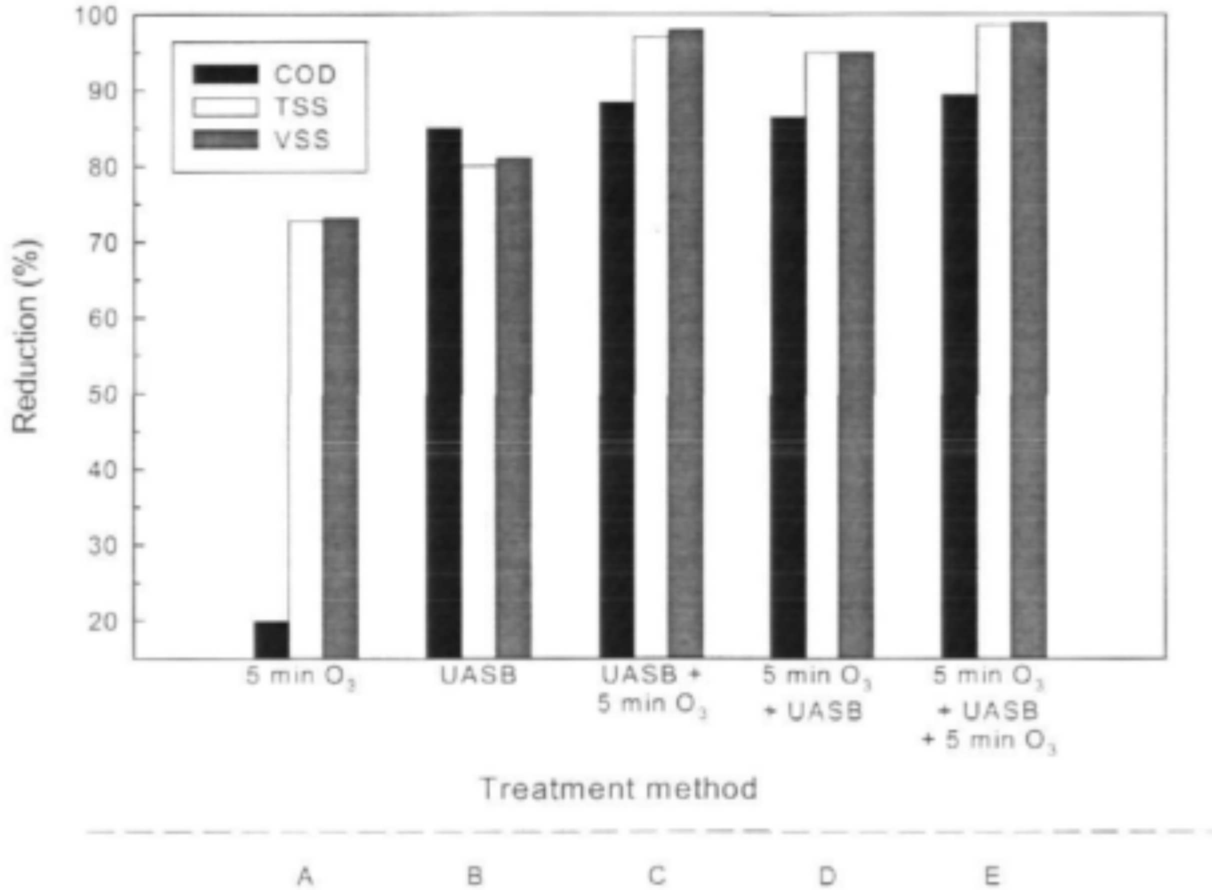

Figure 5.3. COD, TSS and VSS reduction during various ozone/UASB treatment combinations for cellar wastewater degradation.

CHAPTER 6

INFLUENCE OF PRE- AND POST-OZONATION ON THE EFFICIENCY OF AN UASB REACTOR TREATING APPLE JUICE PROCESSING WASTEWATER

6.1 Summary

The effects of pre-ozonation on apple juice processing wastewater were determined. A pre-ozonation of 10 min decreased the total chemical oxygen demand (COD) of the wastewater by 19%, while the soluble COD fraction of the total COD increased from 81.7 to 92.4%. The total suspended solids (TSS) in the wastewater also decreased by 36% after a 10 min pre-ozonation. The effects of feeding a pre-ozonated (2.5 min) apple juice processing wastewater on the efficiency of an upflow anaerobic sludge blanket (UASB) reactor was subsequently determined. COD reductions increased from 78.0 to 90.0% after the first day of the pre-ozonated substrate feed. After 26 days of feeding ozonated substrate the OLR was increased from 10.0 to 16.6 kg COD.m^{-3}.d^{-1}. The COD reduction, however, remained constant at between 90 and 95% and the reactor pH and alkalinity increased from 6.9 to 7.65 and 2 600 to 3 200 mg.L^{-1}, respectively. The VFA content also decreased from 650 to 78 mg.L^{-1} and the reactor effluent had an average COD of 465 mg.L^{-1} during this period. Post-ozonation was then done on this reactor effluent. A 10 min post-ozonation reduced the COD and colour of the reactor effluent by 64.8 and 79.0%, respectively. A combined pre-ozonation, UASB treatment, and post-ozonation system reduced the COD of the apple juice processing wastewater from 9 653 to 180 mg.L^{-1} (98.1%) compared to UASB treatment alone that only reduced the COD by 78%.

6.2 Introduction

Large volumes of wastewater with a high organic content are produced during the washing, pressing, juice extraction and dewatering stages of the apples juice production process (Grismer *et al.*, 2002). The necessity of improved on-site wastewater treatment facilities to degrade this wastewater has become unavoidable due to strict export regulations and government legislation (Trnovec & Britz, 1998).

The effectiveness of the upflow anaerobic sludge blanket (UASB) treatment system in the degradation of food processing wastewaters is well documented (Lettinga *et al.*, 1997). The nature and strength of food processing wastewater provides an ideal UASB substrate (Trnovec & Britz, 1998). It is, however, well known that UASB systems are very substrate sensitive. The finely dispersed and complex organic matter, present in apple juice processing wastewater (AJPWW) can have a negative effect on the efficiency of an UASB system (Lin & Yang, 1991).

The use of ozonation for the treatment of wastewater is well documented. It has also been shown that ozonation as a pre-treatment, can improve the biodegradability of wastewaters (Weemaes *et al.*, 2000; Martin *et al.*, 2002). Ozonation enhances the biodegradability of organic matter by increasing molecule polarity and by forming smaller molecular weight substances (Volk *et al.*, 1993; Martin *et al.*, 2002). Several authors (Benitez *et al.*, 1999; Weemaes *et al.*, 2000; Martin *et al.*, 2002) found that a pre-ozonation during anaerobic digestion, increased the methane yield and overall efficiency of UASB systems. Beltrán *et al.* (2000) and Sigge *et al.* (2002) also reported that the COD of food processing wastewaters can be lowered by ozonation and the ozonation of UASB reactor effluents was especially effective in the reduction of the final COD and colour value of wastewaters. Andreozzi *et al.* (1997) did, however, find that the pre-ozonation of phenol containing olive oil mill wastewater, prior to anaerobic digestion, had an inhibitory effect on the methanogenic bacteria due to the formation of azelaic acid.

The aims of this study were to evaluate the effect of ozone as a pre-treatment on AJPWW, the effect of the pre-ozonated AJPWW on the efficiency of an UASB reactor, and as a post-treatment on the effluent from an UASB reactor treating the AJPWW.

6.3 Materials and methods

Wastewater

The AJPWW used in this study was obtained from Elgin Fruit Juices (Pty) Ltd. (Elgin, South Africa). The substrate batches were kept at -18°C until required. The wastewater was dark grey in colour and very murky due to the presence of high concentrations of suspended solids, had a COD of 7115 (±952) $mg.L^{-1}$ and a pH of *ca.* 4.5. The wastewater was supplemented with 100 $mg.L^{-1}$ urea and 100 $mg.L^{-1}$ K_2HPO_4 to prevent nitrogen and phosphorus deficiencies and the pH adjusted as required with 1 M sodium hydroxide (NaOH) or phosphoric acid (H_3PO_4). Potassium hydrogen carbonate ($KHCO_3$) was added at times to increase the buffering capacity of the substrate. The substrate was also enriched with trace elements (1 $mL.L^{-1}$ substrate) once a week (Nel *et al.*, 1985).

Anaerobic Treatment

A laboratory-scale UASB bioreactor operated at 35°C, as described in Chapter 4 of this report, was used.

Ozonation

Ozonation of the AJPWW was done in a continuous mode, bubble column and ozone was bubbled upwards through the glass column. The bubbling column had a length of 900 mm and diameter of 65 mm. An ozone generator (Parc Scientific, Ifafi) producing 15.5 $g.h^{-1}$ O_3 at a flow rate of 4 $L.min^{-1}$ was used for all ozonation trails. All ozonated samples were analysed in triplicate. The raw reactor substrate at a pH of 6, was ozonated for different times (1, 2.5, 5 and 10 min) during the pre-ozonation study. The UASB reactor effluent was also ozonated for different times (1, 2.5, 5 and 10 min) during the post-ozonation tests.

Analytical methods

The following parameters were monitored according to the APHA (Standard Methods, 1998): pH; alkalinity; total suspended solids (TSS); volatile suspended solids (VSS); chemical oxygen demand (COD); and ozone production was measured using an iodiometric titration.

The total volatile fatty acids (TVFA) and biogas composition were determined using the methods described in Chapter 3 of this report.

To determine the effect of ozonation on the biodegradability of the AJPWW, the activity test method of O'Kennedy (2000), was used. Biomass from the laboratory-scale UASB reactor treating the unozonated AJPWW (day 10) was used. The apple juice processing wastewaters (12 mL) was ozonated for different times (0, 1, 2.5, and 5 min) and added to 3 g of this reactor biomass, sealed in vials and incubated for 25 h. Biogas and methane production were measured after 5, 10, and 25 h.

6.4 Results and discussion

Pre-ozonation

The total and soluble COD content, and the percentage soluble COD after each ozonation are shown in Table 6.1. The effect of pre-ozonation on the AJPWW is shown in Fig. 6.1. It can be seen that total COD reduction was enhanced with increasing ozonation times. The COD reduction of 5% after a 1 min ozonation increased to 19% after 10 min

Table 6.1. Total and soluble COD contents and percentage soluble COD of the raw AJPWW after different pre-ozonation times.

Ozonation time (min)	Total COD (mg.L^{-1})	Soluble COD (mg.L^{-1})	Soluble COD (%)
0	7 301	5 972	81.7
1.0	6 967	5 761	82.7
2.5	6 645	5 564	83.7
5.0	6 266	5 430	86.6
10.0	5 948	5 499	92.4

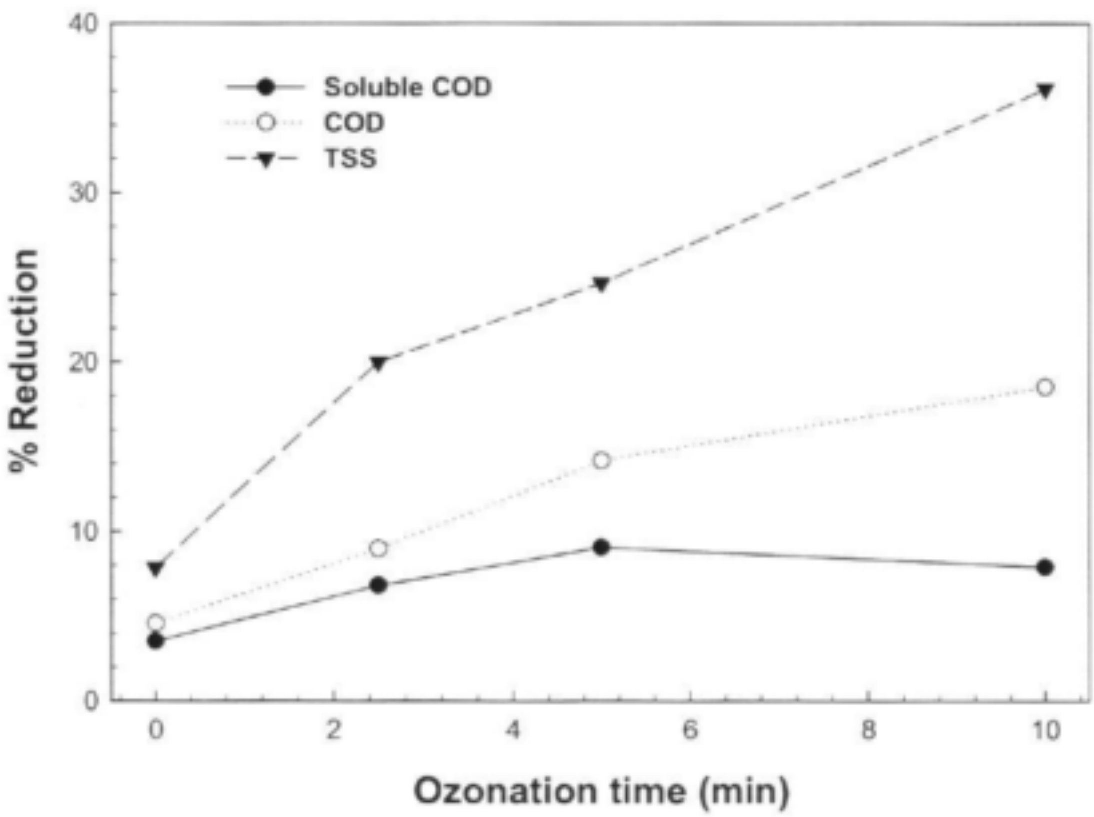

Figure 6.1. Effects of the raw AJPWW pre-ozonation on the COD, soluble COD and the TSS contents at various ozonation times.

ozonation. The TSS content in the raw AJPWW decreased as the ozonation time increased and a 36% reduction in TSS content was observed after a 10 min pre-ozonation (Fig. 6.1).

The data also showed that the percentage soluble COD increased from 81.7 to 92.4%, after the 10 min ozonation (Table 6.1). The lower reduction in the soluble COD content after a 10 min ozonation (Fig. 6.1) can probably be ascribed to the fact that the percentage of soluble COD had increased (Table 6.1) as ozonation reduced the TSS (Fig. 6.1) and insoluble organics present in the AJPWW. An increase in the soluble COD of wastewater will usually result in an increase in biodegradability (Volk *et al.*, 1993). These reductions in COD content, after the ozonation of the untreated AJPWW, are in accordance with results reported by other authors. Benitez *et al.* (1999) achieved a 20 to 30% COD reduction in winery wastewater after ozonation while Beltrán *et al.* (2000) achieved a 40% COD reduction using a pH sequential ozonation system in the treatment winery wastewater. Chang & Sheldon (1998) also achieved a 47 – 62% COD reduction after the ozonation of a meat processing wastewater. The larger COD reductions that occurred in the studies could be due to a variety of factors, including a longer ozonation time, higher ozone concentration, better mixing a wide variation in wastewater characteristics like a low initial COD, presence of ozone scavengers or a more favourable wastewater pH and redox potential.

Biodegradability after ozonation

The use of activity tests to determine the biogas production when identical biomass samples are fed with different substrates can serve as a useful indication of the biodegradability of the different substrates (O'Kennedy, 2000). The effect of ozonation on the biodegradability of the AJPWW is shown in Fig. 6.2 and 6.3. Population activity was monitored in terms of biogas (Fig. 6.2) and methane (CH_4) (Fig. 6.3) production. It can be seen that the amount of biogas produced during the activity test decreases with time (Fig. 6.2). This is to be expected since the amount of substrate is quickly depleted. The amount of methane formed during the activity tests was more constant, indicating that the carbon utilising and methane production is slower. The degradation products of other bacteria are possibly used by the methane producing bacteria (Bitton, 1999) to produce relatively more methane during the latter times of the incubation period.

If the total amount of biogas produced is considered, increased ozonation time resulted in increased biodegradability, as can be seen from the increase of biogas formed after 5 h. After 25 h of incubation, the total amount of biogas produced from ozonated substrates (1, 2.5 and 5 min), was higher than for the control (0 min). Ozonation of the raw AJPWW thus resulted in increased biodegradability of the wastewater, resulting in higher total biogas production.

The total amount of CH_4 formed during the activity tests increased after the 1 and 2.5 min ozonations. The 5 min ozonated substrate did, however, result in slightly lower CH_4 production. After 25 h, the pre-ozonated substrates led to slightly higher CH_4 production.

Effect of pre-ozonation on UASB reactor performance

The effects of a 2.5 min (time chosen due to higher biogas productions during the activity tests) AJPWW pre-ozonation on UASB efficiency were determined and the reactor performance in terms of COD, COD reduction and HRT is shown in Fig. 6.4. The stability of the UASB reactor at the start of the study can be seen in Fig. 6.4. The COD reduction was between 90 and 95% at an OLR of *ca.* 10.3 kg $COD.m^{-3}.d^{-1}$. This status was maintained until day 34 (Fig. 6.4 vertical line A). The first pre-ozonated substrate feeding commenced on day 35 and continued until day 47 (Fig. 6.4 vertical line B). No significant change in the reactor performance was observed during this time. This could have been due to the fact that the UASB reactor was performing very efficiently before the start of the

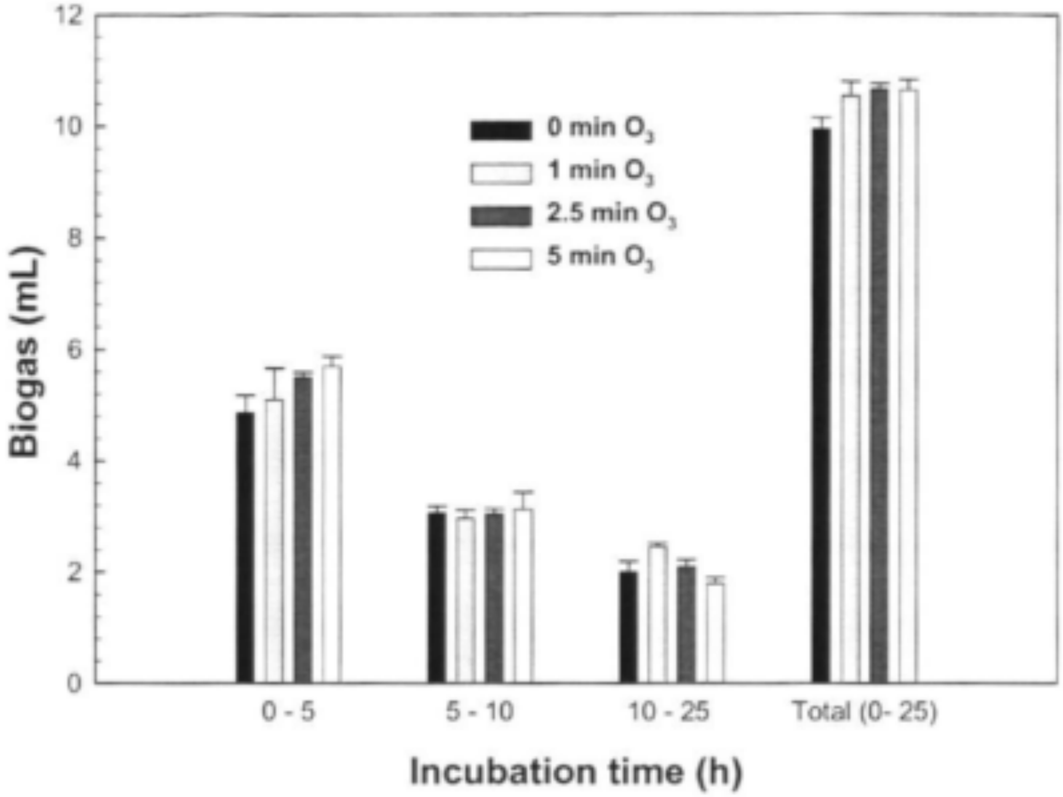

Figure 6.2. Cumulative biogas production during activity tests done on the UASB biomass and the pre-ozonated AJPWW at different times (vertical error bars indicate 95% confidence intervals)

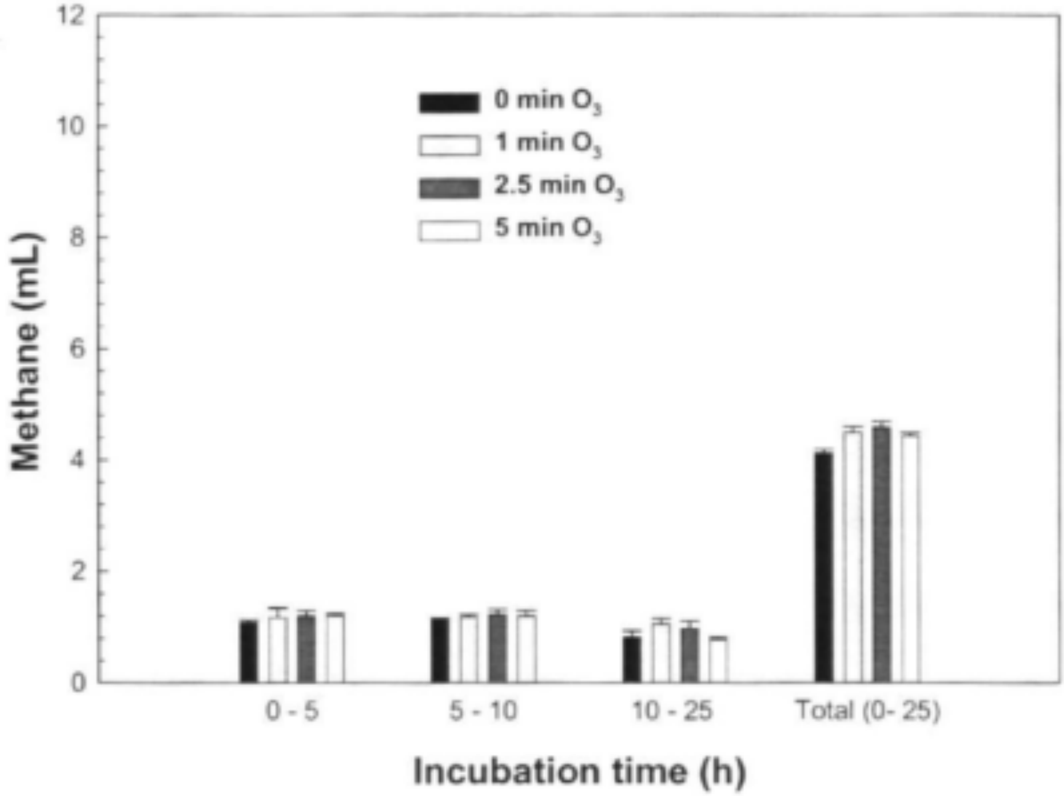

Figure 6.3. Cumulative methane production during activity tests done on the UASB biomass and the pre-ozonated AJPWW at different times (vertical error bars indicate 95% confidence intervals).

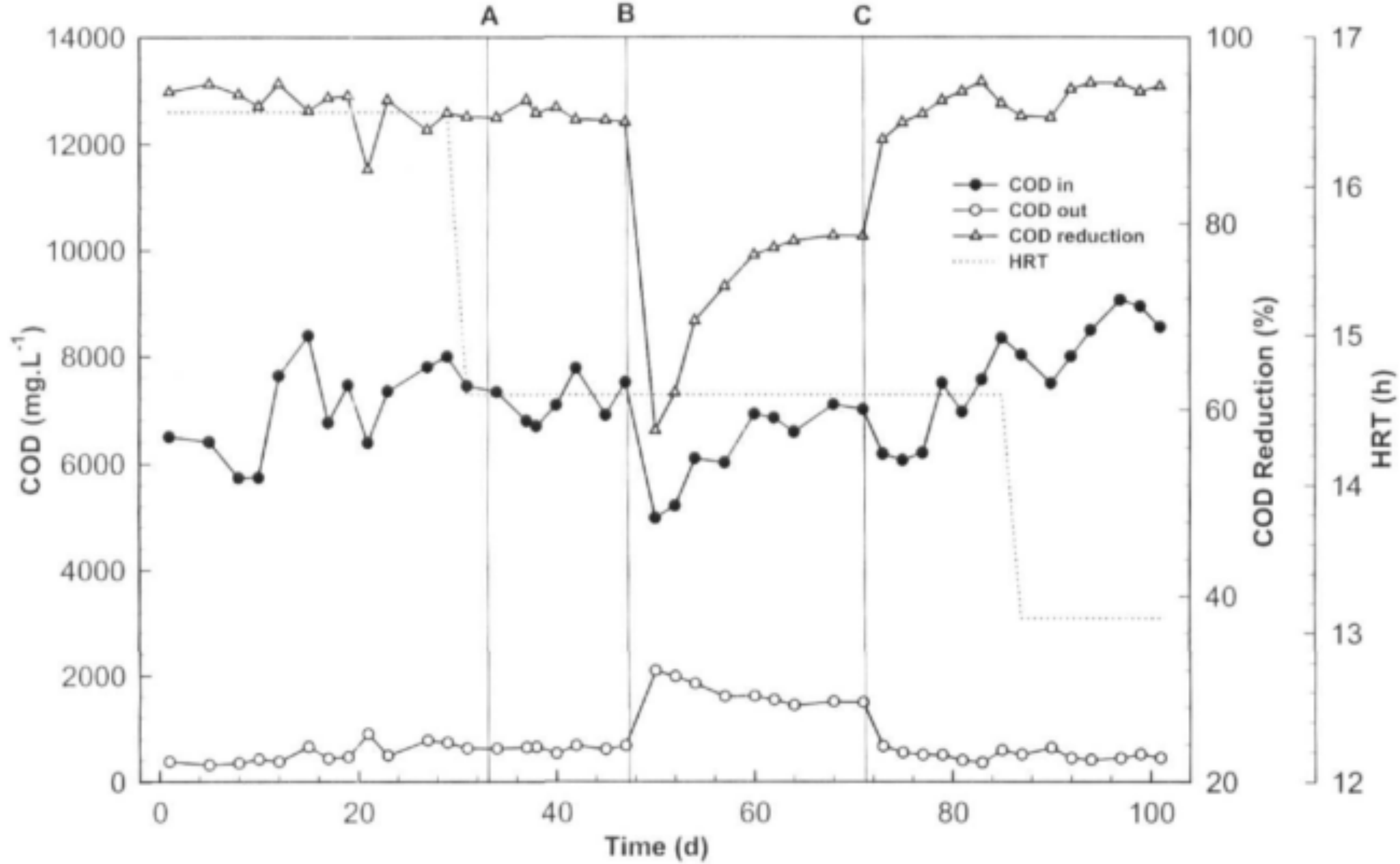

Figure 6.4. Efficiency parameters of the UASB reactor treating AJPWW and pre-ozonated AJPWW. (A - First Pre-ozonated substrate feed started; B – End of first pre-ozonated substrate feed and reduction of 600mL (25%) reactor biomass; C – Second pre-ozonated substrate feed started).

pre-ozonated feed, and improvements were thus difficult to observe. A 25% reduction in microbial biomass within the reactor was made on day 47 (Fig. 6.4 vertical line B) to reduce the active microbial population, and thereby forcibly lowers the reactor efficiency. After the biomass reduction, the substrate COD was intentionally decreased (from 7 512 to 4 979 $mg.L^{-1}$) to prevent possible reactor failure (Fig. 6.4, vertical line B). The reactor was then allowed to stabilise and reach its optimum performance with the reduced microbial population, while gradually increasing the influent COD. Stability was reached at a COD reduction of 78% by day 71. The HRT and OLR at this stage were 14.6 h and 11.5 kg $COD.m^{-3}.d^{-1}$, respectively (Fig. 6.4) and it appeared that the OLR limit of the system had been reached since the VFA content remained relatively high at 600 $mg.L^{-1}$ and no further increases in COD reduction occurred (Fig. 6.4).

A second pre-ozonated substrate feed commenced on day 72 (Fig. 6.4 vertical line C). A sharp increase in COD reduction efficiency from 78 to 90% (Fig. 6.4 vertical line C) occurred after the first day of pre-ozonated substrate feed. The substrate COD decreased from 7009 to 6 188$mg.L^{-1}$ (12%) due to the 2.5 min pre-ozonation (Fig. 6.4 vertical line C), resulting in a 12% OLR decrease from 11.5 to 10.1 kg $COD.m^{-3}.d^{-1}$. The ORR did, however, not decrease after pre-ozonated feed, but stayed constant at 9.1 kg $COD.m^{-3}.d^{-1}$, despite this OLR decrease (12%). The same amount of organic degradation thus took place after ozonation, despite the lower substrate COD content, which resulted in improved organic reduction efficiency. This indicates that some of the non-biodegradable organic constituents were either degraded by ozone or made more biodegradable which led to an increased COD reduction. The lower COD content combined with the possible improvement in biodegradability, thus resulted in a 12% improvement in reactor efficiency (Fig. 6.4, vertical line C). This increased COD reduction after pre-ozonation is in accordance with other authors (Benitez *et al.*, 1999; Martin *et al.*, 2002; and Weemaes *et al.*, 2000), who also experienced improved reactor efficiencies after a substrate ozonation.

Reduction in substrate pH

Reactor performance in terms of pH stability, alkalinity and volatile fatty acid (VFA) content improved after pre-ozonated substrate feed commenced. Stability in pH was also maintained when substrate pH was sequentially lowered to 6.0, while VFA decreased to below 100 $mg.L^{-1}$, indicating improved reactor stability and better methanogenic performance.

Post-ozonation

The effects of post-ozonation of an UASB reactor effluent, in terms of COD and colour reduction, are shown in Fig. 6.5. The reactor effluent produced during the pre-ozonated substrate feeding stage (Fig. 6.4 from day 72 onwards) had an average COD of 469 $mg.L^{-1}$ and a pH of *ca.* 7.5 and was used for the post-ozonation treatments. The effect of a 10 min post-ozonation on the reactor effluent resulted in a 79% colour reduction (Fig. 6.5). Sigge *et al.* (2002) reported similar results in the post-ozonation of a cannery and winery UASB effluent where a *ca.* 80% colour reduction occurred in both effluents after a 10 min post-ozonation.

Ozonation was also effective in reducing the COD of the reactor effluent. Increases in ozonation time led to increases in COD reductions from 31.1% after 1 min of ozonation to 64.8% after a 10 min ozonation. These COD and colour decreases will increase the suitability of the wastewater for irrigation, discharge or reuse purposes. Similar increases in COD reduction with increased ozonation time were also reported by other authors treating food processing effluents (Beltrán *et al.*,

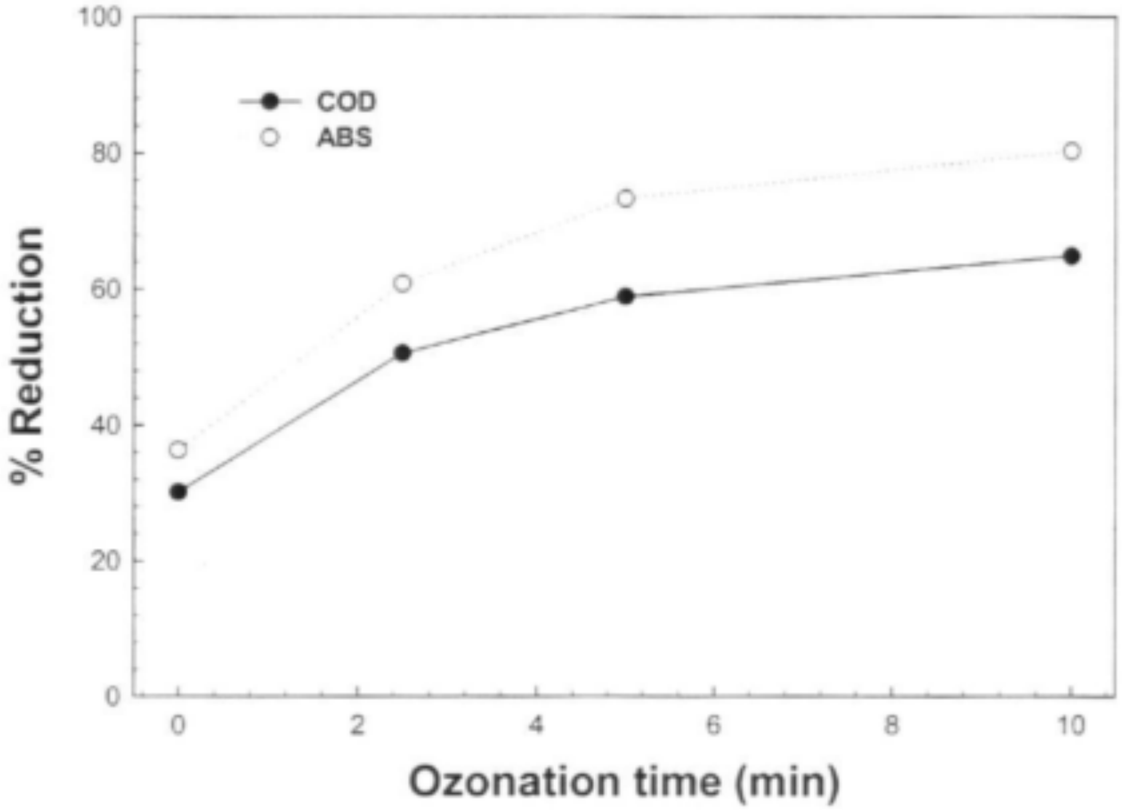

Figure 6.5. Effects of post-ozonation on the COD and colour content (abs at 450 nm) of an UASB reactor effluent treating an AJPWW.

Table 6.2. The COD concentrations at the different stages of the treatment.

Treatment stage	COD ($mg.L^{-1}$) before	COD ($mg.L^{-1}$) after	COD reduction (%)
UASB treatment	7 010	1 540	78
Pre-ozonation of raw apple juice processing wastewater	7 641	6 190	19
UASB treatment of pre-ozonated winery wastewater	6 190	469	92
Pre-ozonation + UASB treatment	7 010	469	93
Post-ozonation of effluent from UASB treating pre-ozonated winery wastewater	469	180	62
Pre-ozonation + UASB + post-ozonation	7 010	180	97

1997 and 1999; Sigge *et al.*, 2001 and 2002). A non-linear COD and colour reduction occurred over time, and was ascribed to the fact that some of the effluent constituents do not react to ozonation (Sigge *et al.*, 2002).

A combined pre-ozonation - UASB treatment - post-ozonation system as used in this study reduced the AJPWW COD by 97% (Table 6.2). The UASB treatment alone resulted in a 78% COD decrease and ozonation alone (10 min) resulted in a 19% COD reduction. The reactor effluent with a COD content of *ca.* 1 700 $mg.L^{-1}$ was produced before the pre- and post-ozonations (Fig. 6.4, vertical line B to C) compared to an effluent with a COD content of 180 $mg.L^{-1}$ after the application of ozone as a pre- and post-treatment (Table 6.2). These improved COD reduction efficiencies are in accordance with the findings of Benitez *et al.* (1999), Martin *et al.* (2002) and Weemaes *et al.* (2000) who reported that enhanced reactor performance and reduction efficiencies are achieved by a combined ozonation, anaerobic digestion system compared to the application of the processes individually.

6.5 Conclusions

The combination of ozonation and UASB technology resulted in increased COD reductions and could be a technically viable treatment option for the AJPWW treatment industry. The higher reduction by a combined process compared to ozonation and UASB treatment individually indicated that the two treatments can complement each other if applied in the correct manner. It was also shown that the long term use of a pre-ozonated reactor substrate does not inhibit reactor performance but actually increases the potential loading capacity of the UASB system. Post-ozonation of reactor effluents is also effective in reducing the COD and colour of the effluent with a significant amount since the wastewater produced had a COD content (180 $mg.L^{-1}$) of below the legal irrigation limits of South Africa (400 $mg.L^{-1}$) (Republic of South Africa, 2004). A summary of COD concentrations at various stages of treatment is given in Table 6.2. COD concentrations of below the South African discharge limit (75 $mg.L^{-1}$) were, however, not achieved and a longer post-ozonation time or further biological treatment would have to be applied.

CHAPTER 7

EVALUATION AND OPTIMISATION OF A MOBILE UNIT INCORPORATING A SCALED-UP 600 L UASB REACTOR AND PRE- AND POST-OZONATION

7.1 Summary

The scale-up of the mobile unit UASB reactor, with pre- and post-UASB ozonation was investigated on a winery wastewater only. The scale-up was done only on winery wastewater due to logistical and practical reasons. The Bergkelder winery is situated within 2 km of the laboratory, while the closest apple juice processing plant is more than 80 km away, making daily monitoring and sampling impractical. Pre-ozonation of the raw winery wastewater (average COD = 5 370 $mg.L^{-1}$) resulted in an average COD reduction of 22%. UASB treatment of the raw winery wastewater in a pilot-scale 600 L UASB resulted in a maximum COD reduction efficiency of 84%. Treatment of pre-ozonated wastewater in the pilot-scale UASB resulted in the COD reduction efficiency of the UASB increasing to between 87 and 93%. The increased COD reduction efficiency was ascribed to increased substrate biodegradability. Variations in organic loading rate (OLR) did not influence COD reduction efficiency. Post-ozonation further reduced the UASB effluent COD, increasing the total COD reduction of the combined pre- and post UASB ozonation treatment to between 91 and 95%.

7.2 Introduction

Wine production is an agricultural activity of major economic importance to South Africa. Not only are many thousand jobs created but, valuable foreign currency is obtained through export of the wine products. One negative aspect of the processing is that large quantities of wastewater are generated (0.7 – 3.8 $m^3.ton^{-1}$ of grapes processed) mainly by the washing, rinsing, cooling and sanitising operations in the cellar (Water Research Commission, 1993; Bezuidenhout *et al.*, 2002). These wastewaters vary in organic load and pH, depending on the season and activities in the cellar. Wineries are under increasing legislative pressure to reduce their water intake and dispose of their effluents in an environmentally responsible manner.

Various methods of treating food and beverage processing wastewaters have been investigated (Bitton, 1999). Ozone has also been shown to be effective in reducing COD, removing colour and making organic compounds more biodegradable, but very little research on the use of ozone as a pre-treatment to anaerobic digestion may be found in the literature. In one study, the use of ozone in combination with hydrogen peroxide (H_2O_2) and ultra-violet (UV)-light to treat a winery waste before anaerobic digestion was investigated and COD reductions of 20 – 30% were reported with a good methane yield increase (Benitez *et al.*, 1999). Anaerobic digestion of vinasse pre-treated with ozone plus UV light in the presence of titanium dioxide also led to a decrease in COD and total organic carbon and increased the methane yield and rate of anaerobic digestion by 25% (Martin *et al.*, 2002). Weemaes *et al.* (2000) reported that the anaerobic digestion of ozonized wastewater sludge enhanced methane production and accelerated the digestion rate, while in contrast Andreozzi *et al.* (1998) found that ozonated olive oil mill effluents (OME) had a stronger inhibitory effect on methanogenesis than un-ozonated OME when treated with ozone prior to anaerobic digestion. Ozone as a pre- and post-treatment step to the UASB treatment of fruit cannery and winery wastewaters has also been shown to be feasible. The COD reduction efficiency of the UASB reactors increased when fed pre-ozonated wastewaters, methane yield increased and no detrimental effects on the microbial population of the reactors was observed. These studies on the use of ozone in combination with anaerobic digestion were were all done on laboratory-scale where variations in organic load, substrate composition and pH are less drastic than in industrial scenarios. Simulation of conditions similar to those encountered at wineries would be beneficial in determining the commercial feasibility of combining ozonation with anaerobic treatment of winery wastewaters.

The aim of this study was firstly to determine the efficiency of a 600 L pilot-scale UASB process while treating winery wastewater, and secondly to investigate the use of ozonation as a pre- and post-treatment option to the pilot-scale UASB process.

7.3 Materials and methods

Wastewaters

Wastewater was obtained from a large winery, Bergkelder (BK) (Distell, Stellenbosch) which produces a variety of red and white wines and some distilled products. This winery was used for the source of winery wastewater for logistical supply and consistency reasons. Due to the nature of the cellar operations, the wastewater COD varied extensively, from a minimum of 2 613 $mg.L^{-1}$ to a maximum of 7 603 $mg.L^{-1}$. The average COD content of the wastewater during this study was 4 200 $mg.L^{-1}$ with an average pH of 4.46 (3.39 – 5.46). The average total Kjeldahl nitogen (TKN) and orthophosphate phosphorous (PO_4^{3-}) content of the wastewater were 12.3 $mgN.L^{-1}$ (7.2 – 19.6 $mg.L^{-1}$) and 24.7 $mg.L^{-1}$ (11.4 – 40.3 $mg.L^{-1}$), respectively.

Anaerobic digestion

The 600 L mobile unit UASB reactor (Fig. 7.1) was used and operated at 35°C and the hydraulic retention time (HRT) was initially set at 48 h for days 1 – 15. The HRT was reduced to 36 h from day 16 – 37 and set at 24 h from day 38. The HRT was kept at 24 h until the end of the evaluation period. The wastewater substrate was fed semi-continuously to the reactor by means of an impeller pump controlled by an electronic timer. A re-circulation pump maintained an upflow velocity of approximately 2 $m.h^{-1}$. Substrate pH was not adjusted, but the reactor was supplemented with an nutrient- buffer stock solution on a daily basis. The supplementation included the addition of 250 g CaO (lime), 40 g nitrogen (N) in the form of 86 g urea and 4 g phosphorous (P) (18 g KH_2PO_4) per day. The supplementation was done in two equal feedings per day. This supplementation was done in order to maintain reactor alkalinity, as well as supplying a source of N and P. The pH, COD, alkalinity and orthophosphate phosphorous of the reactor effluent were monitored. The UASB reactor effluents were subjected to a post-ozonation treatment. Feeding of pre-ozonated winery wastewater was commenced on day 114 and the resulting UASB reactor effluent was again treated with ozone and considered the "pre- and post-UASB treatment" sample. The different treatment combinations studied are summarized in Table 7.1.

Ozonation

Pre-ozonation was done in the mobile unit's 1 000 L equilibration tank. The ozone was introduced into the tank by means of a venturi system. The outlet end of the venturi was situated at the bottom of the 1 000 L tank to facilitate maximum mixing within the tank. Post-ozonation was carried out using a venturi, circulating contactor

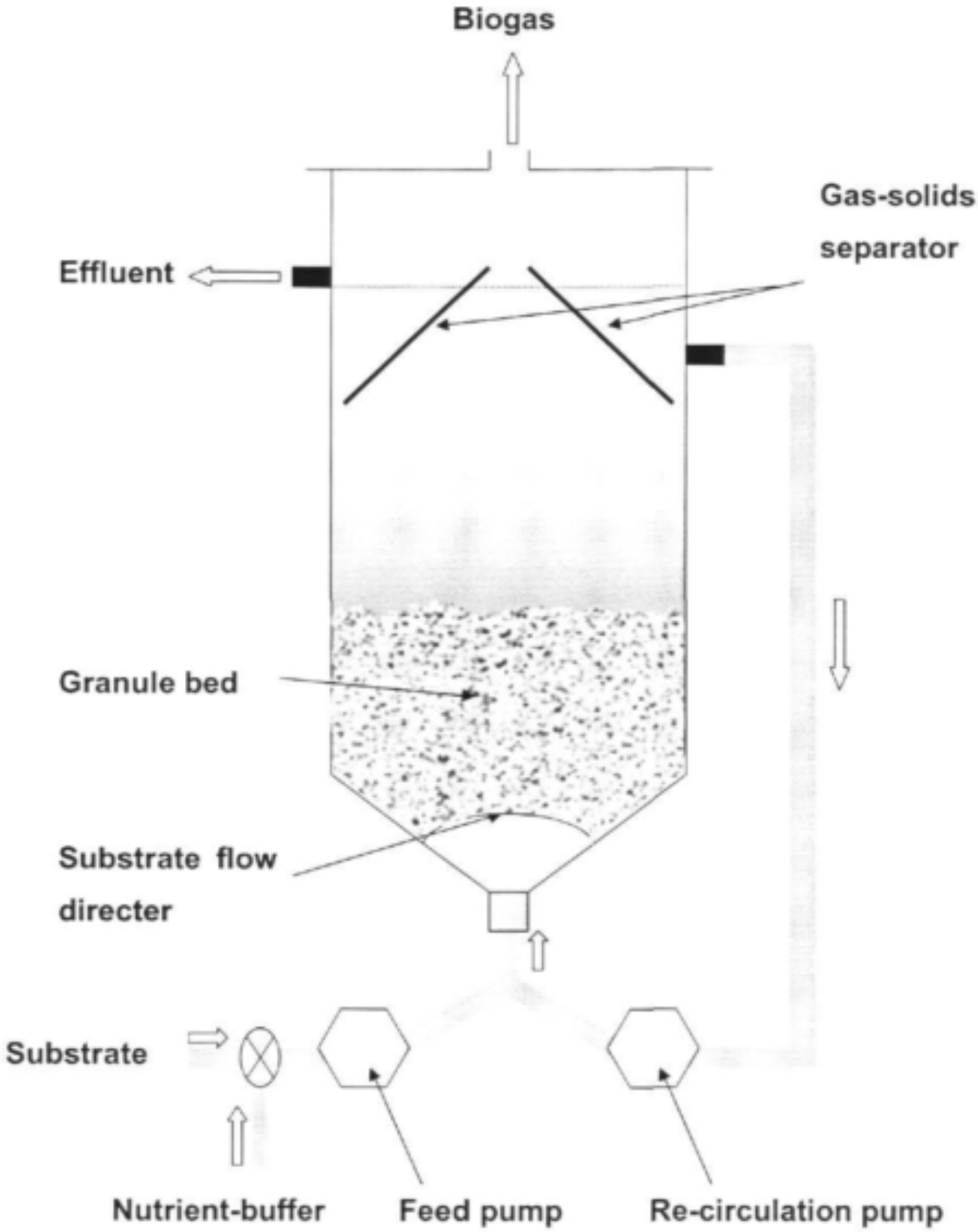

Figure 7.1. Schematic diagram of the 600 L UASB reactor (h = 200 cm; ϕ = 70 cm; granule bed height = 46 cm) used to treat the winery wastewater.

(Fig. 7.2). The contacting column consisted of a closed PVC tube (l = 103 cm; ϕ = 11 cm) filled with stainless steel turnings to enhance mixing. A stainless steel impeller pump was used to circulate (flow rate = 50 $L.min^{-1}$) the UASB effluent through the contacting system. The ozone was introduced into the system by means of the venturi installed beneath the contactor on the inlet side (Fig. 7.2). Pressure in the contacting system was regulated at 1 bar to increase the ozone residence time. An ozone generator (Parc Scientific, Ifafi) capable of producing 9.0 g $O_3.h^{-1}$ was used on both systems. A flow rate of 4 $L.min^{-1}$ was used, resulting in an ozone concentration of 38 $mg.L^{-1}$. Post-ozonation of 25 L batches of UASB effluent was done for 4 min, resulting in an ozone dose of 24.3 $mgO_3.L^{-1}$. Pre-ozonation of the winery wastewater was done in the 1 000 L tank. The ozonation time was 2.5 h, resulting in an ozone dose of 21.9 $mgO_3.L^{-1}$.

Table 7.1. Pre- and post-UASB ozonation treatment combinations of winery wastewaters and UASB effluents.

	Treatment description
1	UASB treatment of winery wastewater
2	Post-ozonation of UASB effluents
3	Pre-ozonation of winery wastewater
4	Pre-ozonation + UASB treatment of winery wastewater
5	Pre-ozonation + UASB treatment + post-ozonation of UASB effluent

Analytical methods

The pH, COD, alkalinity, orthophosphate phosphorous and TKN of the wastewaters and reactor effluents were monitored (Standard Methods, 1998). The ozone production was measured using an iodiometric titration (Standard Methods, 1998). The COD, orthophosphate phosphorous and TKN was determined colorimetrically using a DR2000 spectrophotometer (Hach Co. Loveland, CO) and standardised procedures (Standard Methods, 1998). Volatile fatty acids (VFA's) were determined gas chromatographically. All analyses were done in triplicate.

7.4 Results and discussion

Anaerobic digestion

The mobile test unit's 600 L UASB was used to treat a winery wastewater. During the first 15 d the reactor was operated at a HRT of 48 h (Fig. 7.3 – region A). During this period the influent COD varied between 2 667 and 4 285 $mg.L^{-1}$. An average COD reduction of 77.6% was observed during this period. The effluent pH varied between 6.79 and 7.00. The HRT was reduced to 36 h for the period, days 16 – 37 (Fig. 7.3 – region B). During this period the influent COD varied between 2 613 and 6 588 $mg.L^{-1}$. An average COD reduction of 83.1% was observed during this period (Fig 7.3. – region B). The effluent pH varied between 6.75 and 6.98. The HRT was again reduced on day 38 and set at 24 h for the remainder of the evaluation (Fig. 7.3 regions C and D). During the period from day 38 – 113 (Fig. 7.3 – region C) raw winery wastewater feed continued and influent COD's varied between 2 895 and 7 603 $mg.L^{-1}$ (average = 4 435 $mg.L^{-1}$). During this period the COD reduction varied between 74 and 84%, with an average of 81.0% (Fig. 7.3 –.

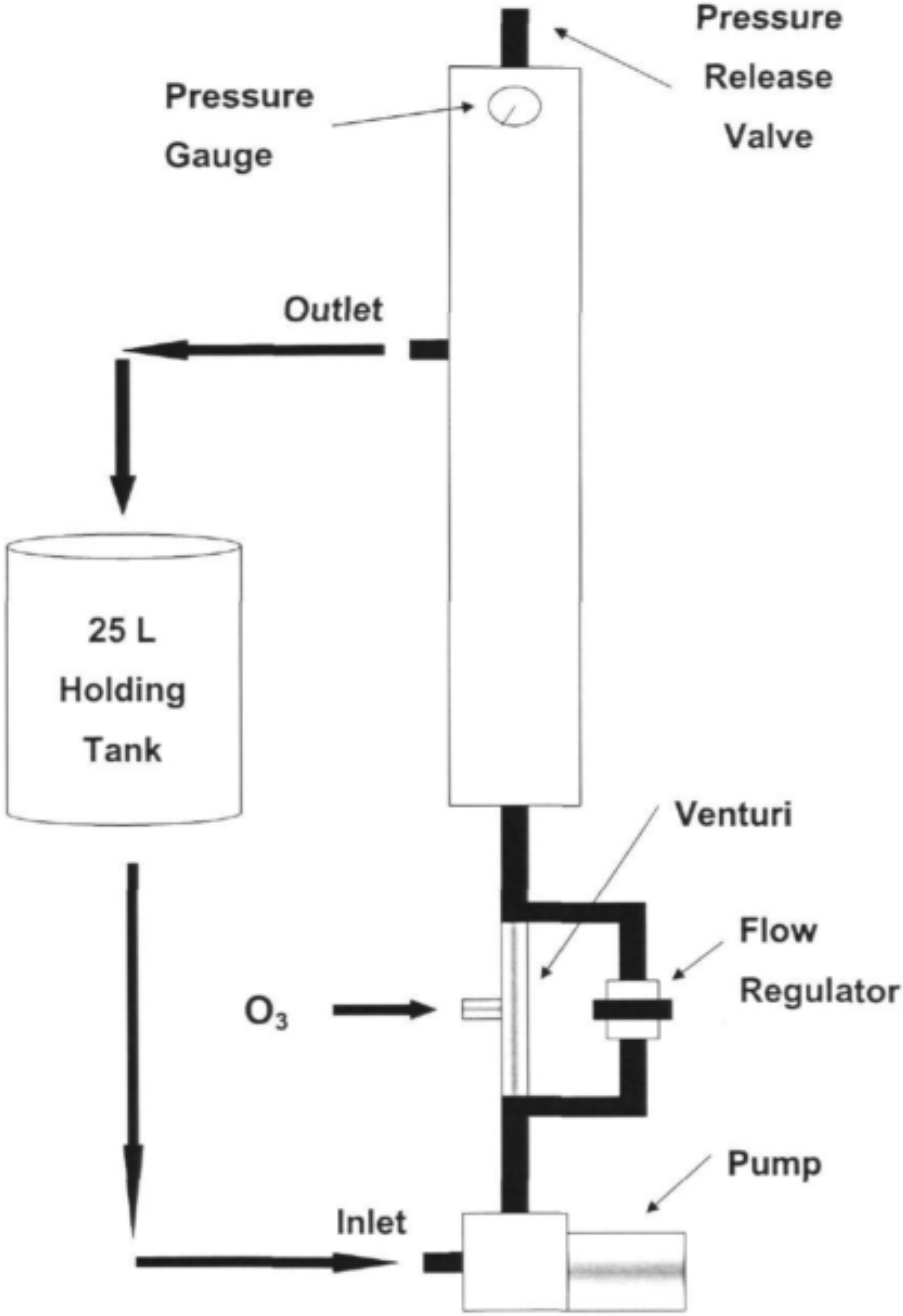

Figure 7.2. Schematic diagram of the purpose-built venturi, circulating contactor system used for the pre- and post-ozonation of winery wastewater and UASB effluent.

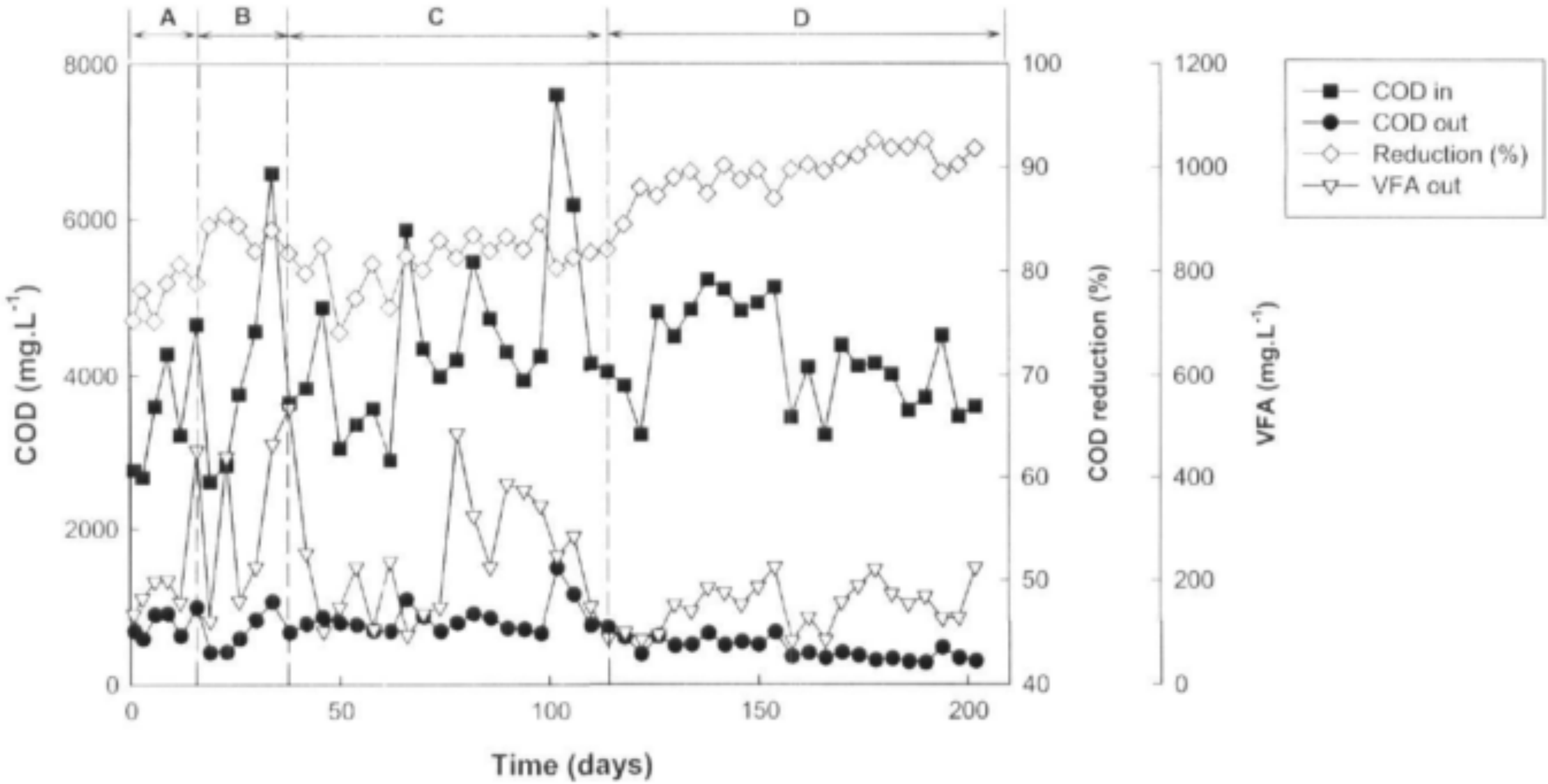

Figure 7.3. COD reduction efficiency parameters of the UASB reactor treating a winery wastewater during different periods of the evaluation (A – 48 h HRT; B – 36 h HRT; C – 24 h HRT; D – 24 h HRT with pre-ozonation of winery wastwater).

region C). The volatile fatty acid (VFA) content in the UASB effluent during this period varied considerably between 95 and 536 $mg.L^{-1}$ (Fig. 7.3 - region C). The effluent pH varied between 6.73 and 6.92.

The COD reduction efficiency attained in this study was somewhat lower than in similar studies. Reductions in COD of between 84 and 93% were reported for winery and distillery wastewater UASB treatment (Müller, 1998; Ronquest & Britz, 1999). A possible reason for the lower efficiency obtained in the case of this 600 L mobile unit UASB may be ascribed to the compositional variability of the specific winery wastewater used and the fact that most studies in the literature are done on laboratory-scale UASB's. For example, the COD in this study varied between 2 613 $mg.L^{-1}$ and 7 603 $mg.L^{-1}$, the pH between 3.39 and 5.66 and the influent VFA's between 300 and 1 356 $mg.L^{-1}$. The reason for the compositional variation is the diverse nature of activities in the winery and the grape pressing season.

Anaerobic digestion of pre-ozonated winery wastewater

Pre-ozonated wastewater feed was used as substrate from day 114 to day 202 (Fig. 7.3 – region D). The COD of the raw winery wastewater during this period averaged 5 371 $mg.L^{-1}$. It was thus found that pre-ozonation of the raw winery wastewater resulted in an average COD reduction of 22%. The COD reduction compared favourably with previous results reported in the literature. Benitez *et al.* (1999) reported COD reductions of 20 – 30% after ozonating winery wastes. Reductions in COD of up to 25% were reported during the ozonation of wine vinasses (Martin *et al.*, 2002; Benitez *et al.*, 2003). Reductions of between 40 and 65% of the COD have also been reported for cannery, yeast production and poultry processing wastewaters (Chang & Sheldon, 1989; Filipović-Kovačević & Sipos, 1995).

After the pre-ozonated substrate feed had commenced on day 114 the COD reduction efficiency gradually increased from about 81% to above 87% on day 122 (value calculated in terms of the pre-ozonated influent) (Fig. 7.3 – region D). The COD reduction remained between 87 and 93% for the remainder of the evaluation, with an average COD reduction efficiency of 89%. During the period of day 114 to 202, the UASB effluent COD averaged 455 $mg.L^{-1}$, representing a total (Pre-ozonation + UASB) COD reduction of 92%. The volatile fatty acid (VFA) content in the UASB effluent during this period (days 114 – 202) (Fig. 7.3 – region D) varied between 84 and 225 $mg.L^{-1}$. The effluent pH varied between 6.78 and 7.05.

Pre- and post-UASB ozonation of wastewater and UASB effluents

The UASB reactor effluent averaged 835 $mg.L^{-1}$ for the period between day 38 and 113 (Fig. 7.3 – region C). Post-ozonation of the UASB reactor effluent resulted in an average additional COD reduction of 18%, giving an average final COD of 685 $mg.L^{-1}$ (total COD reduction averaging 85%).

During this evaluation it was found that the UASB effluent varied between 348 and 565 $mg.L^{-1}$ during the period of day 114 to 202 (Fig. 7.3 – region D), with an average COD of 455 $mg.L^{-1}$. Post-ozonation of these effluents represented the "pre- and post-UASB treatment" sample. Reductions in COD of the UASB effluent averaged 17%, resulting in effluents with COD's between 289 and 468 $mg.L^{-1}$. This further 17% COD reduction represents a total COD reduction (from the initial average raw wastewater COD of 5 371 $mg.L^{-1}$) of 93% on average.

7.5 Conclusions

The use of ozone as a combined pre- and post-UASB treatment option for winery wastewaters was shown to be feasible on a 600 L pilot-scale with COD reduction efficiencies of between 77 and 81%. Post-ozonation of the UASB reactor effluent was found to be effective in further reducing the COD, with a reduction averaging 22% (Table 7.2). It was shown that with the mobile 600 L unit, pre-ozonation increased the biodegradability of the wastewaters, as the COD reduction efficiency of the UASB reactor increased. The COD reduction efficiency was found to improve even though the influent COD levels varied. This indicates a stable process, capable of functioning at below optimum conditions, making it ideal for wineries where wastewater composition varies form day to day.

Table 7.2. Efficiency of different treatment stages and combinations of treatment stages in terms of average COD reductions.

Treatment stage	COD ($mg.L^{-1}$) before	COD ($mg.L^{-1}$) after	COD reduction (%)
UASB treatment (region C)	4 435	840	81
Post-ozonation of UASB effluent (region C)	840	685	18
UASB + post-ozonation (region C)	4 435	685	85
Pre-ozonation of raw winery wastewater	5 370	4 210	22
UASB treatment of pre-ozonated winery wastewater (region D)	4 210	455	89
Pre-ozonation + UASB treatment (region D)	5 370	455	92
Post-ozonation of effluent from UASB treating pre-ozonated winery wastewater	455	377	17
Pre-ozonation + UASB + post-ozonation	5 370	377	93

It was found that the COD reduction efficiency of the mobile unit's UASB with pre- and post-ozonation was 93% (Table 7.2). Although the COD was not lowered to below the South African legal limit of 75 $mg.L^{-1}$ for discharge to a natural water resource, the reductions did lower the COD to below the legal limit of 400 $mg.L^{-1}$ for irrigation.

It has thus been shown that the use of ozone as a pre- and/or post-treatment to anaerobic digestion is a feasible option (depending on environmental considerations and specific industrial conditions) for use by wineries generating wastewaters from the production of a variety of red and white wines and even some distilled products. Wastewater treatment efficiency can be improved, providing financial benefits to industries involved and contributes to the sustainability of our fresh water resources.

CHAPTER 8

ECONOMIC CONSIDERATIONS

8.1 Background

The research from this study has shown that pre- and post-ozonation is an effective technology in improving the efficiency of anaerobic digestion of food processing wastewaters. Before further research is done into the full-scale application of ozonation technology as a pre-treatment to anaerobic digestion, estimates need to be made to determine whether the technology is also econimically feasible.

A basic cost estimation for the production of ozone has been made. However, certain variables such as capital equipment cost, maintenance and labour have not been included in the calculations. Averages of research results obtained during this study have been used as benchmark and a few varaible scenario's have been included to illustrate potential costings.

8.2 Basic experimental assumptions

An ozone generator (Parc Scientific, Ifafi) was used, producing an average of 8 $g.h^{-1}$ ozone. The average ozone concentration was 140 $mg.min^{-1}$ at a flowrate of 4 $L.min^{-1}$. The best ozonation results were obtained in the venturi, circulating PVC contactor (as described in Chapter 7 of this report). Ozone doses varying between 25 and 45 mg $O_3.L^{-1}$ wastewater were applied and COD reductions of between 10 and 20% were achieved in wastewaters with initial COD concentrations of 5 000 – 10 000 $mg.L^{-1}$. These COD reductions, during pre-ozonation, were found to improve the COD reduction efficiency of the anaerobic digestion process.

8.3 Calculations

Average lab-scale scenario

Based on the average efficiency of a pre-ozonation treatment, an average ozone dose of 35 mg $O_3.L^{-1}$ applied to a wastewater with a COD of 10 000 $mg.L^{-1}$ and achieving 15% COD reduction, would equate to the following:

35 mg $O_3.L^{-1}$ wastewater oxidises 1 500 $mgCOD.L^{-1}$ (15% COD reduction)
1 mg $O_3.L^{-1}$ wastewater oxidises 43 $mgCOD.L^{-1}$

Ozone generator power consumption = 140 W
Ozone generation = 7 – 9 g.h-1
Average cost of 1 kWh = R0.35

0.14 kWh required to produce 8 g O_3
0.0175 kWh required to produce 1 g O_3
0.0175 kWh costs (0.0175 x 0.35) = R0.0061

thus 1 000 mg O_3 costs R0.0061

35 mg $O_3.L^{-1}$ wastewater oxidises 1 500 $mgCOD.L^{-1}$
but 1 000 mg O_3 costs R0.0061
thus 35 mg O_3 costs R0.00021

Cost per L to oxidise 1 500 $mgCOD.L^{-1}$ = R0.00021
<u>**Cost per m^3 to oxidise 1 500 $mgCOD.L^{-1}$ = R0.21**</u>

8.4 Cost of industrial ozone production

Ozone generator power consumption = 18kW
Ozone generation = 1 000 $g.h^{-1}$
Average cost of 1 kWh = R0.35

18 kWh required to produce 1 000 g O_3
0.018 kW required to produce 1 g O_3
0.018 kWh required to produce 1 g O_3
0.018 kWh costs (0.018 x 0.35) = R0.0063

thus 1 000 mg O_3 costs R0.0063

This figure compares well to the lab-scale ozone generation cost of R0.0061/1 000 mg O_3

8.5 Cost of industrial implimentation

If the same basic experimental assumptions (8.2 and 8.3) are used, and applied to an industrial scenario, the following cost calculations can be made:

An average sized winery, such as Rupert and Rothschild Fredericksburg (R-RF) will generate an average of 5 000 L wastewater per day, thus a total of 1 825 m^3 per year

Ozone required per day to achieve 15% COD reduction in wastewater with a COD = 10 000 $mg.L^{-1}$:

$$35 \text{ mg } O_3.L^{-1} \times 5\,000 \text{ L} = 175 \text{ g } O_3.d^{-1}$$

Thus, ozone production required per hour = 7.3 g $O_3.h^{-1}$

Cost of ozone generator with a 10 g $O_3.h^{-1}$ output = R15 000-00

Take lifetime of generator = 10 years

Thus, capital cost = R1 500-00 per year

Thus, unit cost = R1 500-00 per year/ 1 825 m^3 per year
= **R0.82 per m^3**

Total running cost per m^3 for first 10 years = R0.82 + R0.21 = **R1.03**

Thereafter running cost per m^3 = R0.21

CHAPTER 9

CONCLUSIONS AND RECOMMENDATIONS

As mentioned in Chapter 1, the objective of this research programme was to investigate the efficiency of utilising combinations of ozone and UASB technology to treat winery and apple juice processing wastewaters. This was done by:

1. Evaluating and optimising UASB reactors treating winery and apple juice processing wastewaters. The efficiency of the UASB process was monitored by determining the COD reduction efficiency, pH stability, loading rates, biogas production and reduction of wastewater specific components;
2. Evaluating and optimising the pre- and post-UASB ozonation treatments in terms of optimum ozone dose and reaction time. The efficiency of the combined process was also monitored by determining the COD reduction efficiency, pH stability, loading rates, biogas production and reduction of wastewater specific components;
3. Evaluating and optimising the results obtained in lab-scale trials on pre- and post-UASB ozonation on a 600 L pilot-scale UASB process. The efficiency of the UASB process was monitored by determining the COD reduction efficiency, pH stability, loading rates, biogas production and reduction of wastewater specific components;
4. Furthermore, based on the results obtained in the different studies, recommendations concerning the cost efficiency of the pre- and post-ozonation treatment processes were made.

The research in this study focussed firstly on the use of anaerobic digestion as a treatment option for certain apple and wine processing wastewaters, secondly, the use of ozonation technology as an additional treatment step to anaerobic digestion (more specifically the UASB process) and thirdly, on scaling-up the combined treatment process to a pilot-scale (600 L) UASB system. The following conclusions were made from the results obtained:

1. It was shown that anaerobic digestion of winery wastewaters in an UASB process was feasible, even though it is known that cellar wastewaters are nutrient deficient substrates and are usually difficult to treat. The lowest efficient operational substrate pH was found to be 5.73 for a substrate with COD less than 5 000 $mg.L^{-1}$. Higher substrate loads at this pH led to drastic decreases in the effluent pH and alkalinity. At a substrate pH of 6.0, it was possible to successfully treat wastewaters (COD reduction = 84%) at a HRT of 19.7 h and a corresponding OLR of 9.75 kg $COD.m^{-3}d^{-1}$ producing an effluent with a COD of 1 200 $mg.L^{-1}$. Although legal limits of 75 $mg.L^{-1}$ and 400 $mg.L^{-1}$ for disposal in a natural resource and irrigation, respectively, were not met, these reductions could possibly have cost-saving implications for the wine producing industry.

2. From the results obtained during this study it is clear that the UASB design is feasible for the effective treatment of an apple juice processing wastewater. COD reductions were in the region of 85 to 90% throughout the study. The high organic loads fed during the increased OLR stage had no drastic effect on the system's efficiency. This study indicated that UASB systems can cope with the large increases in OLR during an apple processing season. Excessive sludge overflow did, however, occur at times, especially during the start of the study, due to the low sludge density and settling ability of the seed sludge. Lower sludge overflow, was however, experienced by the end of the study due to granulation having taken place. The effluent COD varied between 300 and 1 500 $mg.L^{-1}$ and further

treatment will be required before the legal discharge limits of 75 and 400 mg.L^{-1} are met.

3. The use of ozone as a pre- or post-treatment to anaerobic digestion of winery wastewater was shown to be successful in that total COD and colour reduction were increased. Ozonation of the winery wastewaters alone was less effective in reducing the COD (20%) than anaerobic digestion by UASB (65%). Ozonation as a post-treatment to UASB (73%) seemed to be less effective than using ozonation as a pre-treatment to UASB (89%). Ozone as a pre- and post-treatment to UASB, however, achieved the best results in reducing the COD (91%) and colour of the wastewaters. It was also shown that the long-term use of pre-ozonated winery wastewater as UASB substrate improved the total COD reduction efficiency of the UASB reactor (from 65 to 89%), while also increasing the methane production per COD load. Although legal limits for discarding into a natural resource (75 mg.L^{-1}) and irrigation (400 mg.L^{-1}) were not quite met, significant progress was made in reducing COD levels. The use of ozonation, not only as a post-treatment, but also as a pre-treatment to anaerobic digestion is a feasible option in the treatment of winery wastewaters. By using a combination of pre- and post-treatment, significant improvements in the wastewater treatment efficiency can be achieved, which could be beneficial financially and environmentally.

4. The combination of ozonation and UASB technology resulted in increased COD reductions and could be a viable treatment option for apple juice processing wastewaters. The higher reduction by a pre- and post-UASB ozonation process (97%) compared to ozonation (12%), UASB treatment (78%) and pre-ozonation + UASB treatment (92%) indicated that ozonation and the UASB process can complement each other. It was also shown that the long term use of a pre-ozonated apple juice processing wastewater as reactor substrate did not inhibit reactor performance but actually increased the COD reduction efficiency of the UASB system (78 to 93%). Post-ozonation of reactor effluents was effective in reducing the COD of the effluent to 180 mg.L^{-1}, well below the legal irrigation limit of 400 mg.L^{-1}. COD concentrations of below the South African discharge limit (75 mg.L^{-1}) were, however, not achieved but these reductions could signify possible cost-savings in wastewater treatment penalties.

5. The use of ozone as a combined pre- and post-UASB treatment option for winery wastewaters was shown to be feasible on pilot-scale. The 600 L pilot-scale UASB was shown to be effective in that a COD reduction efficiency of between 77 and 81% was maintained. Post-ozonation of the UASB reactor effluent was found to be effective in further reducing the COD, with a reduction averaging 22%. It was shown that with the mobile test unit pre-ozonation increased the biodegradability of the wastewaters, as the COD reduction efficiency of the UASB reactor increased from 81 to 92%. It was found that the COD reduction efficiency of the mobile unit's UASB with pre- and post-ozonation was 93%. Although the COD was not lowered to below the South African legal limit of 75 mg.L^{-1} for discharge to a natural water resource, the reductions did lower the COD to below (377 mg.L^{-1}) the legal limit of 400 mg.L^{-1} for irrigation. It has thus been shown that the use of ozone as a pre- and/or post-treatment to anaerobic digestion is a feasible option for use by wineries generating wastewaters from the production of a variety of red and white wines. Wastewater treatment efficiency can be improved, providing financial benefits to industries involved and contributes to the sustainability of our fresh water resources.

In this study several potential avenues of investigation were identified, which if implemented could further enhance the efficiency of wastewater treatment in these industries.

1. It is recommended that the efficiency of the ozonation step be further investigated at laboratory-scale to better simulate the application of ozone to wastewaters in industrial-scale applications. More accurate indications of COD reductions and improvement in biodegradability would be obtained. More efficient contacting systems (such as static mixers) would permit higher flowrates and mixing efficiency of the ozone and wastewater, resulting in cost savings on ozone requirements. A more efficient contacting process could also reduce the time required for ozonation and thus increase the volume capacity of the treatment process. It is also recommended that intermittant ozonation of the wastewater and its effect on UASB efficiency be investigated as a possible cost-saving advantage;

2. A further recommendation is that a specific cost analysis of available ozonation systems, for full-scale applications, be done so as to determine the specific cost of ozonating particular volumes of wastewater. More precise predictions regarding the amount of ozone required to bring about specific reductions in wastewater components, which are of concern, will be able to be made.

3. It is also recommended that a further investigation be made into the identification of polyphenols present in winery and distillery wastewaters. Identification of these polyphenols is important for two reasons. Firstly, it has been stated in the literature that certain polyphenols may be toxic towards specific microorganisms. Secondly, it may be useful in predicting the resultant polyphenol by-products formed during oxidation – which could also be toxic;

4. It would also be of great value if more research were conducted into waste minimisation at specific industries. Firstly, by investigating the potential cost-saving implications on the waste treatment process itself and, secondly, the potentially positive effect on the efficiency of the waste treatment process (due to a reduction in the concentration of certain wastewater components).

With the availability of South African made ozone generators incorporating new innovations, the cost of using ozonation in wastewater treatment has been considerably reduced. Commercialisation of this new South African technology will further reduce the cost. Implementation of these wastewater treatment technologies along with further efficiency improvements, as outlined above, will not only benefit these industries financially, but also enhance their image of being environmentally responsible and ensuring a sustainable and profitable business.

CHAPTER 10

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