BIOTREATABILITY OF LIQUORS FROM WET OXIDATION OF SLUDGES AND INDUSTRIAL WASTEWATERS

by

YOUSAF KHAN

Thesis submitted as partial fulfilment for the degree of

Doctor of Philosophy in Civil Engineering

February 1997

Division of Environmental Engineering
Department of Civil Engineering
University of Newcastle upon Tyne
NE1 7RU
United Kingdom

BIOTREATABILITY OF LIQUORS FROM WET OXIDATION OF SLUDGES AND INDUSTRIAL WASTEWATERS

by

YOUSAF KHAN

Thesis submitted as partial fulfilment for the degree of
Doctor of Philosophy in Civil Engineering

February 1997

Division of Environmental Engineering
Department of Civil Engineering
University of Newcastle upon Tyne
NE1 7RU
United Kingdom

THE FIRST THING THAT A POOR MAN DESIRES IS HIS BELLYFUL,

WHATEVER THE PHILOSOPHY OR RELIGION YOU TEACH HIM.

(Bey-Bey)

To

My beloved Son

♥

Barryally Zarak Khan

ACKNOWLEDGEMENTS

This present work would not have been completed without support from many quarters. First and foremost, a warmest and sincere admiration is extended to my supervisor, Professor G. K. Anderson for his invaluable and continuous guidance throughout the study period. I am also grateful to Prof. M. B. Pescod, Mr D. J. Elliott, Mrs L. M. Evison, Mr Simon Holbrook of Unilever plc Dr James Bloor, Dr Speece and Dr G. P Noone of Anglia Water, for their general support and guidance.

I would also like to extend my appreciation to the staff of the Environmental Engineering Group, especially to Mrs Patricia. E Johnston, Miss Amanda Allan Mr John Hamilton, Mr John Moor, Mrs John Baugh, Mr J. T Moor, Mr D. Edgar, Mr W. D. Craigie, Mr J. L Allan, Mr J. E. Edmonds Mr K. Scholefield, Mr K. Tweddle and Mr Les Hepple for their expert advice and technical/non-technical assistance.

I am thankful to Dr Tameez Ahmad, M S Razzaq Abasi, Raja Rafhat Iqbal, Farid-uddin Khan, Obaid-ullah, Haji Liquat Ali, G. P Singh, Sannam Mumtaz, M. A. Malik, Manzoor ahmad, Murtaza Malik, Zulfiqar Ali and Dr Jamil Ahmad for their assistance, friendship and encouragement during my stay at Newcastle.

The financial support of the Ministry of Education, Government of Pakistan for this study is gratefully acknowledged. I am also very much thankful to those organisations who provided financial help in the final year of this study especially university of Newcastle upon Tyne, especially Professor G. K Anderson, and Mr A. B. Williamson of Ryklow Trust.

I would like to express my immense appreciation and thanks to my wife, Dr Shagufta Khan, for her full support. Last but not least I would like to acknowledge the unconditional support of my Baba, Bebbey, brothers Ali Khan, Idrees Khan, Wali Khan, Dr Nusrat, Mohammad Ayub Khan, Mahfooz-ullah, Haroon Jan Khan, Saddiq-ullah, Tehsin-ullah, Irfan Ahmad, Farukh Seer Khan, Shahzada Jalal Khan, Dr Shahzada Ali Khan, Zafar Rahmat Afridi, Dr Javeed Iqbal, Dr Saddiq, Dr Ilyas, Dr Tariq Saffi, Dr Farhat, Dr Jan Sultan, Dr Yasmin, Khatoon Bi-Bi, Mohammad Tariq Jan, relatives and friends in Pakistan whose acknowledgements, to my work encouragement and Dua'a have led to the completion of this project.

ABSTRACT

As environmental awareness increases, it will become increasingly difficult to discharge pollutants to the environment without treatment. New and improved technologies can only be based on a knowledge of a large number of factors for each situation. These can be divided into: legislative requirements, environmental impacts, economics, and technical feasibility. Meeting all these criteria will often mean that no single technology will be sufficient to completely alleviate the problem. Hence, a combination of technologies can often be employed. Industrial wastewater, which is often very difficult to treat by conventional treatment, and the large volumes of sludge produced by the wastewater industry have opened up the potential for wet oxidation, which could be very effective in destroying many hazardous organic wastes, and also very effective in reducing the volume of sludge to be disposed of. The decant liquor from WO is often very concentrated and contains low molecular weight organic compounds, mostly acetic acid, but which could be treated to some degree by a biological treatment process.

The Wet Oxidation (WO) process is recommended for the oxidation of organic effluent with a solids concentration of between 1% to 25% but which are too toxic to be biologically treated or too diluted to be incinerated.

This research project was a continuation of a previous study by Luduvice (1992) and, when possible, most of his recommendations were investigated, including the use of pure oxygen instead of air in the reactor, the biotreatability of the heat liquor and an evaluation of the chemical characteristics of the liquor. It was not, however, possible to develop a continuous Wet Oxidation process capable of operating at both subcritical and supercritical conditions.

This thesis describes the ability of wet oxidation to treat different organic wastewaters and sludges under conditions which included the stoichiometric requirement of oxygen being provided and with further biological treatment being given to the decant liquor. The organic wastewater and sludges tested were from different origins and characteristics, including paracetamol wastewater, detergent wastewater, from industries plus raw primary sludge and activated sludge from a biological wastewater treatment plant.

Tests were carried out at temperatures varying between 160°C and 300°C at retention times of 10, 15, 30 and 60 minutes in a 3.78 l stainless steel reactor. Temperature proved to be the most significant parameter, followed by retention time and oxygen overpressure. A considerable reduction in sludge volume and organic content was obtained in most runs, which in general produced an effluent liquor with a high oxygen demand and relatively stable residual solids. The residual WO solids, when dried were found to be capable of removing colour from a textile-dye wastewater, implying that dried WO sludge may have adsorption properties similar to that of activated carbon.

Simplified empirical equations were developed from the experimental data. The equations adequately described the transformation pattern of the organic and inorganic components of the activated sludge in a WO environment. The empirical equations further demonstrate a direct relationship between the influent VTS and the transformed organic and inorganic components in the liquor after WO.

The purpose of this study was also to demonstrate the feasibility of reducing the strength of heat treatment liquors to that approximating domestic wastewater. A range of aerobic and anaerobic biological treatment systems was investigated. Aerobic biological processes proved to be very effective and robust in COD and BCOD removal compared to the anaerobic biological processes.

CONTENTS

CHAPTER 5 WET OXIDATION OF SLUDGES AND WASTEWATER............82

LIST OF ABBREVIATIONS AND SYMBOLS

BOD_5	Biochemical Oxygen Demand (5 day)
°C	Degree Celsius
T'	Mean temperature at which 50% destruction occurs.
σ	Standard deviation;
aa	Acetic acid
ABS	Alkylbenzene Sulphonates
AD	Active Detergent
AS280 °C	Activated Sludge Liquors Treated at 280 °C
atm	Atmosphere
BCOD	Biodegradable Chemical Oxygen Demand
COD	Chemical Oxygen Demand
CST	Capillary Suction Time
EPA	Environmental Protection Agency
EU	European Union
F/M	Food/Microorganism
HDL	Heavy Duty Liquid
HEQ	Hamburg Ester Quaternary Ammonium Surfactant
HRT	Hydraulic retention time
JLR	Jet Loop Reactor
LAS	Linear Alkyl Benzene Sulphonate

LES	Sodium Lauryl Ether Sulphate
MLSS	Mixed Liquors Suspended Solids
MLVSS	Mixed Liquors Volatile Suspended Solids
MPa	Mega Pascal
n	no of moles
OLR	Organic Loading Rate
P	Pressure
PAH	Polyaromatic hydrocarbon
P_{air}	Air Partial Pressure
PAP	Para-amino Phenol
P_{O2}	Oxygen Partial Pressure
psi	Pounds per square inch
P_t	Total Pressure
P_v	Vapour Pressure
R	Gas constant (8.317 j/mol. °C)
RT	Retention time
SBR	Sequencing Batch Reactor
SCOD	Soluble Chemical Oxygen Demand
SCWO	Super Critical Wet Oxidation
SRT	Solids retention time
SS	Suspended Solids
SVI	Sludge Volume Index
T	Temperature
TCOD	Total Chemical Oxygen Demand

tDS	Total Dry Solids
TS	Total Solids
UFAF	Up-flow Anaerobic Filter
UNEP	United Nation Environmental Protection Agency
USEPA	United States Environmental Protection Agency
V	Volume
VFA	Volatile Fatty Acid
VS	Voaltile Solids
VTS	Volatile Total Solids
WAO	Wet Air Oxidation
WO	Wet Oxidation
WWTP	Wastewater Treatment Plant
Z	Fraction of oxidizable VS destroyed;

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1

INTRODUCTION

Our planet is under siege. The assault on the atmosphere- the greenhouse effect, ozone depletion and increasing air pollution offer a still unquantified threat to human life. The dumping of hazardous waste, wastewater, sludges etc. and landbased sources of pollution present a similar threat to the ocean. We are destroying a tropical forest the size of Austria every year and more than a hundred species of wild plants and animal are lost forever each day (Tolba, 1982, 1992).

Only recently have humans shown much concern for the quality of their environment . For thousands of years they have been quite happy to use natural resources without any thought for the effect they were having upon their world. Nevertheless, it was only after the industrial revolution, which began at the end of the eighteenth century that anthropogenic pollution became a significant problem, demanding action from governmental agencies deriving authority from legislation.

Not all the signs however are negative. Throughout the 1970s and into the 1980s, UNEP was able to report progress in some important areas. The environmental monitoring capacity was being rapidly improved in many parts of the world, and Ministries of the Environment were being set-up in an attempt to deal with the environmental threat in a more coherent way. Associated with the growth of interest has been the introduction of new legislation emanating from national and international sources, such as, the European Union, that seeks to influence the relationship between development and the environment.

Treatment and disposal of sludges from wastewater treatment plants are receiving great attention all over the world. Most plant operators would probably agree that sludge disposal represent 90 % of their headaches. This is especially true for treatment plants located in thickly populated areas. At present, and in the future, the adoption of secondary treatment will greatly increase the quantity of biological sludges, which in turn are particularly difficult to dewater, with traditional chemical conditioning being commonly used.

In UK the production of sludge in 1991-1992 was 1.107×10^6 dry tonnes/year (Anderson, 1995). By the year 2000, the production of sewage sludge in UK is expected to double (Hall, 1995). Wigston (1994) predicted in 1994 that sludge production in the UK will increase by around 65% in the current decade and that it will more than double compared with the 1994 figure by the year 2006. Sludge treatment is likely to remain a major part of the total wastewater treatment cost. Today, sludge treatment may exceed 50% of the total wastewater treatment budget (Noone, 1994).

Disposal of hazardous and toxic industrial wastewaters has acquired great importance all over the world and needs to fulfil stringent regulations. Awareness of the harmful effects of the hazardous organic matter present in many industrial wastewaters has developed an interest in establishing treatment technologies for these industrial wastewaters. Public awareness and stringent statutory regulation make the treatment of hazardous wastewaters compulsory. Technologies used for treatment of such wastewaters should preferably aim at the destruction of the hazardous materials to harmless end products.

In any conventional analysis of treatment processes up to the final disposal of the wastewater or sludge, it is usual to attempt to optimise one or more of several variables. Factors usually considered for optimisation are: economics, stabilisation of organics, biodegradability, energy production, dewaterability, odour control, and public health. In optimisation analysis the cost plus other relevant factors required for a particular situation should be taken into account. However, the lowest cost solution may not be the most acceptable, due to public health considerations. Any system which could optimise more than one variable should be more acceptable.

Public awareness of the environmental impact of dumping sludge and industrial wastewater in the ocean is increasing day by day. It is envisaged that in the near future the dumping of sludge in the ocean will cease altogether (Hall, 1995). The increased cost of landfill and haulage will open the way to finding new and acceptable technologies for sludge and industrial wastewater handling. In such a scenario it is expected that thermal reduction and destruction processes will gradually increase their role in the wastewater disposal market.

Wet air oxidation (WAO), when air is used for aqueous oxidation, or simply wet oxidation (WO), when pure oxygen is used, could be one of those alternative thermal technologies. It was developed in late 1950s in the USA as a viable alternative in industrial wastewater and domestic sludge treatment, although its initial success was forgotten due to its capital and operation costs. Due to changes in environmental law in USA, maximum industrial waste streams will require that treatment facilities be installed (Pradt, 1972).

Wet air oxidation is a physical-chemical process. At high temperatures (150-370 C subcritical or critical above 374°C) and pressures (5-30 MPa) the process may be used to treat liquid wastes (domestic and industrial). The process is effective for wastes with a significant organic matter content and for which conventional aerobic and anaerobic biological treatment processes are inefficient because the effluent is either poorly biodegradable or very toxic to biological processes. The basic principle of this method is to enhance contact between oxygen and the aqueous solution containing the toxic or nontoxic organic pollutants. High temperatures in a closed system prepare the pollutant for oxidation, and high pressure provides oxygen to react with the organic matter and produces, inorganic salts and simpler forms of biodegradable and non-biodegradable compounds or may result in complete oxidation to carbon dioxide and water.

The primary aim in the case of sludge is to make the sludge easily settleable and filterable. Most sludges contain an average of 5 % solids and the weight to be disposed of may be reduced by a factor of 10 to 20 if the liquid can be separated from the solids by WAO.

This research is a continuation of the previous work carried out by Luduvice (1992). Luduvice's work was concerned mainly with the effects of temperature, and retention time on the conditioning of selected sludges, at low over-pressure in the presence of air (WAO). The organic sludges treated by Luduvice were of different characteristics and origin, including raw primary, anaerobically digested, activated and thickened activated sludge from domestic wastewater treatment plants, organic sludges from a brewery, paper repulping plant and a diary waste. The main purpose of his research was to investigate the ability of WAO to treat the selected sludge from a variety of sources. Emphasis was given to the effects of operational parameters as well as to the characteristic of the effluent liquors. Luduvice's work has been fully described in his Ph.D. thesis. The summary of Luduvice (1992) recommendations are given below:

> "The use of pure oxygen, instead of air, as the oxidising agent is recommended in an attempt to increase the total chemical oxygen demand (TCOD) oxidation rate. A more comprehensive evaluation of the treatability of the effluent liquor to biological treatment is also recommended. This should take into consideration the effect that temperatures might have on the production of toxic compounds for bacteria both anaerobic and aerobic. Investigation into a suitable use for the residual solids is also recommended. The possibility of developing a continuous wet oxidation process unit capable of operating at both sub-critical and super-critical conditions should also be considered."

Based on the recommendations of Luduvice's, the current study is concentrated on:

i) the use of pure oxygen insead of air for sludges and industrial wastewasters in wet oxidation system, and

ii) the biotreatability of the heat liquors from (i)

The specific aims of the present study is presented in detail in Chapter 3.

CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

Due to the increase in industrialisation, the complexity of environmental management is continually increasing and the contaminants must often be either contained or destroyed. If left to conventional treatment processes the destruction of hazardous and toxic organic wastes and sludges will remain a permanent problem in the future (Frisch and Gloyna, 1992).

Future environmental management will be controlled by two factors, environmental impact and economics (Chermisinoff, 1987). In the past, much of the sludge from the wastewater industries was dumped at sea. Present and future Directives and legislation in the EU will stop this practice, and hopefully will lead to other sludge treatment methods. The cost involved in disposing of large volumes of sludge and the problems faced in dewatering the various sludges has enhanced interest in evaluating different methods of sludge dewatering.

Sludge dewatering and wastewater treatment requirements are based on the two following main factors:

(i) technological progress and increased knowledge which allow for a diversification of treatment systems, and

(ii) because of energy costs, the search for more economical solutions better adapted to local conditions has, in certain cases, placed a much higher value on products which were formerly considered only as waste (Leglise, 1981). The two main sludge conditioning systems are:

(i) chemical conditioning, i.e. the addition of a chemical, such as a coagulant or flocculant which improves the filterability of the sludge, and

(ii) heat conditioning, i.e. heat treatment which modifies the hydrophilic structure of the sludge and improves its thickening and filterability characteristics (Leglise, 1981).

One process being considered for the treatment of wastewaters and sludges is pre-treatment by wet air oxidation (WAO). Wet air oxidation has been shown to have considerable potential for advanced wastewater treatment facilities, since it could replace a number of stages in conventional treatment, i.e. primary sedimentation, biological oxidation of settled sewage, and sludge treatment and disposal. It could avoid the difficulties which sometimes arise as a result of inhibition of biological processes and might be effective in destroying toxic organic compounds which are resistant to such processes.

In addition to the above, heat treatment of sludges and wastewaters can destroy 80% of the organic content of a sludge and more than 99% of some organic compounds such as phenols (Khan, 1992). The heat treatment process for conditioning sewage sludge has been in use for over 50 years but even so, there is still uncertainty concerning the biodegradability of the heated liquor produced at higher temperatures (above $270\,^{0}$C) and the nature of the material remaining after biological treatment. This uncertainty remains regarding both aerobic and anaerobic biological processes despite a number of reports in the literature which indicate that heat treated liquor can be at least partially treated (Friedman and Smith., 1987).

This chapter will review the literature regarding the chemical changes which take place during the heat treatment of wastewater and sludges and the treatability of the liquors produced.

2.2 WASTEWATER AND SLUDGE DISPOSAL POLICIES

In a scenario such as the Urban Waste Water Treatment (UWWT) Directive (91/271/EEC) which requires all sewage discharges above a population equivalent of 2000 to be treated according to the sensitivity of the receiving water in specified phases, by 31 December 2005, the production of sludge will increase significantly:

(i) due to additional secondary and tertiary treatment and
(ii) due to the complete ban on ocean disposal by 31 December 1998 (Hall, 1995; Garbutt, 1995).

It is clear from the above that all sludge must ultimately be disposed of on to land in the form of landfill material or on to agriculture land. In such a situation it is also clear that high temperature processes could increase their role in the treatment of organic wastewaters, as well as in sludge disposal.

Landfill disposal of toxic industrial wastewaters and sludge will not be sustainable in the future due to economic and stringent environmental standards. Thermal drying of sludges and disposal to landfill will cease in countries where regulations will limit the organic matter deposited in landfills. Consequently in the future, due to environmental regulations, it has been claimed that sludge will only be acceptable in landfills as an incinerator ash (Hall, 1995).

The high cost of disposal of liquid hazardous waste by landfilling and incineration could increase the role of wet air oxidation as an alternative treatment (Wilhelmi and Knopp, 1979). Environmental regulations for hazardous waste in landfilling and stack emissions from incinerators could also increase the role of wet air oxidation for the treatment of hazardous industrial effluents (Anon, 1984). In areas where land values are high and are thickly populated, WAO could be one of the treatment options due to its compactness, as well as creating less air pollution.

The general trend in the future for sludge disposal will be dominated by application on to land followed by incineration with ultimate disposal to sea and to landfill being the least attractive options (Hall, 1995). The way ahead for the wastewater treatment and sludge disposal industries is:

i) to ensure that the substantial sums devoted to the treatment and disposal of sewage continue to be used to maximum effect, and

ii) to ensure that future environmental policy has a sound scientific basis and provides good environmental value for money (Calcutt and Moss, 1984).

2.3 WASTEWATER TREATMENT AND SLUDGE DISPOSAL

The use of biological systems for the removal of organic compounds from wastewater is an established and proven technology. The systematic treatment of wastewater in Europe dates back to 1850 when it was common to treat sewage by land spreading. These methods were replaced by trickling filters. As the quantities of wastewater increased, more intensive methods were considered and the theory of activated sludge was first described in 1914 in a report to the Society of Chemical Industry. Such considerations mean that today, conventional aerobic sewage treatment is nearly 100 years old. The anaerobic biological process for the treatment of sludge was first developed in France at about the same time and employed on a large scale in the UK in 1900 (McEldowney et al., 1993).

These biological systems (aerobic and anaerobic) are effective in the degradation of structurally simple carbonaceous and nitrogenous compounds so protecting receiving waters by reducing the organic content and hence the biochemical and chemical oxygen demand (BOD_5 , COD) of the effluent entering the receiving water. Anaerobic systems score in term of volumetric loading and energy requirements, and in fact that sludge yields are lower. However, aerobic systems have considerable potential for a wide variety of wastewaters to achieve higher degrees of BOD_5 reduction,and nutrient removal and are less sensitive to the effects of toxic organic compounds entering the system (Anderson, 1993).

In the UK today wastewater treatment involves at least primary and usually secondary treatment systems which remove up to 95% of the BOD_5 before discharge. In the EU the treated wastewaters are supposed to have a BOD_5 , and SS of 25 mg/l and 35 mg/l respectively when the receiving water dilutes this effluent eight-fold (Ellite, 1993). The inorganic nutrients may be removed either chemically or biologically. Such advanced wastewater treatment reduces the possibility of contributing to eutrophication of the receiving water. In certain instances, where wastewater is to be recycled for human use, a final sterilisation step is incorporated before it is passed to a water reclamation plant.

The final disposal of wastewater sludges and the concentrated contaminants removed by any treatment process has been one of the most difficult and expensive problems in the field of wastewater treatment. New and improved treatment methods will be required to provide higher levels of treatment not only for domestic wastewater but also for problems in the field of wastewater treatment. New and improved treatment methods will be required to provide higher levels of treatment not only for domestic wastewater but also for the removal of specific compounds (metals, VOCs etc.). The removal of these contaminants in turn will lead to the production of a large volume of sludge (Metcalf and Eddy, 1991).

In the EU sludge production and disposal are entering a period of dramatic change driven by EU legislation. Current sludge production and disposal in the EU are shown in Figure 2.1. The introduction of the UWWT design in the EU will result in at least 50% more sludge being produced by the end of 2005. In the next decade such disposal to all the established outlets could become increasingly difficult or in the case of sea disposal and conventional incineration (for hazardous sludge) will become illegal (Hall, 1995).

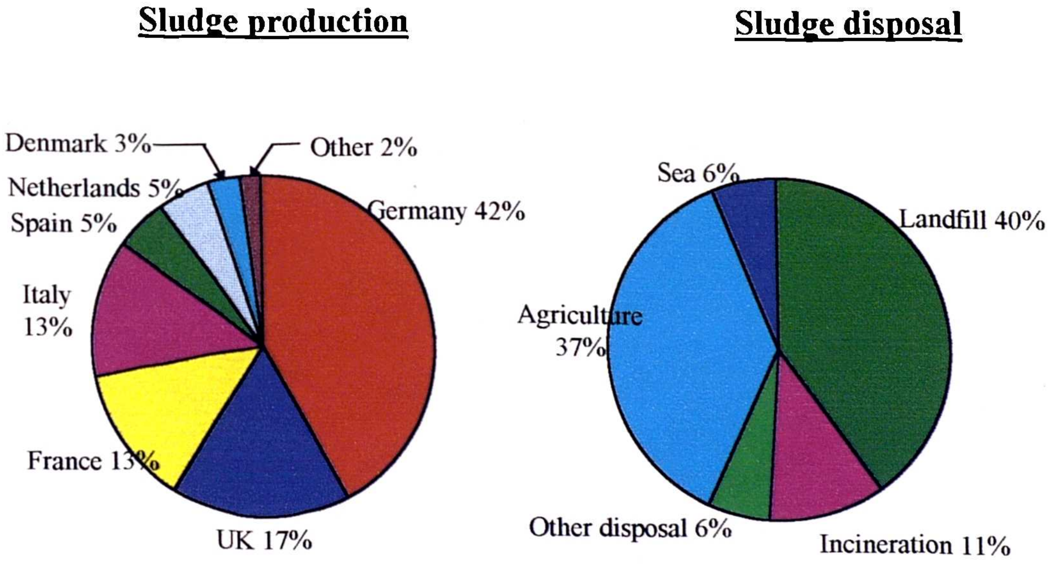


Figure 2.1. Sludge production, and disposal in the European Union (Source: Hall, 1995)

2.3.1 Current Sludge Disposal Routes

Six countries in the EU dispose of over 50% of their sludges to landfill, compared to only four countries which use most of their sludge in agriculture. The amount disposed of to landfill ranges from 8% (UK) to 90% (Greece, Luxembourg), and the corresponding range for agricultural use is 10% (Greece, Ireland) to 60% (France). In the UK 500,000 tDS/year, in Germany 730,000 tDS/year and in France 500,000 tDS/year is recycled to agricultural land (Hall, 1995). Sludge utilisation on farmland is well developed in Europe and is still considered to be a low cost disposal route (Luduvice, 1992).

In a survey of 193 sewage treatment plants in the UK only 37 did not dispose of sludge to agricultural land (Gray, 1989). The reason for these 37 plants not disposing of their sludge onto farmland was the high concentration of heavy metals. However, future competition for void space and more restricting guidelines in landfill management imply that haulage distance and cost will increase greatly in the near future (Calcutt and Frost, 1987; Davis, 1989). Full details of the EEC directive regarding utilisation of sewage sludge for agricultural purposes are given by Bruce et al., (1990).

At present (Fig. 2.1) in the EU only 6% of the total sludge is disposed of to sea. Such disposal is practised by only three countries, Ireland 12845 tDS/year, Spain 3500 tDS/year and the UK currently 334,000 tDS/year, but this practice will be totally stopped by 1998 (Hall, 1995).

Incineration is not a full disposal method by itself but a type of thermal reduction process. Thermal destruction of sewage sludge by incineration is used as a treatment method for about 4% of the total sludge production in the UK (Barrion, 1989), 29% in France, and 10% in Denmark (Calcutt and Frost, 1987). Until recently it has been unpopular because high costs of fuel have made it unattractive compared to other methods of sewage sludge treatment and disposal. In the EU incineration accounts for only 11% of the current sludge disposal but the quantity incinerated, has increased by 38% compared with 1984 (Hall, 1995).

The feed sludge cake for incineration must generally contain more than 15% solids because of the limitation on the maximum evaporating capacity of the furnace. Additional fuel may be required when the feed sludge cake contains 15 - 30% solids. Sludge cake containing more than 50% solids may create a temperature in excess of the upper limit for a standard furnace and could damage the furnace (Metcalf and Eddy, 1991).

2.3.2 Future Sludge Disposal Routes

It is clear from the above discussion that landfill disposal of sludges will not be sustainable in the future because of higher costs, more strict environmental standards and the policies to promote recycling. The limits being suggested for the organic content of material disposed of in landfill should promote recycling. In future, especially in Germany, Denmark, France and possibly in other EU members states, sludge may only be acceptable in landfills as incinerator ash (Hall, 1995).

Sludge utilisation for agricultural purposes is considered by most of the EU States as the most appropriate disposal method. Disposal by this route is controlled by three main factors; heavy metals, organic contaminants and the presence of pathogens. There are a number of other minor sludge disposal routes (sacrificial land etc.) and recycling outlets (compost production, forestry, land reclamation etc.) which will definitely play an increasing role in sludge management in some countries.

In the future, especially in the EU, it is expected that the proportions, as well as the quantities, of sludge being disposed of to the different outlets will change considerably.

There may be a significant increase in incineration and decrease in sludge disposal to landfill. It is expected and estimated that by 2005 , landfilling in the EU, will become the smallest outlet (17%) followed by incineration (38%) and predominated by recycling (45%) (Hall, 1995).

2.3.3 Conventional Wastewater Treatment

In any conventional wastewater treatment process, other than stabilisation pond systems, three main means (physical, chemical and biological) are used for the removal of contaminants:

(i) Physical Unit processes

The methods in wastewater treatment in which physical forces predominate are known as physical unit operations and are typified by screening, mixing, flocculation, sedimentation, flotation and filtration.

(ii) Chemical Unit Processes

Treatment methods in which the removal or conversion of contaminants is brought about by the addition of chemicals or by other chemical reactions are known as chemical unit processes. Precipitation, gas transfer, adsorption, and disinfection are the most common examples used in wastewater treatment.

(iii) Biological Unit Processes

Treatment methods in which the removal of dissolved and colloidal biodegradable organics are brought about by biological activity are known as biological unit processes. Basically these biodegradable substances are converted into gases that can escape to the atmosphere and into biological cell tissue which can be removed by settling in a sedimentation tank or other similar device. A typical conventional wastewater treatment plant is shown in Figure 2.2.

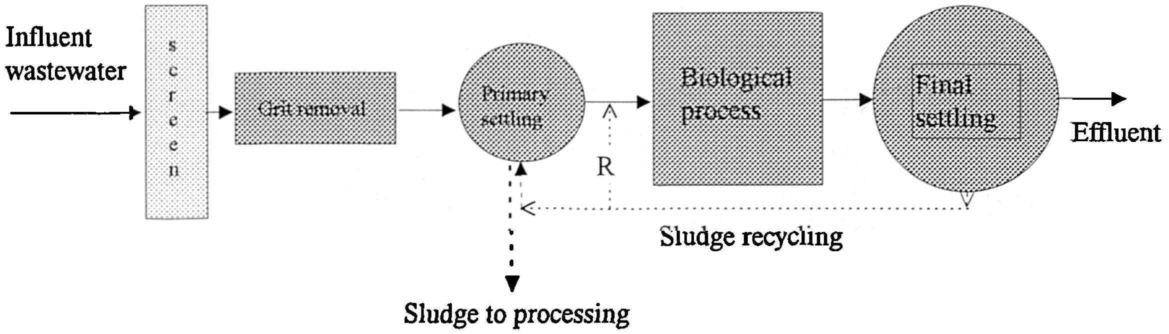


Figure 2.2 Process flowsheet for treatment to meet secondary-treatment standards

2.3.4 Advanced Wastewater Treatment

Advanced wastewater treatment processes applied to domestic wastewater imply the removal of nitrogen and phosphorus prior to its discharge to a water course or the removal of refractory organic compounds that are not converted during conventional biological treatment (McEldowney et al., 1993).

There are a vast number of technologies available which can be used and which can be divided into those technologies which result in the destruction, a phase shift, the concentration or the immobilisation of the pollutants. These treatment processes can be broadly divided into physical, chemical, thermal and biological processes. Such technologies are shown in Table 2.1 (Allen and Ikalainen, 1988).

Table 2.1 Identification and screening of toxic and hazardous waste treatment technologies

Technology	Applicable to sediment matrix	Applicable to water matrix	Applicable to PCB treatment	Applicable for metals removal
Biological				
1. Advanced biological methods	Yes	No	Yes	No
2. Aerobic biological methods	No	Yes	No	No
3. Anaerobic biological methods	Yes	No	No	No
4. Composting	Yes	No	No	No
5. Land spreading	Yes	No	No	No
Physical				
6. Air stripping	No	Yes	No	No
7. Soil aeration	Yes	No	No	No
8. Carbon adsorption	No	Yes	Yes	No
9. Flocculation/ppt	No	Yes	Yes	Yes
10. Evaporation	Yes	Yes	No	No
11. Centrifugation	Yes	No	No	No
12. Extraction	Yes	No	Yes	No
13. Filtration	Yes	No	No	No
14. Solidification	Yes	No	Yes	Yes
15. Granular media filtration	No	Yes	No	Yes
16. *In situ* adsorption	Yes	No	Yes	No
17. Ion exchange	No	Yes	No	Yes
18. Molten glass	No	No	Yes	No
19. Steam stripping	No	Yes	No	No
20. Supercritical extraction	Yes	No	Yes	No
21. Vitrification	Yes	No	Yes	Yes
22. Particle reaction	No	No	Yes	No
23. Microwave plasma	No	No	Yes	No
24. Crystallisation	No	Yes	No	No
25. Dialysis/ electrodialysis	No	Yes	No	No
26. Distillation	No	Yes	No	No
27. Resin adsorption	No	Yes	No	Yes
28. Reverse osmosis	No	Yes	No	Yes
29. Ultrafiltration	No	No	No	No
30. Acid leaching	Yes	No	No	Yes
31. Catalysis	No	No	No	No
Chemical				
32. Alkali metal dechlorination	Yes	No	Yes	No
33. Alkaline chlorination	No	No	No	No
34. Catalytic dehydrochlorination	No	No	Yes	No
35. Electrolytic oxidation	No	No	No	No

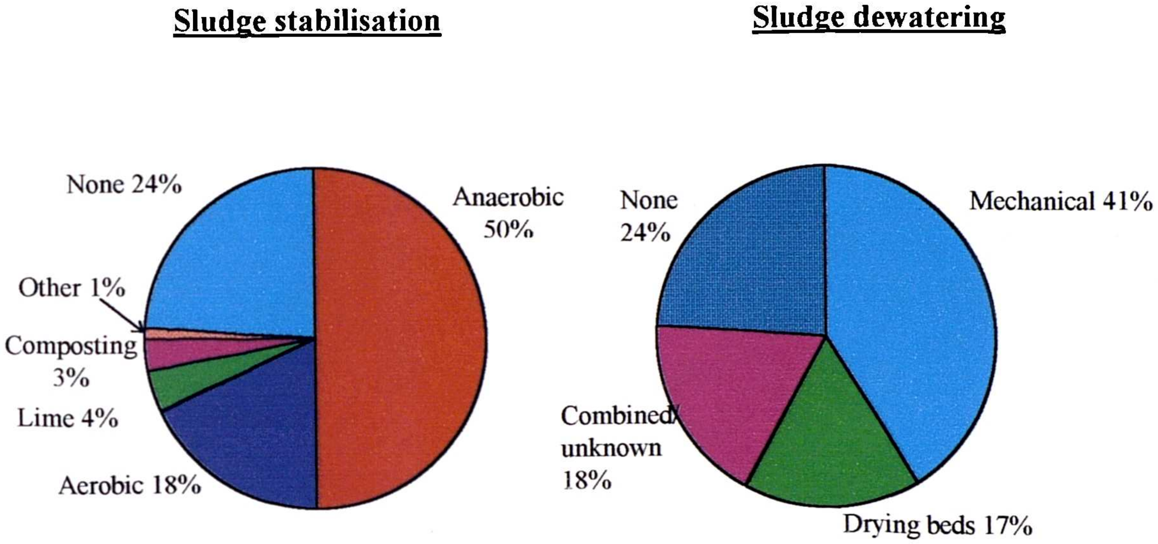
Table 2.1 **continued.**

Technology	Applicable to sediment matrix	Applicable to water matrix	Applicable to PCB treatment	Applicable for metals removal
36. Hydrolysis	No	Yes	No	No
37. Chemical immobilisation	Yes	No	No	Yes
38. Neutralisation	Yes	No	No	No
39. Oxidation/H_2O_2	Yes	Yes	No	No
40. Ozonation	No	No	No	No
41. Polymerisation	Yes	No	No	No
42. Ultraviolet photolysis	No	No	Yes	No
Thermal				
43. Electric reactors	Yes	No	Yes	No
44. Fluidized bed reactors	No	No	Yes	No
45. Fuel blending	No	No	Yes	No
46. Industrial boilers	Yes	No	Yes	No
47. Infrared incineration	Yes	No	Yes	No
48. *In situ* thermal destruction	No	No	Yes	No
49 Liquid injection incineration	NO	No	Yes	No
50. Molten salt	No	No	Yes	No
51. Multiple hearth incineration	Yes	No	Yes	No
52. Plasma arc incineration	No	Yes	Yes	No
53. Pyrolysis processes	Yes	No	Yes	No
54. Rotary kiln incineration	Yes	No	Yes	No
55. Wet air oxidation	No	Yes	No	No
56. Supercritical water oxidation	Yes	Yes	Yes	No

(Source: Allen and Ikalainen, 1988).

2.3.5 Treatment of Organic Sludges

Sludge is a complex material, the quality of which depends upon the characteristics of the wastewater. At moisture contents greater than 90% sludges behave as liquids, whereas below 90% they behave as non-Newtonian fluids exhibiting a plastic rather than viscous fluid (Gray, 1989). The water held within the sludge is either free or bound. In sludges with a moisture content of more than 95%, 70% of the water is in a free or readily sludges with a moisture content of more than 95%, 70% of the water is in a free or readily drained form, and the remainder is bound to the sludge and more difficult to remove, with 20% present as floc or particle moisture, 8% chemically bound, and 2% as a capillary water. Although most of the free water can be removed by gravity settlement, some of the bound water can be removed by coagulation, or heat treatment and dewatering equipment (Gray, 1989).


Sludge stabilisation

Sludge dewatering

Figure 2.3. Sludge Treatment in the European Union (Source: Hall, 1995)

In the EU about 75% of wastewater treatment plants stabilise sludge before recycling or disposal as shown in Figure 2.3. Anaerobic digestion is likely to be the chosen method of treatment at the larger plants. However, some countries (such as the Netherlands) clearly prefer extended aerobic biological wastewater treatment on all sizes of plant in order to minimise sludge production, whilst others, (such as the UK) will generally of lime or composting are minor sludge treatment methods in the EU. In the EU almost all member states dewater most of the sludge produced prior to recycling or disposal (Hall, 1995). The liquid sludge is usually disposed of to sea or spread on sacrificial or agricultural land. Most of the sludge is dewatered by mechanical means. With the improvements in coagulants, and the design and operation of mechanical equipment, mechanical systems for sludge dewatering have greatly improved (Gray, 1989; Metcalf and Eddy, 1991; Hall, 1995).

At present in the EU drying beds are a popular sludge treatment method for small works but for larger works thermal drying plants are becoming more popular, of which there are over 100. This is an attractive option for wastewater treatment plants where sludge incineration is used for final sludge treatment prior to landfill (Hall, 1995).

There are a number of other sludge treatment processes under development, and in some countries in use, which may overcome many of the disposal problems facing sludge, especially hazardous sludges. To treat sludges by these technologies may sometimes be expensive, but provide residues which will be more acceptable by having less adverse effects on the environment compared to other sludge treatment technologies. The most significant of those technologies are the Vertech, deep-shaft, wet oxidation and super critical wet oxidation processes (SCWO) (Hall, 1995; Svensson, 1995). In addition to the above in the UK vitrification, which is a combustion process in which the operating temperature is sufficient to melt the solid residue and which on cooling produces a vitrified, solid end-product in which metals are immobilised.

Oil from sludge (OFS) may be the future favourite process for the treatment of suldge (Boon et al., 1995).

2.4 THERMAL TREATMENT PROCESS DESCRIPTION

The purpose of heat treatment of sludge is to stabilise and condition primary and waste activated sludges so that the need for additional chemical treatment in the dewatering process is either reduced or eliminated or in the case of industrial wastewater (phenol, cyanide, pharmaceutical etc.) the toxic components of the waste stream are either fully or partially destroyed. Thermal treatment can also be used in place of other sludge stabilising systems such as aerobic or anaerobic digesters. The different thermal treatment processes are:

i) Zurn process
ii) BSP-Porteous process
iii) Neptune-Nichols or Farrer process
iv) Zimpro process (WAO)
v) Vertech oxidation technology (WAO)

The Neptune-Nichols and Zurn processes are essentially the same and do not use direct steam injection into the sludge, instead sludge is heated indirectly by a heat exchanger. These two processes are used for sludge conditioning only, because no oxygen is provided for oxidation. The Porteous, Zimpro and Vertech processes use sludge-to-sludge heat transfer by heat exchanger, and direct air (oxygen) injection. A brief processes comparison is given in Table 2.2. Particular characteristics of each waste stream, combined with local environmental regulations and conditions will determine which of the processes given in Table 2.2 should be selected and used. This study will concentrate in detail on wet air oxidation (Zimpro process) and in brief on the latest development, Vertech.

Table 2.2. Thermal Conditioning Systems

Parameter (col. 1)	Zurn (col. 2)	Neptune-Nichols (col. 3)	BSP-Porteous (col. 4)	Zimpro (col. 5)	Vertech (col. 6)
Air Injection (Oxygen)	No	No	No	Yes	Yes
Residence time at maximum temp (min)	45-60	30	30-60	20-30	30-40
Heat supply	Hot water boiler	Hot water boiler	Steam generator	Steam generator	Steam generator
Heat transfer	Heat exchanger: hot water recirculation	Heat exchanger: hot water recirculation	Steam injection	Steam injection	Steam injection
Reactor sludge waste heat recovery	Heat exchanger water heating	Heat exchanger water heating	Heat exchanger water heating	Heat exchangers sludge to sludge	Heat exchangers sludge to sludge
Operating temp. (C)	150-204	202	177-204	150-204 for sludge 150-280 for hazardous waste	260-320

Source: Heyda et al., (1980), and for col. 6 Buning (1992)

2.4.1 Vertical Vessel Oxidation Technology (Vertech)

The WAO principle has led to the development of different processes, all ensuring destruction of organic matter in the aqueous phase. The US Environmental Protection Agency (EPA) in 1975 supported a pilot plant on the Vertech WAO process which was built in Colorado (Mc Carthy, 1982). McGrew et al., (1986) and Longmont, (1987) reported the feasibility of the Vertech process for the treatment of sewage sludge. The first

Vertech WAO process started on June the 5th 1984 at Longmont, Colorado. The Vertech or Deep Well Reactor consists of a tube and shell reactor suspended within a deep well. The Vertech system described above was installed in a 1500m deep, drilled and concrete encased unit. The concentric tubes of the reactor separate the down flowing and the upflowing streams. Oxygen or air is injected into the waste stream, and the mixture flows out of the bottom of the downcomer line in the reactor and rises vertically through the outer tubing. The weight of the liquid provides the pressure required to achieve the reaction conditions [De Bekker et al., (1989), De Bekker (1990), Metcalf and Eddy (1991), Shanableh and Gloyna (1992), Buning (1992)].

Vertech oxidation can also be in the subcritical and supercritical ranges wherein the supercritical deep well process, WAO may attain maximum reactor temperature and pressure above the 'critical point' of water (Smith and Raptis, 1986). Liquids with appreciable vapour pressure may be caused to boil over a wide range of temperatures by decreasing or increasing the pressure. Water boils at room temperature if the pressure above it is reduced to about 0.4 psia . On the other hand, the boiling point of water in a steam boiler operating at 200 psia is 194.4°C. In WO process part of the organic matter is chemically oxidised in an aqueous phase by dissolved oxygen in a specially designed reactor in which the water temperature is elevated to between 250 and 300°C. To maintain a temperature in this range without boiling the water requires pressures between 577 and 1246 psia, respectively. The oxidizability of sludge solids, as well as the oxidation rate, increases markedly with temperature. However, the maximum temperature that can be used in such a reactor is set by the 'critical temperature' above which water can no longer exist in liquid phase, regardless of pressure. This temperature is 374°C. The 'critical pressure' that suffices to keep water in liquid form just below this critical temperature is 3200 psia.

Comparison of design criteria for sub-critical and supercritical wet oxidation(SCWO) are given in Table. 2.3.

Table 2.3 Conceptual Supercritical and Subcritical Design Criteria

Parameter	Subcritical	Supercritical
Well Depth (m)	1200-1700	2400-3058
Temperature, °C	260-320	400-510
Pressure, (MPa)	10-14	220-310
Detention time, (min)	30-40	0.1-2
COD removal, (%)	80-85	100
Oxidant	Oxygen gas	Oxygen gas
Injection point	lower 1/2	lower 1/20
Velocity, (m/s)	1.2-2.7	1.5-4.6
Applicability	Sludge, organic wastes, some hazardous wastes	All organic wastes; all hazardous wastes
Removal efficiency (%)	80-99.9	99.99±

Source: Smith and Raptis, (1986)

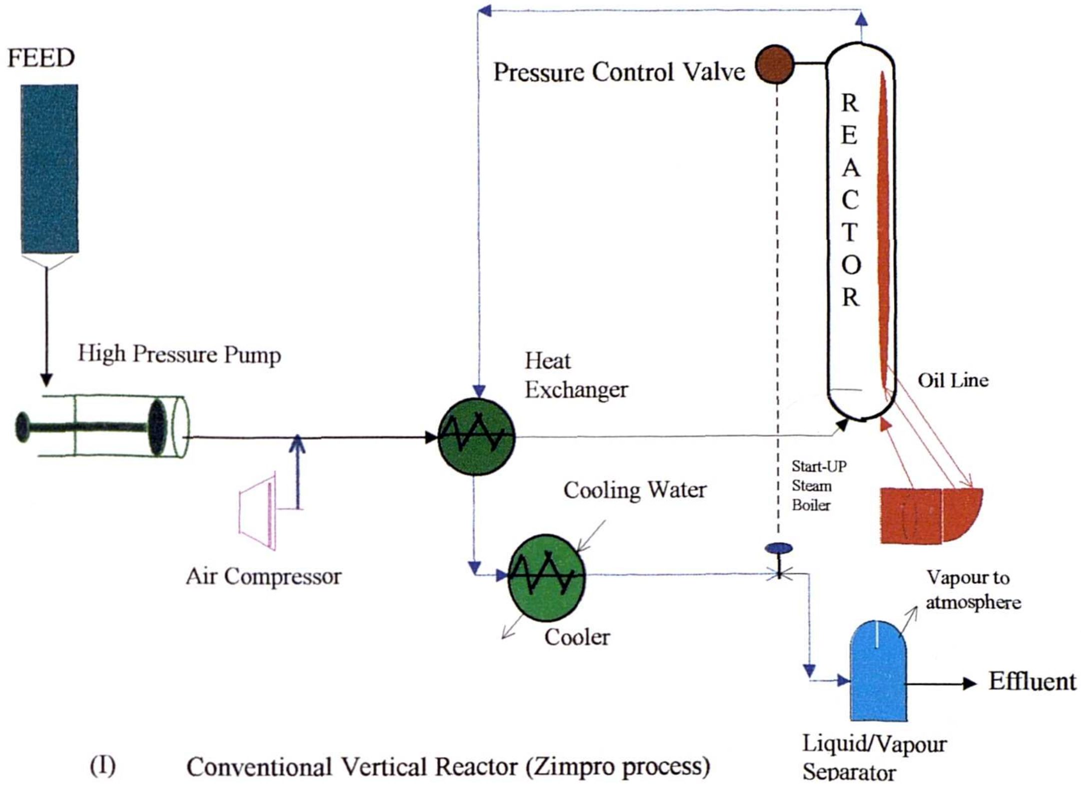
2.5 WET OXIDATION

2.5.1 Process Description

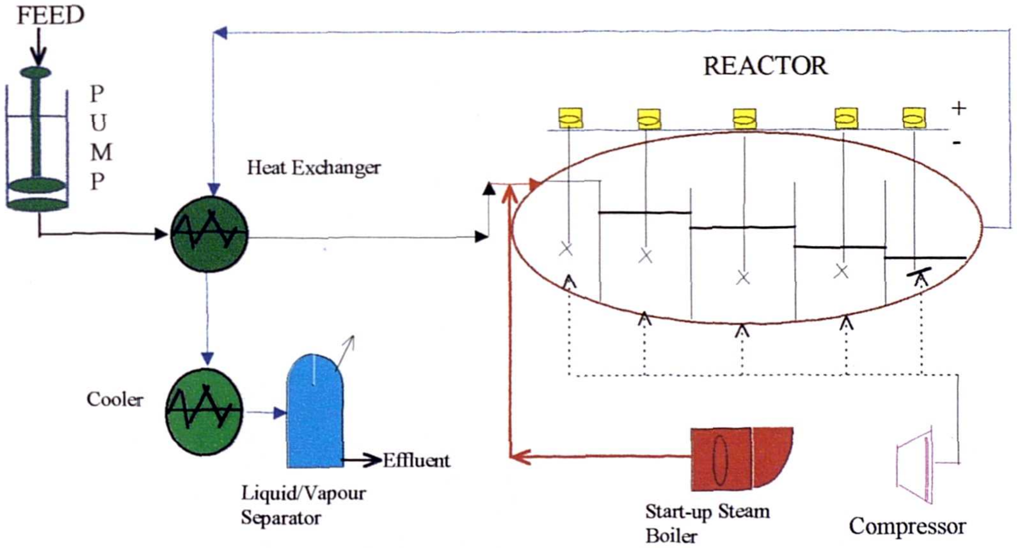
Wet air oxidation (WAO) is the oxidation of organic matter in the liquid state under high pressure and high temperature and involves feeding compressed air (WAO) or pure oxygen (WO) into a pressure reactor. Hurwitz and Dundas (1959) have defined WAO as a chemical oxidation process of the combustible material present in water solutions or suspension at high temperature and pressure. Laboratory-and pilot-scale plants were originally developed in 1944 by Zimmerman Inc. and used very effectively for the treatment of industrial wastewater and sludges (Zimmermann, 1958).

A conventional WAO reactor usually consists of a single, vertical vessel, fitted either with a mechanical stirrer or a gas diffuser with air or oxygen being sparged at the bottom as shown in Figure 2.4(i). However, Laughlin et al., (1983) reported the use of a multi-compartment horizontal WAO reactor with agitation and air injection in each compartment. This multi-compartment reactor is claimed to be more efficient in overall performance from the single vertical vessel reactor and is shown in Figure 2.4(ii). Thus the feed enters the skid-mounted treatment system at a specified rate and is combined with air or oxygen from a compressor. The effect of the added air or oxygen is to raise the pressure of the liquid and to supply oxygen to the stream. The influent stream is then heated before entering the WAO or WO reactor. The first heater is a double-pipe heat exchanger in which the cold, incoming feed is heated by material leaving the reactor. The combined effect of high pressure pumps and heat exchanger give a temperature of 200-230 C to the incoming stream for a reactor operating at 260°C. To raise the temperature of the reactor beyond 260°C the reactor itself or the incoming stream is also provided with a hot oil pipe, or a steam heater.

The waste to be treated remains in the reactor for a specified period of time. The high pressure in the reactor serves two purposes. Firstly it provides oxygen for the oxidation of organic matter and secondly it minimises evaporation of the liquid, which prevents precipitation of salts and fouling of the equipment. The treated stream then moves through the heat exchanger where it raises the temperature of the incoming stream. The treated stream then moves through to a cooler, where its temperature is reduced to 50-



(I) Conventional Vertical Reactor (Zimpro process)



(II) Multi-Compartmental Reactor

Figure 2.4 Basic flowsheet of WAO installations

$70\,^\circ C$, then to a separator where it is flashed into a gas and a liquid stream. The gas which is mainly CO_2 , with some traces of organic compounds, is cooled with water and and usually disposed of to the atmosphere which would not be desirable in the near future. The scrubber water and liquid stream, if high in organic matter proceed for further biological or chemical treatment and dilution prior to discharge to the receiving water.

The three process parameters of WAO are temperature, pressure and retention time. Among these, temperature is the most important and it has, in fact, been claimed by some researchers that the reaction rate relies only on temperature (Foussard et al., 1989; Ploos and Amstel, 1973). The required oxygen partial pressure depends on the rate of the reaction and the mass transfer characteristics of the system (Baillod et al., 1979). When water is heated the vapour exerts a pressure called vapour pressure. For each temperature there is a corresponding constant vapour pressure (VP). The VPs exerted by water vapour at different temperatures are given in Fig. 2.5 which were drawn from the experimental laboratory scale wet oxidation apparatus. When using pure organic liquid, like pure detergent, the liquor pressure may follow a different pattern than Fig. 2.5. In the WAO process the total pressure in the reactor must be greater than the VP at a corresponding temperature. This extra overpressure provides oxygen for oxidation and can be expressed as:

$$P_t = P_v + P_{air} \qquad (2.1)$$

$$P_{O2} = 0.21P_{air} \qquad (2.2)$$

(Source: Luduvice, 1992)

From the above equations (2.1 and 2.2) it is clear that if pure oxygen is to be used then five times less pressure would be required and vice versa. When designing a WAO unit, one should be aware of the following:

i) required pumping capacity for WAO system,

ii) reactor and heat exchanger dimensions, and

iii) compressed air equipment (Hurwitz and Dundas, 1960).

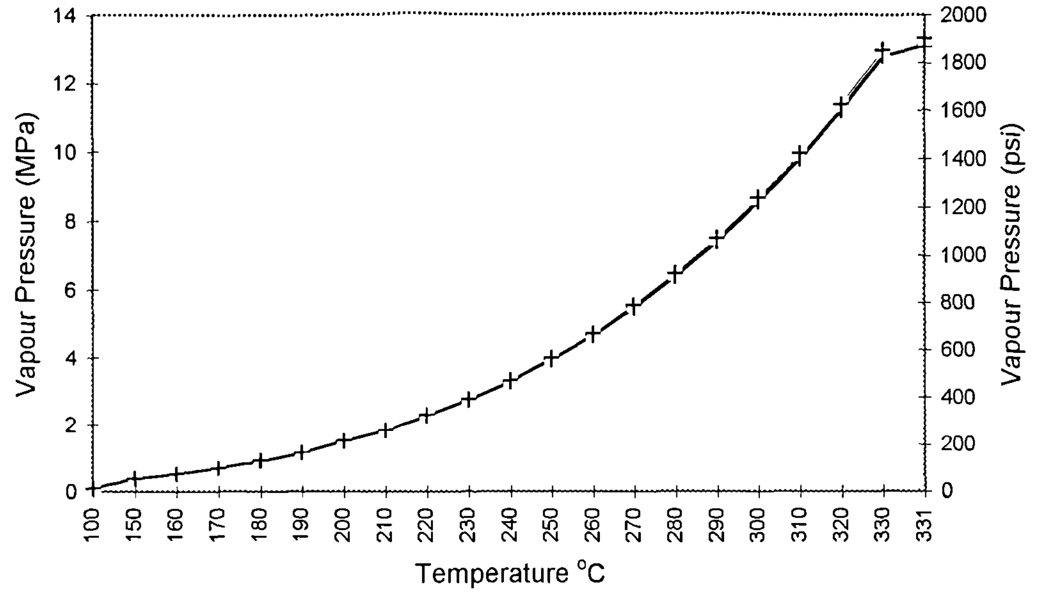


Figure 2.5 Water VP at different temperature

Complete utilisation of the oxygen available must be guaranteed since the air supply system is an expensive part of the process (Teletzke, 1964). Mechanical agitation inside the reactor will greatly increase the oxygen transfer but it will also increase the unit capital and operating costs (Laughlin et al., 1983). In general the cost of a WAO system is proportional to the flow rate, system pressure and the degree of oxidation required (Pradt, 1972). The cost of the reactor and the compressor typically account for 40% of the total capital cost

(Baillod et al., 1985). The size of heat exchanger and the long retention time in the heat exchanger can greatly increase the capital and maintenance costs due to corrosion problems (Baillod et al., 1980; LeBrun et al., 1984). The cost of heating can be reduced by effectively recovering the heat from the WAO. Heat recovery in the heat exchanger is possible when the COD of the influent stream is equal to 10 g/l or more, because by oxidation of 10 g/l COD or more, provide sufficient heat energy to heat the incoming stream to higher degree and hence subsequently reduced the heat requirement of the WAO system, whereas in conventional incineration a COD value of 300 to 400 g/l is required to achieve autogenous operation (Dietrich et al, 1985; Akse et al., 1987).

Most industrial wastewaters and organic sludges treated at high temperature and pressure produce liquors which are highly corrosive, due to acids formation during this process and there is a need for an appropriate reactor design to allow for this. Especially important is the material of construction of the reactor which can significantly affect the economics of the process. This has been one of the major reasons why the process was not widely used at most wastewater treatment facilities. However, due to the introduction of carbon steel and titanium combinations the process is gaining renewed interest in the wastewater industry (Dover, 1991).

Electrical energy can be produced from the effluent stream heat using a gas turbine but this energy would not be sufficient to supply all the power to the air compressor of a WAO unit (Akse et al., 1987) although this statement is contradicted by a BBC2 programme on the Renewable Energy Research (1994), who claimed that sufficient energy can be produced by using isobutane as the heat transfer medium.

In the past, the oxygen for wet air oxidation has been provided from air but the increasing demand for nitrogen for air conditioning and other industries has reduced the price of pure oxygen since it is now a by product of the nitrogen production, thus improving the economic viability of WO systems (Luduvice, 1992). Pure oxygen is very toxic and injurious to health. 100% O_2 has been demonstrated to exert toxic effects not only in animals but also in bacteria, fungi, cultured animal cells, and plants. The toxicity is claimed to be due to the production of the superoxide anion (O_2^-), which is a free radical, and H_2O_2. When 80-100% O_2 is administered to humans for periods of 8 hours or more, the respiratory passages become irritated, causing substernal distress, nasal congestion, a sore throat, and coughing. Exposure for 24-48 hours also causes lung damage (Ganong, 1995). Consequently if pure oxygen was used it would imply additional attention to safety. High volatile organics such as oil mist may ignite in the presence of oxygen (Brooks, 1968).Pure oxygen compared to air could increase the plant sludge handling capacity by six times due to nearly six times more oxidation than air (Longmont, 1987), however, the high cost of pure oxygen could limit the use of pure oxygen compared to free air in WAO.

2.5.2 Destruction of Specific Compounds

The effects of WAO on raw primary sludge, digested primary activated sludge and raw activated sludge were originally studied by Hurwitz et al., (1960). They reported less than 20% COD reduction at a temperature below 150 °C and one hour retention time. Temperatures of 220 °C and above were required to achieve 80% COD reduction. Hurwitz and Dundas (1960) found that at low temperature (100 to 150 °C) WAO of sludge occurred slowly and reached equilibrium (optimum RT beyond which no further oxidation takes place) only after several hours. On the other hand the reaction reached an equilibrium in minutes, while operating at 300 °C.

Teletzke et al., (1967) reported that organic matter in sludge containing protein, lipids, starch and crude fibre were removed by WAO. In his research, at 225°C, removals were about 80% for protein, 95% for lipids, 97% starch, 94% for crude fibre and 72% for COD. Among the above groups of organic matter Teletzke (1967) found that starch was most readily oxidised at temperatures between 150°C to 250°C. Below 200°C, lipids were the most resistant to WAO. Wu et al., (1987) reported that VS destruction of anaerobically digested sludge depends upon the influent solids concentration. The operating conditions for this study were as follows: temperature 125°C to 300°C, pressure 48 bar, retention time one hour plus heating up and cooling down time, and volatile solids (VS) in range of 1% to 4%. They found that VS destruction increased as the temperature increased from 180°C to 250°C, below 180°C there was very little destruction of VS. The removal of VS at temperatures greater than 260°C remained unchanged at about 85%. Friedman et al., (1988) investigated the destruction of volatile suspended solids (VSS) and volatile solids (VS) of digested sludge at 270°C and one hour retention time was 80% and 63% respectively. The destruction of COD and VSS was increased greatly between 250°C and 270°C when VSS destruction increased from less than 60% to more than 80%, the COD destruction also shifted from less than 30% to more than 45%. Foussard (1989) found that theoretical oxygen demand (TOD) destruction ranged from 10% to 99% for different pure compounds , wastewaters and sludges. Shanableh and Gloyna (1992) investigated that during the WAO of activated sludge at an oxygen partial pressure of 82 bars, a retention time of one hour and at a temperature 300 to 350°C, the COD reduction was in the range of 85% to 92%.

On the pure chemical side, research has been carried out on soluble organics such as methanol and formaldehyde (Stepanyan et al., 1972), propionic acid (Day et al., 1973), glucose (Skaates et al., 1981), acetic acid (Frisch and Gloyna, 1992) phenol (Jogleker et al., 1991) and TNT red water (Hao et al., 1992). Sufficient destruction of the above compounds has been claimed by all the above researchers.

2.5.3 WAO of Industrial Wastewater

Researchers have successfully used WAO for the treatment of toxic, high strength industrial wastewaters. Many wastewater streams originating in the chemical process industries contain high concentrations of organic material which may be difficult to treat by conventional methods. Out of 65 priority toxic compounds or classes of compounds recognised by the USEPA, 10 were studied by Randal et al., (1980) who obtained 99% destruction by the WAO process. WAO has been successfully tested for sulphite waste liquor, Kraft liquor, whey from cheese plants and other diverse streams such as slaughterhouse waste and refinery effluents (Zimmermann, 1958). Researchers have also investigated the WAO of shipboard waste, cellulose slurries and oil in waste emulsions (Schatzberg et al., 1974).

Phenols are one of the most common and important of such organic chemicals. They can be found in the effluent streams of refineries, chemical plants and steel mills. Pruden and Le (1976) studied the destruction of phenol and nitrilotriacetic acid (NTA). NTA was adopted in Canada as a partial substitute for , and a complementary agent to sodium tripolyphosphate in detergent manufacture (Pruden and Le, 1976). Other than phenol, cyanide is also a very toxic pollutant present in industrial effluents such as photographic bleaching, metal finishing, iron and steel manufacturing and pharmaceutical industries.

Kalman et al., (1989) studied the destruction of cyanide, while treating pharmaceutical wastewater and achieved an almost complete removal of cyanide from the wastewater, with a 75% reduction in COD. Similar results were observed by Laughlin et al., (1983), Mishra and Joshi (1987). A paracetamol waste, which contains mainly para-amino-phenol and other inorganic pollutant has been successfully treated using WAO by Sterling Organics (Dover, 1991).

The application of WAO for the reclamation of black liquor, a residual of the pulp and paper industry, has been studied by Flynn (1976). Randal (1983), Clifford et al., (1983), Canney et al., (1983, 1984), Ding et al., (1987) and Larson et al., (1988) reported the regeneration of powdered activated carbon (PAC) by using WAO although this has been questioned by Deeney et al., (1989). Kalman et al., (1989) reported severe corrosion problems while treating wastewater with a chloride content of 80 g/l. WAO is also successfully used for the wastewater treatment of spent caustic liquors at different petrochemical complexes in different countries (Horobin, 1994). However compounds such as ketone and 1,2 dichlorobenzene (1,2-DCB) were found resistant to WAO (Randal, 1981, Anon, 1984, Ellis and Canney, 1987).

WAO offers an important alternative to incineration for the destruction and detoxification of dilute hazardous and toxic wastewaters and in some cases for the recovery of inorganic chemicals as well as recovery of energy. Cost comparisons with conventional incineration indicate that WAO is somewhat greater in capital cost, but considerably less expensive to operate (Wilhelmi and Knopp, 1979; Heinbuch et al., 1985). A detailed comparison of WAO and incineration for toxic wastewater is given by Wilhelmi and Knopp, (1879).

2.5.4 Catalytic WAO

Chang (1990) has compiled an extensive review of literature relating to the use of catalysts in WAO. Many of the studies on catalytic WAO have been to reduce the levels of operating parameters such as temperature, pressure and retention time thereby decreasing energy costs. Destruction efficiencies are reported for specific compounds and catalysts under specified conditions. Homogeneous catalysts appear to be more active than non-homogeneous.

Heterogeneous and homogeneous catalysts both form intermediates with reactants, which results in an alternate reaction mechanism. This mechanism is favoured because the overall activation energy required by the catalytic reaction is less than that required by the noncatalytic reaction pathway. By this alternate mechanism, the catalyst participates in the reaction. To illustrate, reactant A may reversibly react with a homogeneous catalyst molecule or an active surface site of a heterogeneous catalyst particle, X, to form an intermediate. This intermediate will either undergo the reverse reaction or irreversibly react to form the product, P and the catalyst.

$$A + X \leftrightarrow AX \rightarrow P + X \qquad (2.3)$$

Unlike homogeneous catalysis, which is kinetically controlled, heterogeneous catalysis depends on mass transport and diffusion as well as kinetics. Heterogeneous catalysis reactions are dependent on the transport of reactants to, and products from, active sites on the catalyst surface. Three transport steps are required for a heterogeneous catalytic chemical reaction:

i) transport of A from the bulk phase into the bulk liquid,

ii) transport of A and B from the bulk liquid to the external surface of the catalyst particle and

iii) diffusion of A and B into the available active sites in the catalyst pores (Frisch and Gloyna, 1992).

Frisch and Gloyna (1992) reported that Imamura et al., (1982, 1986) studied the WAO of acetic acid, n-butylamine, PEG-200, pyridine and ammonia catalysed by homogenous $Cu(NO_3)_2$, Co/Bi (5/1) and Mn/Ce (7/3). In addition to the above, Imamura et al., (1982) also studied Co/Bi (1/1), Sn/Bi (1/1), Zn/Bi(1/1), Ni/Bi (1/1), Bi $(OH)_3$, for acetic acid oxidation. Chowdhury (1974) observed very little effect of different catalysts on wastewater destruction efficiency.

It is clear from the literature that a Mn/Ce catalyst has the highest catalytic activity irrespective of the type of compound oxidised and therefore it appears that Mn/Ce would be more effective for the treatment of wastewaters containing different organic and inorganic pollutants. Mn/Ce, chemically known as MnO_2/CeO_2, shows a high redox potential which suggests a radical destruction mechanism. Due to its nonselective nature, high activity and radical reaction mechanisms, Mn/Ce has highest catalytic activity (Frisch and Gloyna, 1992).

Soluble metallic compounds such as copper may present a toxicity problem in any biological process following WAO and may therefore require further treatment (Frisch and Gloyna, 1992).

2.5.5 Products of WAO and Removal Mechanism

Basic types of organic matter such as proteins, lipids, total sugar starch, and crude fibre are found in raw sludge and in partially oxidised sludge. As the degree of oxidation is increased (temperature, pressure, retention time), the basic classes of organic matter disappear rapidly. The cell structure is broken down and the water, along with cell chemicals, are released. Even at a low degree of oxidation the larger molecules are broken down, producing compounds such as amino acids, VFA, and simple sugars. The hydrolysis effects at the low degree of oxidation cause the resulting product to be readily dewaterable (Teletzke et al., 1967). The probable chemical reaction taking place in a WAO environment for organic matter can be described by the following equation:

$$C_aH_bO_c\,N_aS_eCl_f + O_2 \rightarrow CO_2 + H_2O + NH^{+}{}_4 + SO^{--}{}_4 + Cl^{-} \qquad (2.4)$$

(Source: Metcalf & Eddy, 1991)

The rate of oxidation to CO_2 and H_2O in the above equation is dependent upon the operating conditions (temperature, pressure and retention time) and the nature of the pollutants in the waste stream. It is clear from the above equation that organic nitrogen is converted into ammonia, sulphur into sulphate and halogens into their corresponding anions $\left(Cl\;\; Br^{-}, I^{-}, F\right)$ (De Bekker and Schwoyer, 1989). The ions remain in the aqueous phase and no SO_x and NO_x are produced. If metal is present it will be converted into its highest oxidation state (Dietrich et al., 1985; Klay, 1988).

In wastewater and sludge WAO, insoluble organic compounds are converted to simpler, soluble organic compounds which are then oxidised to carbon dioxide and water.

The effluent is characterised by a high ammonia and volatile acid content. Acetic acid is a residual organic compound prior to complete oxidation (Shanableh and Gloyna, 1992).

WAO or WO end-product quality and concentration were reported to be dependent upon the level of COD removal. Telezke et al., (1967) reported that protein was the most easily solubilized component of sludge, lipids, were converted to fatty acids and sterols and starch and glycogen were hydrolysed to sugars.

Wu et al., (1987) reported the formation of large quantities of volatile acids during the WAO of anaerobically digested sludge. The production of propionic , butyric and valeric acids decreased and acetic acid increased greatly at temperatures above 150°C. Slight acetic acid reduction occurred at temperatures above 225°C (Teletzke et al. 1967; Wu et al., 1987). Acetic acid oxidation was reported to be very slow below 270°C and very rapid at temperatures above 320 C (Foussard et al., 1989).

Sommers and Curtis (1976) reported that when treating sewage sludge at 200°C, more than 50% of the total nitrogen content was decreased and phosphorus was either decreased or unchanged. Wu et al., (1987) reported that at temperatures in the range of 150 C to 250°C, ammonia production was observed to increase with increased reaction temperature, nitrate decreased with increased temperature, the nitrite concentration was low over the entire temperature range and soluble organic nitrogen was increased above 200°C. Fyfe (1992) reported that phosphorus greatly decreased while treating sewage sludge. Wu et al., (1987) suggested the reduction of phosphate level was caused by the formation of calcium and magnesium phosphate salts in the solid phase. Shanableh and Gloyna, (1992) reported that temperatures below 500°C were not sufficient to oxidise ammonia from urea.

Helling and Jefferson (1988) reported that at a temperature below 525°C, ammonia did not oxidise at a measurable rate.

Wu et al., (1987) reported that the effluent pH was slightly alkaline but became acidic as the reaction temperature increased. Metals such as Cd, Mn, Ni, Pb, and Zn were not found in any appreciable amount in the WAO liquor. It was concluded that WAO does not affect metal oxidation over temperature ranges of 200°C to 270°C. Sommer and Curtis (1976) observed the same results but reported high concentrations of metals in settled residues. Friedman et al., (1988) reported that at 230°C the percentage of metals that concentrated in the settled residues was 64% for Ni, 52% for Cd, 94% for Cu, 66% for Pb, 74% for Cr, and 96% for Zn. All the metals, with the exception of mercury, were concentrated in the ash residue, only Fe was found in appreciable concentration in the aqueous phase (Fyfe, 1992).

Fyfe, (1992) reported that n-alkanes was unreactive to WAO, PAH was significantly decreased but the carbazole concentration increased by a factor of 650 while treating raw primary sludge at 280 C. Fyfe (1992) also reported that the lipid constituents aliphatic alcohol and long chained carboxylic acid, appeared highly resistant to WAO. Steroidal alcohol, in particular the faecal sterol coprostanol, appeared less resistant to WAO as compared to the long chained aliphatic alcohols. The reason given by Chaudhary (1976) for the presence of alcohol in WAO liquor was the oxygen starved system. Friedman et al., (1988) reported the presence of formaldehyde in WAO liquor at a temperature of 270°C with concentrations as high as 117 mg/l. Hurwitz and Dundas (1960) reported that the exhaust gas content was mainly CO_2 and nitrogen. Trace hydrocarbons were detected, which exhibited a slight odour of pyridine.

2.5.6 WAO Liquor Strength

The WAO process has been used for different wastes with different aims and objectives as discussed earlier in this chapter. In the case of sludge, heat treatment has the primary objective of increasing the filterability of sludges but in the case of industrial wastewater it is either intended as a complete treatment process for the destruction of toxic and hazardous wastewater or as a partial treatment of the influent stream for inorganic chemical recovery (Flynn, 1976; Wilhelmi and Knopp, 1979). The WAO liquor strength depends upon the influent pollutant and operating parameters.

The cost of disposing of the liquor could add significantly to the overall cost of heat treatment. In the case of sewage sludge it would be advantageous if the process could be operated so that the strength of the liquor is minimised whilst, at the same time, the sludge is adequately conditioned.

Substantial organic and solids loading to treatment facilities by recycle liquors from sludge thermal conditioning has been reported by Heyda et al., (1980). Boyle and Gruenwald (1975) reported that the material balance on the heat treatment system showed that 21% of the BOD_5 and 30% of the SS influent to a 1314 l/sec treatment plant were due to recycle liquor. There was also an increase in colour and turbidity in the plant effluent.

The properties of the decant liquor from WAO are presented by Sommers and Curtius (1976). They found high concentration of volatile solids in the decant solutions. Soluble organic nitrogen in the decant liquor was greatly increased, while almost all ammonia was present in the soluble form. The solid content of decant liquors was varied and was a function of the settling time after the effluent had entered the settling tank. The data collected by Sommers and Curtis (1976) indicated that significant quantities of nitrogenous compounds would be recycled to the head of the treatment plant while phosphorus and metals could be concentrated in the treated sludge. The WAO effluent liquor is high in COD (Friedmann et al., 1988) and contained significant amounts of VFAs (Brooks, 1970).

Randal and Knopp, (1980) reported the liquor strength after the WAO of toxic compounds such as acenaphthene, acrolein, acrylonitrile, 2-chlorophenol, 2, 4-dimethylphenol, 2,4-dinitrotoluene, 1,2-diphenylhydrazine, 4-nitrophenol, pentachlorophenol, and Miller et al., (1980) studied 2, 4-D, glycolic acid, pentachlorophenol, ethylene dibromide, malathion, aroctor 1016 and 1254, and dioxin and found that the process produces effluents with very low levels of pollutants in the parts per billion range in the decant liquor. They further reported that the WAO liquors of the above compounds were low molecular weight compounds such as formic and acetic acid.

2.5.7 Settling and Dewatering Characteristics of WAO Liquor

Hurwitz and Dundas (1960) conducted a pilot-plant study at temperatures in the range of 253 C to 272°C and VS concentration in the range 2.39% to 4.57% and within one hour retention time the effluent had settled to a final volume of 98 ml/l to 116 ml/l. Brooks (1970) reported that the improvement in filterability and settlability were functions of both reaction temperature and holding time. Wu et al., (1987) reported that the settlability improved as the temperature increased. At 7% TS, and a temperature of 275°C, the effluent settled to half the original volume in 30 min, using a 250 ml cylinder. Friedman et al., (1988) reported that the WAO of anaerobically digested sludges reduce the volume of sludges by 90% at temperatures in the range 190°C to 270°C and a settling time of 18 hours.

Hanahan et al., (1960) suggested that proteins and lipids, were bound together by several forces. Those force include hydrogen bonding and stearic formation. The bond between water, protein /lipid structure are ice like (tetrahedral) structures and hydrogen bonding. Teletzke et al., (1967) reported that the hydrolysis of protein and lipid by WAO probably accounted for the increased filterability of sludge.

Heat treatment reduces the specific resistance to filtration of all types of sludge. Hurwitz et al., (1960) reported that the specific resistance of WAO liquor was below $4 \times 10^8 s^2 / g$ at all levels of COD removal in the range of 20% to 83%. Specific resistance values of typical raw primary, raw activated and digested activated sludge were $8 \times 10^9 \; s^2 / g$, $1.87 \times 10^{11} s^2 / g$, and $2.17 \times 10^1 \; s^2 / g$ respectively. Similar results were also observed by Brook (1970). Friedman et al., (1988) achieved a sludge volume reduction of 98°o while using a combination of settling and vacuum filtration at temperatures of 190°C to 270 C. After two hours of settling the wet effluent ash constituted approximately 10% to 15°o of an original activated sludge solid volume (Shanableh and Gloyna, 1992).

2.5.8 Kinetic Studies on WAO of Wastewater and Sludges

Kinetic studies on the WAO of many organic compounds of different wastewaters and sludges have been reported. Day et al., (1973) carried out a kinetics investigation of propionic acid, Taylor and Weygandt (1974) studied the kinetics of selected soluble alcohols, ketones, and acids at temperatures and pressures below 250°C and 136 bar. The WAO of ketones and alcohols exhibited first-order reaction rates. WAO models for phenol and nitrilotriacetic acid (NTA) were developed to describe the effects of pressure, temperature and retention time (Pruden and Le, 1976). Baillod et al., (1979, 1985) reported the kinetics, of phenol and 2-chlorophenol. They also proposed the free radical mechanism to represent the oxidation steps of organic matter in a WAO reactor. Foussard et al., (1989) studied the WAO kinetics of waste streams that included paper mill black liquor, acidic wastes, carboxylic acid and biological sludges. Wu et al., (1987) reported that the relationship between the VS destruction of digested sludges and retention time could be expressed as a cumulative normal distribution function as shown in equation 2.5.

$$Z = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-1/2\left(\frac{T - T'}{\sigma}\right)\right] \tag{2.5}$$

Z = fraction of oxidizable VS destroyed;

σ = standard deviation;

T temperature; and

T = mean temperature at which 50% destruction occurs.

WAO or WO of wastewater and sludge proceeds through thermal decomposition and oxidation. A model for thermal decomposition of sludge was developed by Takamatsu et al., (1970). Their model was based on the fact that solid matter was decomposed into the soluble form through both thermal decomposition and oxidation in WAO (Teletzke et al., 1967). Using an Arrhenius-type non-linear regression technique, first-order reaction rates were given to the reaction pathway.

Ikeda (1972), Taylor and Weygaudt (1974), Pujol (1978), Joglekar et al., (1991), Shanableh and Gloyna (1992), observed a first-order reaction rate to apply to the oxidation of organic compounds. First-order reaction rates with respect to the oxidation of organic compounds was observed by Ploos and Rietema (1973), Foussard et al., (1989), Shanableh and Gloyna (1993) to model sludge oxidation under WAO conditions.

The effect of temperature and pressure were integrated in the reaction constant k_a and k_b (equation 2.6 and 2.7). Sludge was divided into three components (Ploos and Rietma, 1973). The three components were:

(i) easily oxidised (a),

(ii) difficult to oxidise (denoted by b) and

(iii) non oxidizable.

The reaction kinetics were expressed as shown in Equation 2.5 and 2.6

$$\frac{da}{dt} = -k_a.a \qquad (2.6)$$

$$\frac{db}{dt} = -k_b.b \qquad (2.7)$$

The reaction constants were summarized as shown in Table 2.4. The easy to oxidize component of sludge was estimated to be 60^{0}o (Foussard et al., 1989) and others can be find else where.

Table 2.4 Kinetic Constants for Biological Sludge Oxidation (Foussard et al., 1989)

Oxidized Compound	Temp (°C)	P_{O2} (MPa)	$10^3 \times k_a (s^{-1})$	$10^3 \times k_b (s^{-1})$
Run 1 (Sludge)	255	2.2	0.7	------
Run 2 (Sludge)	294	3	2.7	0.11
Run 3 (Sludge)	298	5.3	11	0.21
Run 4 (Sludge)	325	6.2	30	0.28
2-butanol[a]	257	2.5	0.8	---
Sodium acetate[b]	302	5.5	----	0.225
Sludges[c]	255	0.65	28.6	1.9
do.	290	0.44	80	3.52

[a] Taylor and Weygandt (1974); [b] Foussard et al., (1989); [c] Ploos and Rietema (1973)

Although Shanableh and Gloyna (1992) and others have proposed simple and comprehensive models, the applicability of mathematical models outside the experimental conditions where they were developed is still rather doubtful and these models for WAO are no exception (Noone, 1994).

2.6 TREATMENT OF WAO LIQUOR

It is apparent that during WAO, the complex molecules which make up the organic portion of the sludge are broken down to their simpler, usually soluble constituents. The liquor obtained contains suspended solids and simple and complex dissolved organics which exert BOD_5 and COD. In the past the following four treatment techniques have been used for heat treated liquor:

i) adsorption (activated carbon),
ii) chemical oxidation (e.g. ozonation),
iii) chemical coagulation (lime treatment), and
iv) biological treatment.

i) and ii) are very expensive and not very effective, especially when treating liquors which contain high suspended solids. Activated carbon can be used for liquor which often contains hazardous organic compounds (McEldowney et al., 1993). Chemical coagulation can be used for liquor treated at low temperature (<200 ° C) especially the decant liquor from raw and digested sludge which often contains heavy metals and suspended solids.

Biological processes are the most widely used since they are cost effective and can be easily and effectively used for a variety of heat treated liquors.

2.6.1 Chemical Treatment of Heat liquor

Most of the COD/BOD_5 of heat treated liquor is treatable by biological means, but other methods must be adopted either instead of, or in combination with, biological treatment if the liquor is to be completely relieved of its COD or other organic compounds. Evaporation removes most forms of organics from liquor and the distillate can be purified by biological treatment. However, evaporation is very expensive, a disadvantage which also applies to the use of activated carbon (Everett, 1971).

Table 2.5 Chemical treatment of WAO liquor

Chemical	Reactant	%BOD,COD, Colour removed	Reference
Ozone	Primary sludge	10-20%, 50%(colour)	Cutforth, 1991
Alum	Primary sludge	ineffective (BOD & COD)	Cutforth, 1991
Alum+ Cationic Polyelectrolytes	Primary sludge	marginal removal (BOD & COD)	Cutforth, 1991
Lime	Primary and waste activated sludge	11-38 (BOD)	Heyda, 1980
$Al_2(SO_4)_3$	Sewage sludge	44 (COD)	Everett, 1971
A.C.H	Sewage sludge	60 (COD)	Everett, 1971
$FeCl_3$	Sewage sludge	15 (COD)	Everett, 1971
Lime	Sewage sludge	10-80 (COD)	Everett, 1971
$FeSO_4$	Sewage sludge	Ineffective (COD)	Everett, 1971
Polyelectrolyte	Sewage sludge	Ineffective (COD)	Everett, 1971
Activated carbon	Sewage sludge	100 (COD)	Everett, 1971

Other than biological treatment, chemical treatment of thermally conditioned sludge recycle liquors with different chemicals has been explored by many researchers as a method of reducing their impact on wastewater treatment plants. Some of the chemicals tried by different researchers are listed in Table 2.4. Heat treated liquor treated with ozone and chemical coagulation using alum has been considered inappropriate and the use of pre-ozonation before anaerobic digestion, or micro ozonation before chemical coagulation has been suggested by Cutforth, (1991). Heyda et al., (1980) conducted research on heat liquor from wasted activated sludge with lime and reached the following conclusion:

i) at pH 11.5, higher removals of BOD_5 and COD were achieved,

ii) removals of phosphorus, ammonia nitrogen and organic nitrogen were 99%, 27%, and 69% respectively,

iii) SS removal of 94.4% was obtained at pH 9.5 and above,

iv) colour and turbidity was greatly reduced from 4250 to 380 °H and 100 to 3 NTU respectively, and

v) nearly all classes of heavy metals were removed at pH 8.5 and above.

Everett (1971) studied raw heated and biologically treated heat liquor with different chemicals as shown in Table 2.5 and tried to remove almost all COD of the liquor. Everett (1971) suggested that biotreatment followed by activated carbon can remove almost 100% of the SCOD of heat treated liquor.

2.6.2 Biological Treatment of WAO Liquor

Although much research work has been carried out on the biotreatability of WAO liquor, incredible though it seems, even in 1995, there was considerable uncertainty concerning the biodegradability of heat treatment liquor (Noone, 1994). This is in spite of the fact that the process has been in operation for well over 50 years.

Although the volume of the heat treated liquor is usually small its effects on the treatment plant are significant. Additional treatment demanded by heat treated liquors may result in over loading of those plants without sufficient excess capacity to accommodate these additional loads. For other biological treatment plants that have not yet reached their design loadings heat treatment liquor loads may force premature expansion or in the case of direct sewer discharge concentrated heat liquors may be prohibited.

In the past much research has been carried out concerning the optimum processing parameters for heat treatment systems. Additional research devoted to the evaluation of heat treatment liquor treatment is required, consequently this thesis also addresses the operation and performance of separate treatment for heat treated liquor using both aerobic and anaerobic biological process which has been inadequately investigated by previous research workers.

(a) Aerobic Treatment of WAO liquor

Lumb and Barnes (1944), Hirst et al., (1971) considered the use of biological filters to treat diluted heat treatment liquor. The highest BOD_5 loading applied to a conventional filter medium was 0.3 kg BOD_5/m^3.day with 65% removal. A BOD_5 removal of 82% was achieved at a loading of 0.14 kg BOD_5/m^3.day. Lumb and Barnes (1944) used humus tank effluent for dilution of the heat treatment liquor while Berridge and Brendish (1967) and Hirst et al., (1971) used settled sewage for the dilution. Berridge and Brendish (1967) reported results with BOD_5 loading varying from 1.6 to 3.7 BOD_5 kg/m^3.day with a removal ranging from 20 to 93.5%. The proportion of BOD_5 in the feed due to the heat treatment liquor varied from 29 to 69%. Brooks (1968) showed that liquors from WAO plant can be treated biologically. Erickson and Knapp (1972), applied a COD loading of 36 kg COD/m^3.day and 7 kg COD/m^3.day and achieved a removal of 76.5% and 83.6% respectively.

Boyle and Gruenwald (1975) used activated sludge and a biological filter for the treatment of heat treatment liquors and achieved an average effluent BOD_5 of 9 mg/l and 15 mg/l suspended solids but with a high colour. Heyda et al., (1980) used activated sludge for the treatment of WAO liquor (sewage sludge) treated at 150°C to 190°C. They used the following operational criteria for the activated sludge process:

(i) organic loading to aeration tank 1.6 to 2.4 kg BOD_5/m^3.day,

(ii) F/M, 0.4-1 (kg BOD_5/kgMLSS.day)

(iii) MLSS, 4000-5000 mg/l,

(iv) DO, 2-4 mg/l, and

(v) average mean cell residence time 1.3 days.

On the basis of the above design parameters, the following results were claimed:

i) BOD_5 reductions averaged 93% with influent concentrations of 1500-3500 mg/l. Effluent BOD_5 concentration ranged from 10-560 mg/l,

ii) COD reductions averaged 76% with influent concentration of 2800-7600 mg/l. Loadings to the system were in the range of 2.5-4.5 kg COD/m^3.day. Effluent COD concentrations ranged from 340-1930 mg/l

iii) average removal for phosphorus were 89% average ammonia nitrogen and organic nitrogen removal were 66% and 62% respectively,

iv) SS reduction averaged 88% with influent concentration from 600-2000 mg/l,

v) the cell growth coefficient for the recycle liquor generated for this project was determined to be 0.49 kg VS produced/kg BOD_5 removal

vi) the cost/tonnes of BOD_5 removal was $ 370.09.

Leglise, (1981) used the biocarbon system (activated carbon filter). This was a submerged, fixed granular bed, and was continuously fed at the top with the heat liquor to be treated. Air was supplied at the lower part of the bed leaving on undisturbed layer for the removal of SS. The heat liquor was completely treated in one step without secondary clarification, at a loading rate of 6 and 18 kg COD m^3.day, giving removals of 85% and 55^{0}o respectively.

(b) Anaerobic Treatment of WAO Liquor

Anaerobic digestion is the most commonly used process for stabilising high strength organic wastes and has several advantages over other available methods. In addition to a high degree of waste stabilisation, other advantages include; low production of sludge; no oxygen requirement; low nutrient requirement; and production of methane as fuel (Anderson, 1993).

Haug et al., (1978) reported on WAO of waste activated sludge (WAS) treated at 177 C with a retention time 30 min and TS 3%. 60 to 70% of SS were solubilised. The decant liquors were treated by an upflow anaerobic filter. The reduction of BOD_5 and COD were 85% and 76% respectively. Haug (1977) also concluded from this study that potential advantages of the thermal treatment followed by anaerobic digestion of the liquor process include: improved biodegradability; improved dewaterability of the sludge; no separate side stream treatment; net energy production; odour control and sterilisation. Thermal pre-treatment of activated sludge followed by anaerobic digestion resulted in an increase of 60% in methane yield and a 36% decrease in effluent VSS, but in the presence of toxic heavy metals the production of methane could significantly reduce (Hickey et al., 1989)

Vollstedt (1978) studied six different media, including two types of rock, two types of activated carbon, and two types of plastic media to establish the effects of medium size and material. Excellent results were obtained with a 1.2 meter anaerobic packed bed (APB) using 1.58 cm Pall-rings. At a loading of 14.7 kgCOD/m^3-day, 78% BOD_5 removal and 58% COD removal resulted. The anaerobic filter treatment of the thermal conditioning wastes reflected ultimate BOD_5 removals of 84% when operating at a loading of 3.21 kg BOD_5 /m^3.day (Dague et al., 1980). The pilot-plant demonstrated a 78% COD and 80% BOD_5 removal using a design of 1.5 days detention time, a loading rate of 7.1 kg/m^3.day, with the anaerobic filter at 35°C. The gas produced contained 65% to 70% methane. It was suggested that an anaerobic filter for heat treated liquor could be more cost effective than an aerobic process (Salotto, 1981).

Leglise (1981) reported a range of loading rates and removal efficiencies for the anaerobic digestion of heat treated liquors. At 6 kgCOD/m^3.day and 13 kgCOD/m^3.day the removal efficiencies were 85% and 40% respectively. Similar results were achieved by Crawford et al., (1982) and Pinnekamp (1989), while using a packed bed anaerobic biological processes for the treatment of heat treated liquor. Stuckey and McCarty (1984) conducted a research project on waste activated sludge treatment at 175°C followed by anaerobic digestion. They made the following conclusions from their studies.

i) mesophilic bioconvertibility and toxicity were found to be higher than the corresponding values under thermophilic condition. This difference was due to kinetic factors, different microbial populations or both,

ii) bioconvertibility was independent of retention time. However, for toxic compounds longer retention times tended to result in increased bioconvertibilty, possibly due to acclimatization to toxicity, organism selection or enzyme induction,

iii) the toxicity of waste activated sludge (WAS) was due to its solubilization at low temperature, followed by conversion of these soluble products to toxic compounds under more extreme treatment conditions, and

iv) heat treatment changes simple nitrogenous compounds into toxic nitrogenous compounds.

Friedmann et al., (1988) treated WAO liquor anaerobically. They reported failure of the anaerobic digester repeatedly, due to presence of inhibitory substances in the heat treated liquor. The inhibitory substance identified by them was formaldehyde. They reported that 117 mg/l of formaldehyde was in the liquor at a reactor temperature of 270°C. They also reported that the liquor obtained from 230 C and above was very difficult to treat anaerobically. Temperatures above 230°C generated toxins, whilst temperature below this resulted in less VSS destruction and hence more residual solids. Presence of 40 mg/l or more of formaldehyde in an anaerobic environment has inhibitory effects. Cutforth (1995) reported a reduction of 70% COD and 90% BOD_5 at an OLR of 0.5 kg/ m^3.day and a HRT of 50 days, while treating WAO liquor anaerobically.

2.7 SUMMARY OF LUDUVICE'S WORK

The purpose of Luduvice's (1992) research project was to examine the effectiveness of the wet air oxidation (WAO) process at low oxygen overpressure in the destruction of raw primary sludge, anaerobically digested sludge, thickened activated sludge as well as sludges originating from the biological treatment of industrial wastewaters namely a paper repulping plant, and brewery and milk processing plant. Air was used as the main oxidising agent. The main objectives of Luduvice's (1992) work was to:

i) investigate the effects of operational parameters such as temperature, retention time and air overpressure during the destruction of organic compounds in selected sludges,

ii) investigate the concentration of soluble chemical oxygen (SCOD) demand generated during WAO of each of the selected sludges,

iii) investigate the effects of the operational parameters described above on the mass and volume reduction of the different sludges, and

iv) examine the physical and chemical characteristics of the effluent liquor from each sludge.

Luduvice's used seven different temperatures (180, 200, 220, 240, 260, 280, 300 ^{0}C), three different retention times (30, 60, 120 minutes), and two operating pressures (1 and 2 MPa) for each of the organic sludges under consideration. He also carried out catalytic studies using hydrogen peroxide and metallic catalysts (Cu, Fe) in the WAO system in order to improve the destruction of the organic matter and at the same time reduce the level of operating parameters such as temperature, pressure and retention time. The following conclusions were made by Luduvice (1992) from the investigation on the treatability of different organic sludges under wet air oxidation at low air overpressure.

i) low oxygen overpressure WAO proved to be an effective treatment of organic sludges although the limitation in the availability of oxygen produced oxidation results below those reported in the literature for conventional WAO. It is recommended where a high degree of oxidation is not required, reducing capital and running costs. The process also proved to be reliable and capable of handling differences in sludge composition without problems.

ii) the reaction process inside the reaction vessel was found to proceed in two stages: hydrolysation followed by oxidation.

iii) odour and the high concentration of soluble organics in the effluent liquor proved to be the main drawbacks of the process. The former was common to all effluents at different levels and was particularly strong while the effluents were warm. The significant generation of soluble chemical oxygen demand produced an effluent liquor of high oxygen demand. Most of the SCOD was formed from low molecular weight volatile fatty acids with acetic acid in most cases accounting for over 60% of the total VFA concentration, indicating a large potential for biological treatment.

iii) temperature proved to be the critical parameter with retention time of more limited influence. The combination of low temperature and low retention time produced, in many cases, a significant increase in the TCOD concentration of the effluent. A TCOD increase of up to 50% was observed when treating raw primary sludge. An increase in temperature was usually associated with a reduction in the TCOD of the sample.

iv) catalyst systems based on hydrogen peroxide and metal ions failed to produce any improvement in the total oxidation of any of the sludges tested. Its influence was limited to the increase in settleability of effluents treated at temperatures below 220^0C. It also had the disadvantage of producing an effluent liquor of low pH (<4) and increased the concentration of heavy metals in the residual sludge. The use of hydrogen peroxide produced an effluent liquor with less odour.

v) settleability proved to be extremely effective as a solids/liquid separation method for WAO effluents. Apart from the effluent from the dairy wastewater treatment plant sludge, all others were readily settleable and complete separation was normally achieved within twenty minutes for sludges treated above 240^{0}C. Residual solids occupied wet volumes of less than 10% of the original sludge solids for all sludges. Temperature was the main parameter influencing settleability, although retention time played a significant role at low temperatures. Flotation is recommended as a solid/liquid separation method for WAO effluents of dairy wastewater treatment plant sludge.

vi) raw primary sludge was readily oxidised during WAO treatment with TCOD reductions of up to 60% being obtained. It also produced an odourless, readily settleable, tar-like residual solid of high stability. Solids reduction was also very high, reaching over 70%. However the odour released by the effluent liquor while warm, was extremely offensive and by far the strongest of all the effluents produced.

vii) TCOD destruction depended on the sludge, with results varying from 80% for return activated sludge to less than 30% for the brewery wastewater treatment plant sludge.

viii) SCOD followed a similar pattern for all sludges, increasing during the heating-up period and showing a small reduction after retention time above one hour.

ix) total solids (TS) and volatile total solids (VTS) were significantly affected by the process. The raw primary sludge TS concentration was reduced by over 70%, while the sludge from the dairy wastewater treatment plant only achieved a reduction in TS of approximately 20%. The results for the other sludges fell with this range.

x) filterability was greatly affected by the process, with results for capillary suction time (CST) for all effluents being normally below 10 seconds.

xi) acetic acid was the main intermediate product of the process accounting for between 60 - 80% of all the VFA generated. However for dairy wastewater treatment plant sludge, butyric acid was the main intermediate product accounting for around 60% of the VFA concentration present in the effluent liquor.

xii) all sludges were somehow affected by WAO. Raw primary sludge proved to be the most affected while the brewery wastewater treatment plant sludge was the more resistant to the treatment.

A total of 176 WAO tests were carried out by Luduvice on the above cited six sludges, with an average of approximately 21 tests on each. No repetition of any experiment has been observed in his work.

2.8 DETERGENTS

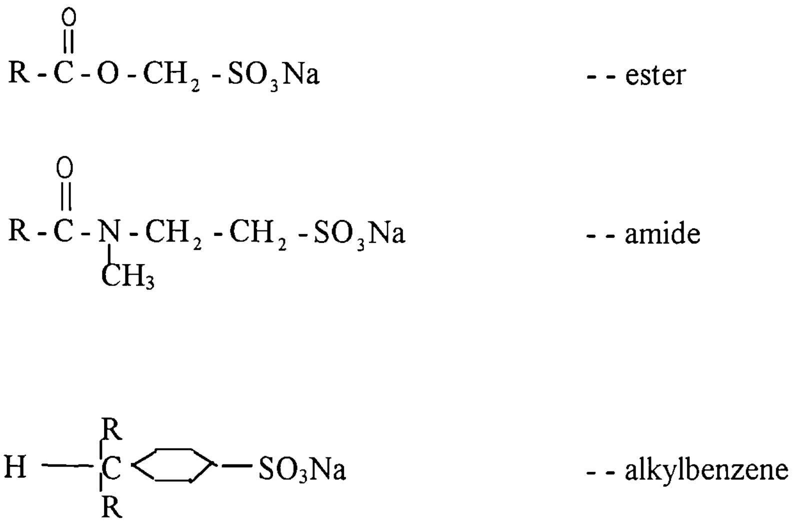
2.8.1 Introduction

Detergent is a surface active agent which can be regarded as a potential pollutant. In general, most detergents are surface active agents, but not all surface active agents are detergents. All surfactants have rather large polar molecules. One end of the molecule is particularly soluble in water and the other is readily soluble in oils. The solubility in water is due to carboxyl, sulfate, hydroxyl, or sulphonate groups. The surfactants with carboxyl, sulphate, and sulphonate groups are all used as sodium or potassium salts (Sawyer and McCarty, 1978). Myers (1988), states that the characteristics for surfactants must be evaluated for detergent application, which are of low c.m.c (critical miscelle concentration), good salt and pH stability, and display biodegradability and good foaming properties. Kelley (1971) reported that until 1940, the use of detergents was limited, and that soap was the dominant cleansing material. The wastewater treatment industries worldwide, and especially in the UK, are now considering recommending to legislative bodies that they should not be too severe on discharges containing detergent (Noone, 1995). Srinivasan (1984), stated that the trend is towards lower soap usage and higher detergent usage in the USA and Europe in contrast to the more dominant position of soaps in Africa and Asia.

2.8.2 Anionic Detergent

An anionic detergent product is one which produces negatively charged surface-active ions in solution. It is derived from sulphonate, sulphate or carboxyl groups. The sodium salt is the most widely used surfactant in industrial and high foaming household detergent (Rosen, 1989, Holbrook, 1995). Sodium salts of sulphates and sulphonates are the most common anionic surfactant. The sulphonates, used for modern detergents, are mainly derived from esters, amides and alkylbenzens (Fig. 2.6).

Unilever use alkylbenzene sulphonates for detergent manufacture (Holbrook, 1995) which are prepared by treating the parent alkylbenzene (from petroleum) with sulphur trioxide sparging. This reaction gives rise to sulphuric acid which is then neutralised to form the sodium salt (Fig. 5.8). Sparging by SO_3 is a very complex process which also gives rise to the formation of dioxane (diethylene dioxide), which is highly undesirable, especially in shampoo manufacture (Holbrook, 1995).



$R-\overset{O}{\overset{\|}{C}}-O-CH_2-SO_3Na$ -- ester

$R-\overset{O}{\overset{\|}{C}}-\underset{CH_3}{\underset{|}{N}}-CH_2-CH_2-SO_3Na$ -- amide

Fig. 2.6 Anionic Sulphonate Surfactants

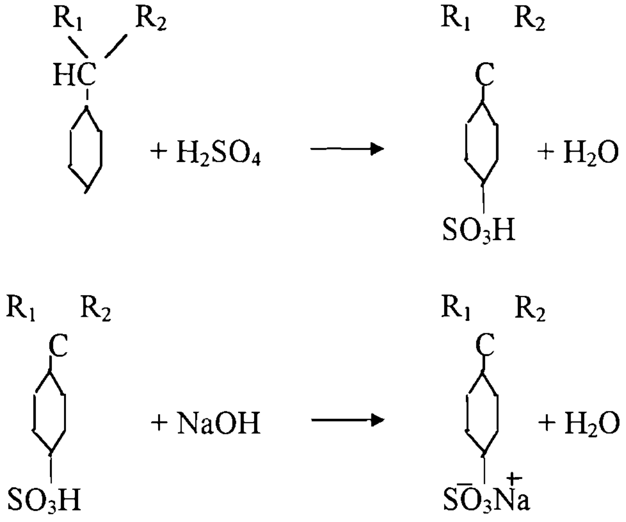
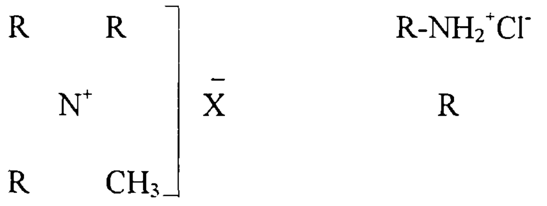


Fig. 2.7 Synthesis of alkylbenzene sulphonate

2.8.3 Cationic Detergent

A cationic detergent produces a positively charged surface-active ion in solution. There are two main types of cationic surfactant, cationic surfactants which consist of long-chain primary, secondary, and tertiary amines, and cationic surfactants of quaternary ammonium compounds. Cationic detergent are weak in detergent power and more expensive than anionic and non-ionic. Cationic detergent have other properties such as fabric softening, water repelling properties, foam depressant and corrosion inhibiting effects. Compounds that have been used as fabric softeners have a quaternary ammonium structure, with R being a hydrophobic, long alkyl chain derived from fatty acids or petro chemical source (Osborn, 1982, 1986; Holbrook, 1995).



(I) (II)

Fig. 2.8 Quaternary ammonium structure of cationic surfactant.

The cationic detergent wastewater used in this study was HEQ (Fig. 2.7, II). The anions of cationic surfactactant are usually halogen for example dodecyltrimethylammoium bromide CH_3-$(CH_2)_{11}$-N-Br.

$$CH_3\text{-}(CH_2)_{11}\text{-}\underset{(CH_3)_3}{N}\text{-}Br$$

2.8.4 Biodegradability of Detergent

Biodegradation of detergent is defined as the oxidation of detergent by microorganisms. There are three kinds of results from biodegradability testing, primary biodegradation, ultimate biodegradation, and environmentally acceptable biodegradation. When detergent molecule oxidised by microbial action to such an extent that those characteristics properties are no longer evident from analytical procedures. Complete or ultimate biodegradation is the one in which complete conversion of the detergent molecules to carbon dioxide, water, inorganic salts, and products associated with the normal metabolic process of the microorganisms. Environmentally acceptable biodegradation is biodegradation to the minimum value necessary to remove undesirable properties of the detergent such as foaming etc. Surfactant concentration in the order of 4 to 5 mg/l interfered with flocculation with the floc floating to the surface instead of settling in the sedimentation tank (Nichols and Koepp, 1961).

Myers (1988) developed the following general rules for the detergent biodegradation:

i) the chemical structure of the hydrophobic group is the primary factor controlling biodegradability, whilst the nature of the hydrophilic group has a minor effect on biodegradability,

ii) the greater the distance between the hydrophilic group and the terminus of the hydrophobic group, the greater is the rate of primary degradation.

Soaps and the sulphated alcohol are readily used as bacterial food. Detergent vary greatly in their biochemical behaviour, depending on their chemical structure (Sawyer and Ryckman, 1957). The detergents with ester or amide linkages are readily hydrolysed. The fatty acids produced serve as sources of bacterial food. The other hydrolysis product may or may not serve as bacterial food, depending upon its chemical structure (Sawyer and McCarty, 1978).

(I) Aerobic Biodegradation of Detergent

Most of the detergents can be easily degraded aerobically. The ability of organisms to degrade detergent depends on the type and structure of the detergent molecule for example a branched-chain detergent molecule (ABS) is more difficult to degrade than a straight-chain (LAS). Linear alkylbenzene sulphonate (LAS) is readily biodegradable at a rate comparable to the other biodegradable organic components in sewage (Swisher, 1967). In activated sludge process, Knopp et al., (1965) investigated that alkylbenzene sulphonate (ABS) which has branched chains could be reduced by up to 85%, but the LAS was reduced by 99%.

Anionic detergents like alkane sulphonates, ester and amide sulphonates are readily biodegradable although their common impurities, principally non-linear analogues, are metabolized more slowely (Pandia, 1990).

Cationic detergent can be degraded aerobically. Sullivan, 1983 investigated that cationic surfactants were biodegradable. The intermediate prodcuts were short lived and biodegraded to carbon dioxide. By varying the position of the ^{14}C label, it was shown that all carbon positions were approximately equally susceptible to ultimate degradation.

It has been reported in the literature that aerobic biodegradation of ABS, LAS and cationic detergent are very high due to the pesence of enzymes such as mono-oxygenases and dehydrogenases which are believed to be involved in the aerobic degradation of ABS, LAS and cationic detergent (Knopp et at., 1965; Cain, 1981; Sulliven, 1983). However, under anaerobic conditions, such enzymes are not able to function due to the absence of oxygen (Little and Williams, 1978).

Punchiraman and Hassan (1986) reported that the alkyl chain of the branched ABS is not known to be degraded under anoxic conditions, however the benzene ring could be partially degraded (Taylor et al., 1970).

For the alkyl sulphate surfactant type, the removal of the sulphonate group from the LAS is an important step in their biodegradation because the sulphonate group is far more stable biologically than the sulphate (Holbrook, 1995). The probable biological degradation of LAS by reported by Pandia (1990), is shown in Fig. 2.7.

Pandia (1990) reported that an alkylbenzene sulphonate has three likely points of metabolic attack: the alkyl side chain, the sulphonate group on the ring, and the ring it self. Swisher, (1963) found that the terminal methyl group of the alkyl side chain is initially attacked by bacteria. Alkane sulphonate, ester, and amide sulphonates are readily biodegradable, although their non-linear structure, metabolised very slowly (Pandia, 1990).

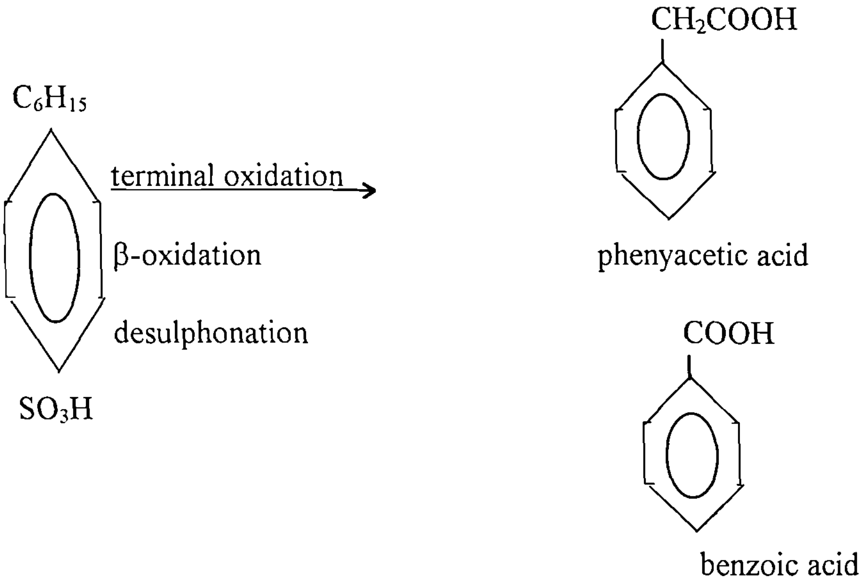


Figure 2.9 Bacterial Degradation of LAS (source: Pandia, 1990)

Anionic detergents in the presence of cationic detergents are less toxic to biological process than each alone. Anionic surfactants which are usually present in wastewater at a higher level than that of quaternary ammonium compounds form stoichiometric complexes and this reaction by itself may reduce or even eliminate toxicity (Pandia, 1990).

(II) Anaerobic Biodegradation of Detergent

It has been reported in the literature that for ABS (alkylbenzene sulphonates) in concentrations of 1000 mg/l an anaerobic digester performed well and showed no inhibitory effects on the anaerobic system (Punchirman and Hassan, 1986). An anaerobic digester inhibited by anionic detergents was recovered by adding catatonic long-chain aliphatic amines (Swanwick and Shurben, 1969). Like ABS, linear alkylbenzene sulphonates (LAS) are also resistant to biodegradation under anaerobic biological systems (Pandia, 1990).

2.8.5 Detergent Nuisance

The presence of detergent in a river water can lead to a reduction in the rate of reoxygenation. This will reduce the rate of self-purification of the river and have an unfavourable effect on fish and other animal life in streams. The toxicity levels of LAS, to aquatic organisms are in the range of 0.1 to 8.2 mg/l; the longer chain lengths of LAS, the higher the toxicity (Brown et al., 1978). Eyanoer et al., (1985) found that the toxicity of detergent (LAS) to fish (Puntius gonionotus Bleeker) varied considerably according to the hardness of the water.

Phosphate compounds, for example sodium tripolyphosphate (STTP) which is used in detergent, may contribute to nutrient levels of water bodies may cause eutrophication. When phosphate exceeds 0.1 mg/l it sustains algal growth and 1 mg/l of phosphorus will permit a lush algal growth (Pandia, 1990).

2.9 SUMMARY

As environmental awareness increases, it will make it difficult to discharge pollutants to the environment without treatment. New and improved technologies can only be based on knowledge of a large number of variables for each situation. These variables can be grouped as: legislative requirements, environmental impacts, economics, and technical feasibility. Meeting all these criteria will often mean that no single technology will be sufficient to completely alleviate the problems. Hence mixed technologies can often be employed. Industrial wastewater which is often very difficult to treat by conventional treatment and the large volumes of sludge produced by the wastewater industry open up the potential for wet oxidation, which is very effective in destroying many hazardous organic wastes, and also very effective in reducing the volume of sludge. The decant liquor which is often very concentrated and contains low molecular weight organic compounds, mostly acetic acid, can be treated by any biological treatment. In the past very little work has been done on the comparative biotreatability of the heat treatment liquor such as which biological process would be best suited for a particular waste stream.

CHAPTER 3

AIM OF STUDY

A number of wastewater treatment facilities throughout the world are using thermal conditioning as a sludge processing method. The final product of this process is a highly concentrated liquor which often contains substantial quantities of COD, BOD, Nitrogen and other organic and inorganic pollutants which may need further treatment. Much research has been carried out in the past on heat treated liquor using anaerobic processes and some using aerobic processes. Most of the heat treated liquor used for such biological and chemical treatment research was produced at temperatures in the range 150 C to 225 C. There appears to be no information in the literature concerning the treatment of liquors produced at 280 C and above as a substrate for anaerobic and aerobic processes.

This work is a continuation of a previous study carried out by Luduvice (1992) on sludges but which was concerned mainly with the effect of temperature and retention time at lower over pressure. The study by Luduvice, describes the ability of WAO to treat different organic sludges under conditions below the stoichiometric requirement for oxygen of each of the sludges. Most of the recommendations given by Luduvice (1992) are to be investigated in the present study as mentioned in Chapter 1.

The main purpose of this research project was to examine the effectiveness of wet oxidation (WO) at low, and high oxygen overpressure process in the destruction of raw primary sludge, wastewater from detergent and paracetamol industries. Pure oxygen was used as the oxidising agent. More specifically the objectives were:

i) to investigate the effects of pure oxygen on the oxidation of domestic primary and activated sludge at different temperature, pressure and retention times,

ii) to investigate the optimum operating conditions for the destruction of organic matter in industrial wastewaters including:

    a) wastewater from the production of detergents, and

    b) wastewaters from the production of paracetamol,

iii) to develop a relationship between the influent volatile total solids (VTS) and the formation of heat transformed compounds such as soluble chemical oxygen demand (SCOD), ammonia (NH_3), volatile fatty acids (VFA) and formaldehyde (HCHO),

iv) to investigate the biotreatability of heat treated liquor.

CHAPTER 4

EXPERIMENTAL EQUIPMENT AND PROCEDURE

4.1 INTRODUCTION

The experimental work for this project was divided into two separate chapters i.e., Chapter 5 and Chapter 6:

i) wet oxidation of sludge and wastewater, (Chapter 5; AppendixB), and

ii) biotreatability of selected heat treated liquors (Chapter 6; AppendixC)

Throughout this study approximately 220 control tests were carried out on five different organic sludges and wastewaters and more than one hundred tests were carried out on selected organic wastewaters and sludges to prepare a feed for biological treatment. The control tests were performed with the objective of determining the destruction efficiency of the WO process on different wastes over a range of operating conditions.

The experimental equipment and laboratory procedures involved in the present research, in particular the reaction vessel for WO, and the aerobic and anaerobic laboratory-scale reactors are described in detail. The experimental work was carried out mainly from May 1993 to September 1995, with some disruption due to breakdown of the WO equipment, from time to time. The effluent from WO varies considerably depending upon the type of wastewater or sludge treated and the WO treatment conditions. Due to different industrial wastewater and sludge the following equipment was used:

(i) WO reaction vessel,

(ii) upflow anaerobic filter (UFAF),

(iii) laboratory-scale membrane activated sludge process(MAS),

(iv) sequencing batch reactor (SBR), and

(v) jet loop reactor (JLR)

The different processes (WO or biological) cited above were used, some with the same and some with different objectives, depending upon the suitability of the treatment process adopted for a particular waste stream. For example the UFAF, SBR and MAS were designed and used for the WO liquor to obtain a comparative result of aerobic and anaerobic biological processes. On the other hand, the high concentration of sulphate in the paracetamol heat treated liquor and other inorganic contaminants made it difficult to be treated by any conventional process other than the JLR process.

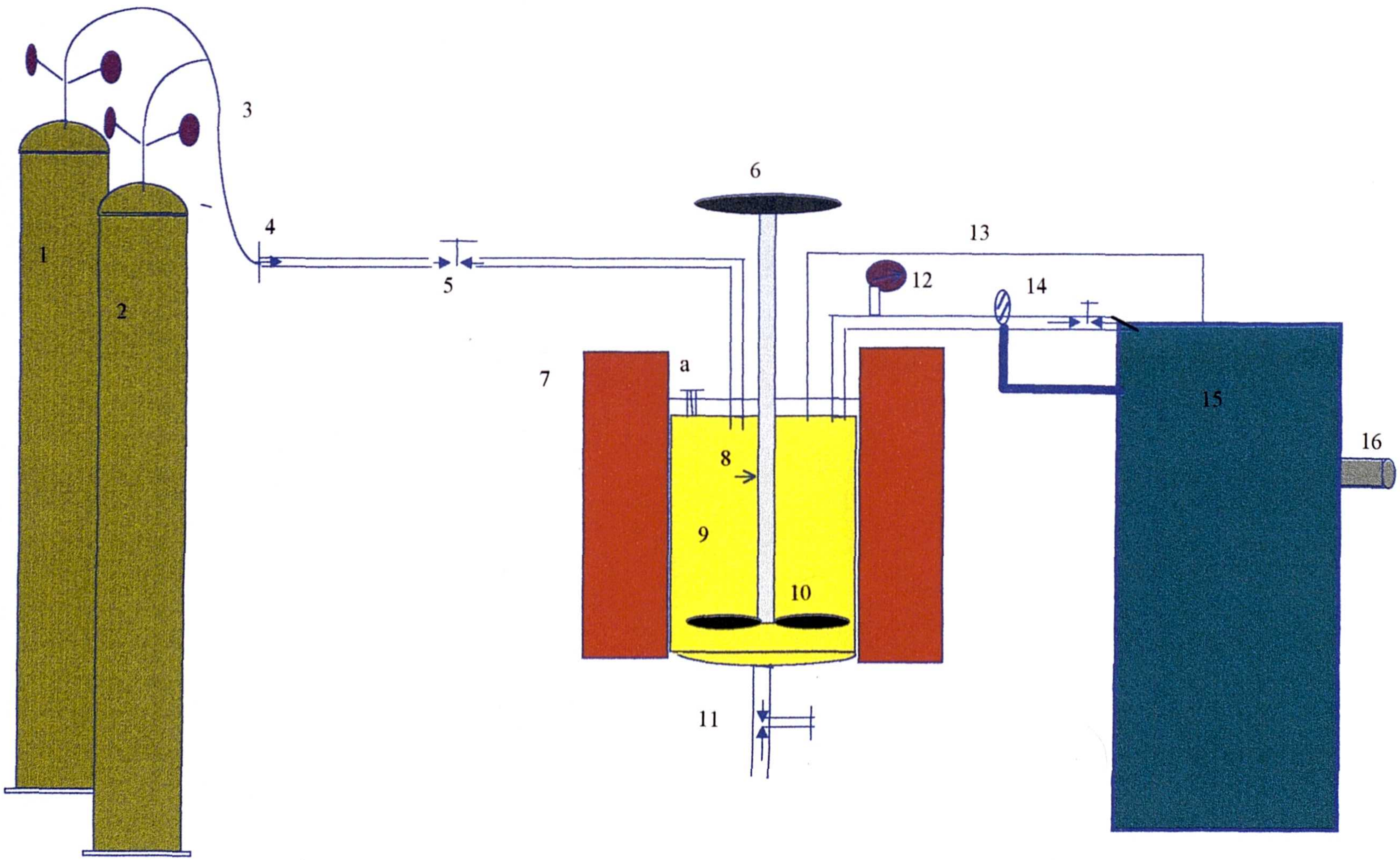
4.2 WO REACTION VESSEL

WAO and WO tests were carried out using a batch reactor (Fig. 4.1) with the following characteristics:

i) total effective volume: 3.78 litres,

ii) maximum pressure rating: 13.1 MPa (1900 psi, or 135 bar),

iii) manufacture and materials: the reactor vessel and ancillary equipment were manufactured by Charles Cook and Sons (Model No. 1042). The body of the 316 ASTM A182 stainless steel reactor was surrounded by a 1.8 kW electrical heater which was used to heat the liquor and oxygen mixture to the desired temperature,



1. Oxygen cylinder
2. Air cylinder
3. Cylinder regulator and Flexible pipe
4. One-way valve
5. Inlet valve
6. Pulley-motor connection
7. Heating jacket
8. Stirrer shaft
9. Reactor
10. Turbine blades
11. Bottom valve & effluent port
12. Reactor pressure gauge
13. Safety disc bursting pipe
14. Pressure release valve
15. High pressure release tank
16. Discharge pipe to atm.

a. Influent port

4.1 **Schematic diagram of WO reactor assembly**

iv) a six-bladed stirrer mounted on one side and the top was connected to a motor through a belt and pulley system. The stirrer speed could be varied in the range 10 to 500 rpm,

v) one-way gas inlet, outlet and bottom needle values, all rated for 34 MPa (5000 psi),

vi) electrical temperature controller and thermocouple,

vii) safety and rupture discs and inlet port,

viii) a steel angle iron frame to hold the whole assembly at working height. The frame was also fitted with a small chain crane to facilitate the movement of the heater and lid of the reactor,

ix) the autoclave and the gas cylinder were both fitted with a pressure gauge to determine the pressure inside the cylinder and the autoclave,

x) a reactor switch board was fitted with an automatic temperature control and stirrer speed control,

xi) a pressure cylinder at 13.5 MPa and 20 MPa was used for air and oxygen respectively,

xii) gas cylinder regulator rated for 10.5 MPa (1522 psi),

xiii) a gas inlet line was connected by a flexible stainless steel pipe for easy connection between reactor and oxygen cylinder.

In addition to the above, after an accident with the bursting disc and the discharge pipe, the discharge pressure release line was replaced by a large hollow drum as a pressure release system. Other than the hollow drum another safety valve was also fitted so that, in case of high pressure, if the safety disc did not burst at 13.1 MPa for any reason the valve would then reduce the pressure inside the reactor to a maximum operating pressure of 13.1 MPa (1900 psi).

4.2.1 Experimental Procedure

The cold reactor was charged with a sample of known strength (i.e., total solids, VTS, COD etc.) of wastewater or sludge after which all valves were closed. The vapour pressure was read from the pressure gauge of the reactor and at the desired temperature a known amount of oxygen was injected into the reactor. After the required period the treated sample was removed from the reactor. The procedure used during all experimental runs was as follows:

(i) the reactor was loaded with a known quantity of wastewater or sludge,

(ii) the reactor was closed and all fastenings were clamped,

(iii) the heater was mounted around the reactor,

(iv) the thermocouple placed in position,

(v) the stirrer belt was connected,

(vi) inlet and outlet valves were closed,

(vii) the power was switched on and the required temperature set on the temperature controller,

(viii) the reactor was then heated to the desired temperature,

(ix) oxygen or air was then added to the required pressure and stirring started for the required time,

(x) the stirrer and heater was switched off, the heater removed and the oxygen inlet valve was closed

(xi) the electric fan was switched on to cool down the reactor to room temperature,

(xii) the gas content of the reactor was released by slowly opening the gas outlet valve,

(xiii) based on the present research work if the solid contents of the influent waste comprises more than 10 %, disassemble all connecting pipes and stirrer belt. If less than 10 %, collect the treated sample from the bottom valve,

(xiv) after each run the reactor was cleaned with hot water and detergent, and if necessary with acetone followed by hot water and detergent.

For samples with a high concentration of solids the procedure was time consuming and could take 8 hours, depending on the test temperature and retention time. For wastewater and sludge having less than 5% solids the process took about 50% less time. This reduction in time was due to not having to open the top lid of the reactor and disconnecting the pipe but instead using the influent and effluent port for loading and unloading. The use of the second operating method made it possible to carry out three tests a day rather than 1 to 2 tests per day using the former procedure.

During most of the runs the internal pressure was maintained according to the stoichometric requirements of the waste and was always maintained above the vapour pressure of the liquid in order to ensure that the reaction would only occur in the liquid phase (Eq. 4.1).

Total pressure inside the reactor *Vapour Pressure at a particular temperature* + *Oxygen partial pressure* (4.1)

In Equation 4.1, the oxygen partial pressure was calculated from the Ideal Gas Law ($PV \ nRT$) for each sample (Appendix A). For a given temperature, the pressure determined from the gas law is dependent upon the initial COD of the waste.

4.3 LABORATORY-SCALE UPFLOW ANAEROBIC FILTER (UFAF) SYSTEM

The schematic diagram of the laboratory-scale single-phase UFAF system used for the treatment of the WO liquors (thickened activated sludge liquor and detergent heat liquor) is shown in Figure 4.2. The UFAF was designed on the basis of the specification given by Young (1991). The UFAF system was preferred to other anaerobic reactors for its capacity to operate at high organic and hydraulic loading rates and its known stability (Anderson, 1993).

The reactor was constructed from PVC, having an effective void volume of 2.8 litres. The base of the UFAF reactor was made in such a way as to avoid short circuiting in the filter media as shown in Figure 4.2. The UFAF used in the experimental work was a 70 cm long by 7.62 cm inside diameter PVC column. The system pH was adjusted manually on a daily basis and was buffered using $Ca(OH)_2$. The influent and effluent ports were positioned 2 cm from the base and 10 cm from the top respectively. The recirculation line was also connected to the influent port in order to increase the methanogenic activity by recirculating the biomass back to the filter. A variable speed peristaltic pump was used to feed and recirculate the treated effluent into the filter.

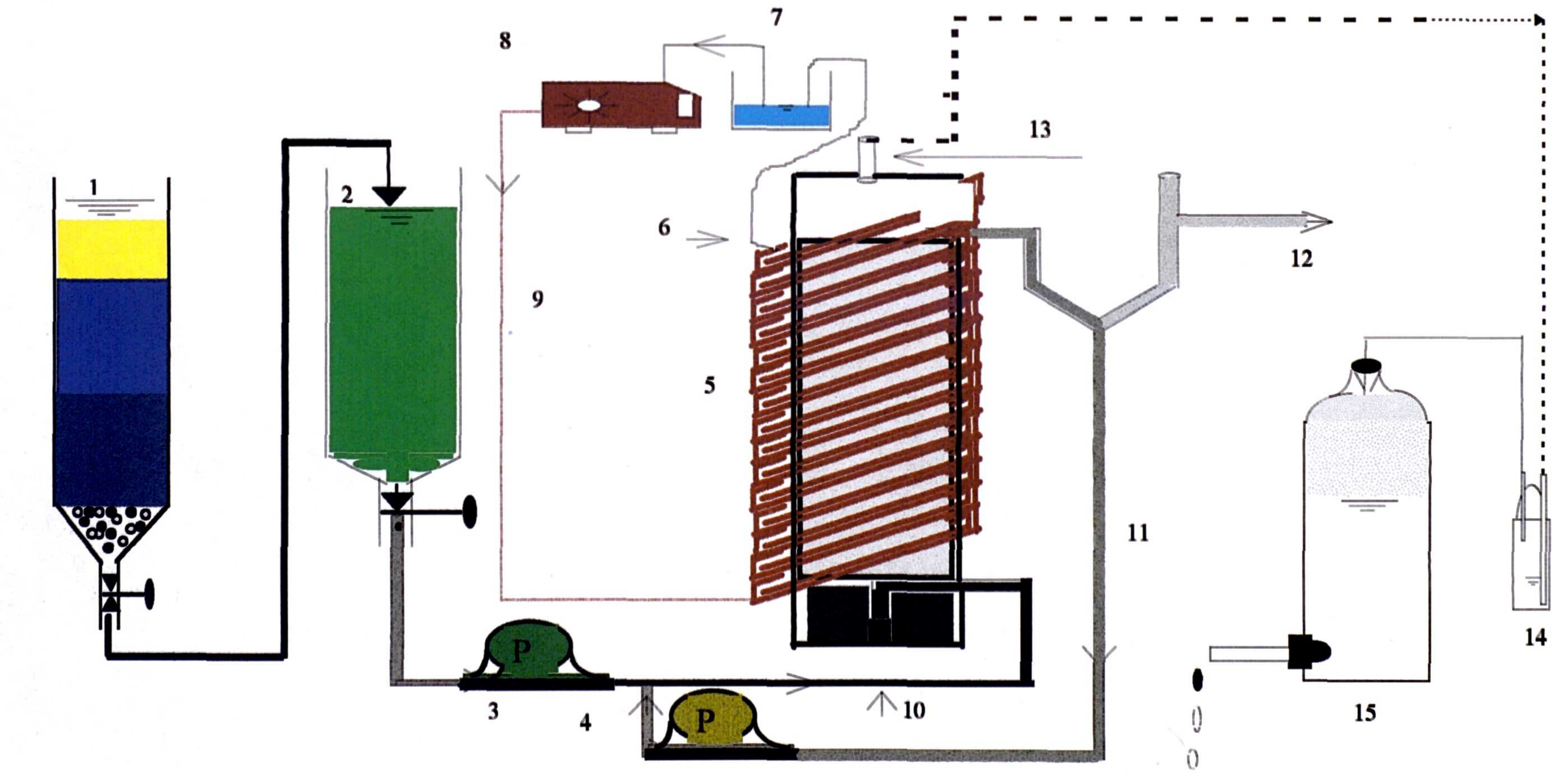
The upflow velocity (UFV) in the filter was initially maintained at 4.5 to 8 m/day in order to allow biomass attachment to the plastic media of the filter. After 30 days the UFV was increased to 17 m/day (Young and Yang, 1989, Young, 1991). It was intended to keep the UFV at this level throughout the study but this proved to be impossible. A gas outlet, was positioned in the flanged top of the UFAF which also had a serum cap set into it in order to enable a sample to be taken for gas analysis. A water-filled aspirator bottle was used to measure gas production by water displacement. The aspirator was of 10 litres capacity and calibrated at 0.1 l intervals. Gas generation could be read to an accuracy of 0.1 litre. The temperature inside the reactor was maintained at $37^{\circ}C$ using a plastic hose around the cylindrical section through which hot water was continuously circulated via a heater water circulator.

The media used for filter packing was of non-porous unplasticized PVC pall rings and was loosely packed. The effective specific surface area of the pall rings was 125 m^2 m^3.

The start-up procedures followed the recommendation of Cutforth (1995) using digested sewage sludge from the Barkers' Haugh wastewater treatment plant. The organic substrate used for the cultivation of the anaerobic biomass was spoilt beer diluted with tap water to obtain the desired feed COD and supplemented with macro and micro nutrients to maintain an influent COD:N:P ratio of 200:5:1 (Appendix A).

Initially the feed was spoilt beer and digested sludge, but after a period of three weeks this feed was changed to only spoilt beer and continued for two weeks. At the end of the 5th week the feed was changed to a mixture of 90% spoilt beer and 10% WO liquor after which the feed to the UFAF was supplemented with WO liquor at the rate of 10% every two weeks until the feed reached 100% WO liquor.

The routine monitoring schedule was carried out throughout the operation period of the UFAF as shown in Table 4.1.



1- Sand Filter
2- Feed Tank
3- Feed Pump
4- Recirculation Peristalitic Pump
5- Upflow Anaerobic Filter

6- Plastic Hose
7- Hot Water Reservoir
8- Heater Water Circulator
9- Hot Water Recirculaion Pipe
10- Feed/Recycle Liquor Line

11- Recycle Line
12- Liquid Effluent
13- Gas Collection Port
14- Dreshel Bottle
15- Aspirater Bottle

Fig. 4.2. Schematic diagram of UFAF reactor

Table 4.1 Monitoring Schedule

Parameter	Frequency	Sampling Location
AD :Influent Effluent	1 x /week 1 x /week	Feed tank Effluent port
SCOD :Influent Effluent	4 x /week 4 x /week	Feed tank Effluent port
NH_3-N :Influent Effluent	4 x /week 4 x /week	Feed tank Effluent port
VFA :Influent Effluent	4 x /week 4 x /week	Feed tank Effluent port
pH :Influent Effluent	Daily	Feed tank Effluent port
Gas	2 x /week	Gas sample port
TKN :Influent Effluent	1 x /week 1 x /week	Feed tank Effluent port
PO_4-P : Influent Effluent	1 x /week 1 x /week	Feed tank Effluent port
Formaldehyde	1 x /2 week	Feed tank Effluent port
Solids SS VSS	1 x /week	Feed tank Effluent port

AD active detergent, cationic or anionic

4.4 LABORATORY-SCALE MEMBRANE ACTIVATED SLUDGE PROCESS (MAS)

The laboratory-scale membrane activated sludge aeration tank had a volume of 3.5 litres and was constructed in PVC with the inside of the tank being lined with a porous material which retained most of the MLSS in the reactor. The feed tank was provided with a magnetic stirrer to maintain a uniform influent feed to the reactor. The organic substrate used for the start-up of the aerobic process was spoilt beer diluted with tap water to obtain the desired influent COD and supplemented with micro and macro nutrients (Appendix A) to maintain an influent COD : N : P ratio of 200 : 5: 1. As the WO liquor concentration was increased in the feed it was not possible to maintain this ratio due to the high concentration of nitrogenous compounds in the liquor. At 100% WO liquor in the feed an average COD : N : P ratio of 100 : 25 : 2.25 was measured.

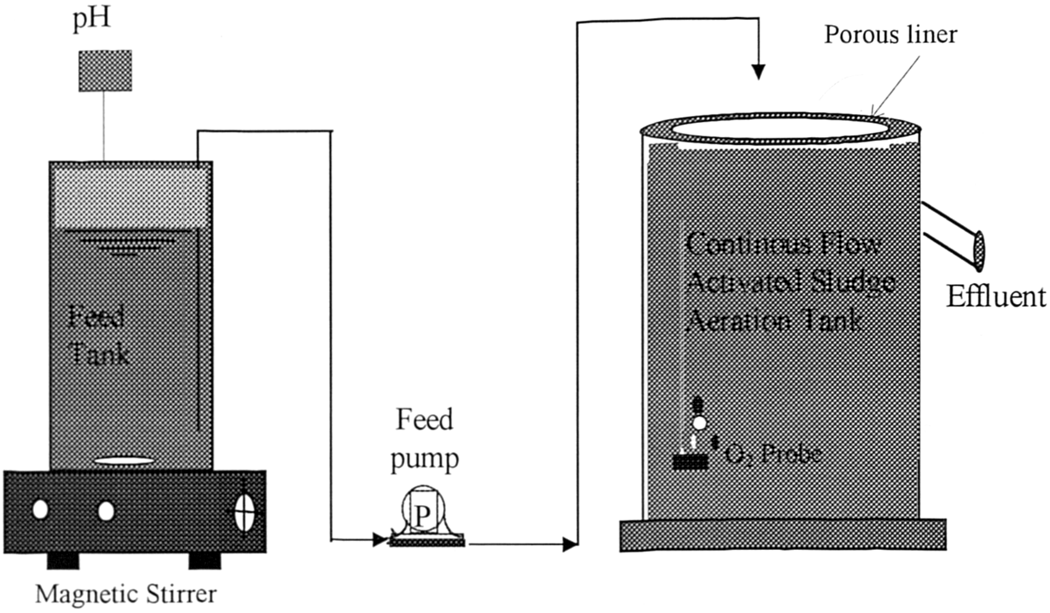


Figure 4.3 Schematic Diagram of the MAS Process

Initially the MAS was filled with fresh activated sludge to seed the aeration tank and diluted spoilt beer. The dissolved oxygen level in the mixed liquor was maintained at 5-9 mg/l. Due to the high organic loading rate (OLR) the reactor was operated at a HRT of 12 hours. After two days feeding with beer wastewater, the reactor was acclimatised with an 25% increase in COD from the WO liquor per day to the MAS until the feed was 100% WO liquor. The reactor schematic diagram is shown in Fig 4.3. The SCOD, MLSS, ammonia, were all monitored on a daily basis while SVI, nitrate and formaldehyde were determined once per week.

4.5 SEQUENCING BATCH REACTOR (SBR)

Sequencing batch reactors (SBR) are gaining in popularity, usually for small wastewater treatment works and in particular for industrial wastewater treatment (Boon et al., 1995). Other than its simple construction and operation, SBR systems provide a wider range of micro-organisms (Irvine and Ketchum, 1989, Oles and Wilderer, 1991). As WO liquors are difficult to treat by biological processes, an SBR system was used to determine if the anoxic stage showed any improvement in the removal of detergent. No literature has been found regarding the degradation of detergent in anoxic stage.

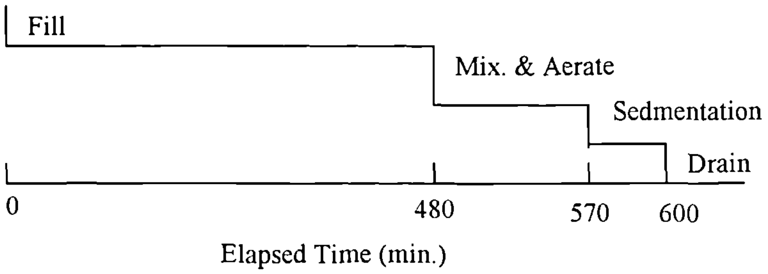


Figure 4.4 Sequence of SBR Phases During One Cycle

A six litre SBR glass reactor was used for the treatment of the detergent liquor with aeration being provided by a diffuser system at the base. Three litres of activated sludge, obtained from the local wastewater treatment plant was mixed with one litre of heat treated detergent liquor and aerated in the SBR system. The acclimatisation period was completed in five days. At the end of acclimatisation period the SBR system was operated at an 8 hour HRT throughout the study. The sequence of SBR process phases during one cycle of laboratory scale experiments is shown in Figure 4.4. Each time the pH and nutrients (COD : N : P) were corrected to 7 and 200 : 5 : 1 ratio respectively. Due to the high OLR, pure oxygen was used for aeration. For control of foaming, due to presence of high concentration of detergent in the feed an antifoaming (polydimethyl siloxane) agent was used. The details of the process parameters loading etc. will be further discussed in Chapter 5.

4.6 PILOT-SCALE JET LOOP REACTOR (JLR)

4.6.1 Introduction

The use of compact reactors is more crucial nowadays since conventional activated sludge processes require extensive land use. In some places like Venice, Hong Kong etc. where industrial activities are highly concentrated, an ever increasing amount of effluents are being discharged into inland and marine water everyday. Land is scarce in such small places and not available for conventional treatment methods for all industrial effluents. A high-rate compact reactor would be an ideal system for the treatment of such wastewater to help improve water quality and at the same time use the minimum amount of land.

The application of heat oxidation processes has considerable potential for the treatment of complex, toxic organic wastewater. The resultant liquor from such a process may however, be best treated using a high performance, small "footprint" system such as the Jet Loop Reactor. One such wastewater is that from the pharmaceutical industry, typified by the production of paracetamol. A North-East England drug company; Sterling Organics, in fact use the Zimpro Air Oxidation process for wastewater treatment. It was therefore decided to investigate the possibility of using the pilot-scale JLR for aerobically treating the Zimpro effluent after first confirming that the effluent from the Zimpro process was similar to that when using the laboratory-scale WO process. It proved necessary to use the Zimpro effluent for the JLR rather than the laboratory-scale WO system since it was not possible to generate sufficient effluent from the latter reactor. The comparison between the Zimpro process and laboratory-scale reactor is given in Chapter5.

4.6.2 Experimental Rig (JLR)

The experimental JLR rig (Fig. 4.5) consisted of the following components: a feed storage tank, a feed pump, a jet loop reactor (JLR) with pump, a degassing tank and settling tank with a return sludge pump, a sludge wasting pump and flow meter for liquid and air.

i) Feed tank: Wastewater was transferred to the reactor via a feed pump at 5 l/hour. pH in the feed tank was maintained daily.

ii) Jet Loop Reactor (JLR): The JLR consisted of a 28 litre effective volume, cylindrical reactor constructed from PVC, with an inner draft tube. The JLR is a concentric tube reactor with two coaxial nozzles and a liquid inlet through the annular nozzle. A liquor/air jet is formed by pumping MLSS plus influent wastewater via a recycling pump through one coaxial nozzle fitted with a central air tube, the air being drawn into the reactor through the air tube by the drop in pressure at the tip of the nozzle. The high velocity gradient in the JLR produces air bubbles with high gas/wastewater interface renewals. The liquid and air from the jet passes into the reactor via the draft tube under the pressure of the recycling pump head. After reaching the bottom of the reactor the mixture of air and liquid rebound upward producing sufficient turbulence in the system to increase the oxygen transfer rate. The diameters of the liquid nozzle and the air tube were 10.5 mm and 3.5 mm respectively.

iii) Degassing tank: The highly aerated liquor from the tubular reactor next discharges into the degassing tank in order to remove CO_2 and traces of other gases. The presence of gases in the liquor would greatly hinder the settleability of the biomass. The rising gas bubbles from the jet keep the small flocs in suspension, which in turn would cause high turbidity in the JLR effluent. A rotating stirring, mild agitation was used to release the dissolved gases to allow bigger floc formation and finally improved settleability. The dissolved oxygen (DO) content in the degassing tank was measured using a DO probe. The effective volume of the degassing tank was 25 litres.

iv) Settling tank: The settling tank was of 55 litres volume with a variable speed return sludge pump and a sludge wastage pump.

When possible the JLR was operated at constant optimum conditions. An air flow rate of 4.5 litre/min. and a dissolved oxygen of 1-2 mg/l in the degassing tank was generally maintained. After the start-up under steady state conditions a constant organic loading rate was used throughout the experimental period.

4.7 ANALYTICAL METHODS

Throughout the operation period, routine laboratory analyses were carried out on a daily or weekly basis depending upon the operation and treatment involved. The analytical methods and instrumentation used in this study are listed in Appendix A.

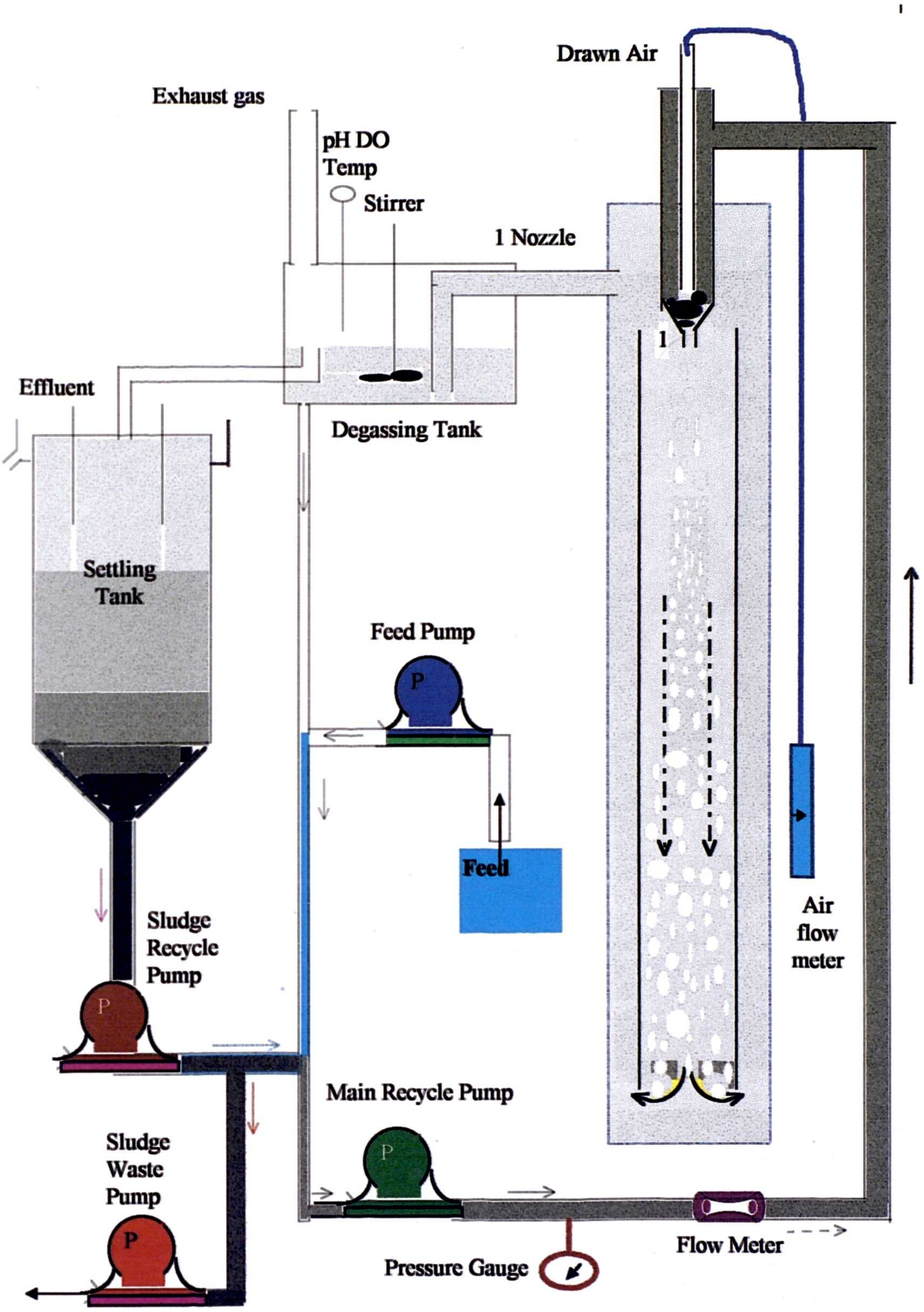


Figure 4.5 Schematic Diagram of the JLR Reactor

CHAPTER 5

WET OXIDATION OF SLUDGES AND WASTEWATER

5.1 INTRODUCTION

The main purpose of using WO treatment is not only to change the sludge to a form which is easily filterable but also to reduce its offensiveness in terms of organic matter concentration. The process parameters that can be controlled are the temperature, pressure, retention time and the total solids concentration of the sludge. The effect of these parameters in the reduction in the CST or specific resistance, COD destruction and solids destruction for various types of sludge have been reported in the literature. Thus, although the effect of the WO process variables on the conditioning and destruction are will known their effects on the liquor strength are less well understood, as is the relationship between influent volatile total solids (VTS) and liquor strength. One of the objectives of the current research is to quantify the effect of process parameters on the strength of the liquor and to establish the relationship between the liquor strength and the organic matter destruction. The cost of disposing of the liquor can add significantly to the overall cost of heat treatment. It would, therefore, be advantageous if the process could be operated so that the strength of the liquor is minimised whilst, at the same time, the sludge is adequately conditioned. As mentioned in the literature review (Luduvice's Work) some data on how this could be done was already available but additional experiments were necessary to see the effects of pure oxygen on the selected wastewater and sludges. The sludges and wastewaters tested comprised of:

i) raw primary sludge (Howdon Wastewater Treatment Plant),
ii) activated sludge (Newton Aycliffe Wastewater Treatment Plant),
iii) detergent wastewater (from Unilever Research plc),
iv) paracetamol wastewater (from Sterling Organics).

Data describing the destruction of domestic and industrial wastewaters and sludges using a batch WO reactor operating under a variety of conditions are presented. The results include the kinetics of activated sludge destruction, active detergent (AD) destruction, production and transformation of intermediate products such as ammonia, acetic acid and formaldehyde in the liquor effluent, ash leachability, and sludge volume reduction.

To assess the potential for WO to destroy or transform the organic matter present in each sludge and wastewater under investigation, total chemical oxygen demand (TCOD) removal and generation of soluble chemical oxygen demand (SCOD) were the parameters of concern, and in the case of detergent wastewater, active detergent (AD) removal was the parameter used to assess the ability of WO to destroy the AD in detergent wastewater. The percentage of TCOD/AD destroyed and the SCOD generated were calculated according to formulae given in Appendix A (1.2A).

Most experiments were carried out by previously calculating the amount of oxygen required for TCOD oxidation. The stoichiometric formulae used for determination of the amount of oxygen required for a particular TCOD are given in Chapter 4.

In order to facilitate the general presentation of this chapter, each sludge and wastewater is considered separately with individual Results and Discussion section.

5.2 WET OXIDATION OF ORGANIC MATTER (TCOD REDUCTION)

5.2.1 TCOD Destruction from Wet Oxidation (WO) of Raw Primary Sludge

(I) Results

The raw primary sludge was collected from Howdon Wastewater Treatment Plant, which is situated in Newcastle upon Tyne, U.K. and receives wastewater from a domestic and industrial population equivalent to approximately one million. The plant is designed to provide primary treatment only, prior to discharge to the North Sea. Due to variations in precipitation at different times of the year and the wide range of discharges from industries, the primary sludge characteristics vary considerably, especially the solids levels. Throughout this study, efforts have been made to overcome the variable characteristics of the sludges by maintaining the total solids (TS) concentration as constant as possible in the sludge prior to WO treatment. Sludges having similar TS level would normally have similar organic and inorganic component fraction.

Careful preparation of each sample was necessary prior to heat treatment in order to obtain consistency in results. If this step had not been taken, then the repetition of experiments and average values of those experiments having different TS would be meaningless. The first batch of sludge collected for a series of experiments was used unaltered but when further experiments were required, either in that range or another range of TS, and sufficient sludge was not available, the TS of the next batch of sludge was adjusted by concentration (settlement) or dilution (water addition).

The results show that at the stoichiometric oxygen requirement (SOR), pressure had little effect on the removal of TCOD. In other words the pressure which provides oxygen equivalent to that of the TCOD in the reactor (SOR) would give similar removal or destruction of TCOD to the situation where the pressure provides two times more oxygen (2×SOR). At the SOR the results show that TCOD destruction and SCOD generation were mainly dependent on temperature whereas retention time (RT), oxygen partial pressure and influent TS concentration had little effect. TCOD destruction varied from 30% to 80% (Fig. 5.1) for temperatures of 200°C to 300°C for other given conditions.

At 200°C, 10 minutes and 60 minutes RT gave a TCOD reduction of 12% and 30% respectively, while at a higher temperature (i.e. >280°C) the TCOD destruction at 10 minutes and 60 minutes RT were similar which suggests that at the SOR a high TCOD removal could be achieved in a short time. Operating at the SOR not only reduced the TCOD but at the same time prevented the production of odours. The conversion of solid COD to SCOD is shown in Fig 5.2. It is clear from this figure that high SCOD is generated at lower temperature (200°C) and short RT (10 minutes) and less SCOD is generated both at high RT and high temperature. The TCOD and SCOD of the sample were 45000 mg/l and 2650 mg/l respectively. At the lower temperature

(200°C) the destruction of TCOD was 12-30% but the formation of SCOD (157%) was the highest. At a higher temperature (300°C) the destruction of TCOD (80%) was greater and the formation of SCOD (25%) was significantly reduced. Out of six repeated samples treated at 300°C, two samples showed no generation of SCOD (Fig. 5.2).

Three different retention times (10, 30, 60 minutes) were used to investigate the effect of retention time (RT) for the destruction of TCOD and the generation of SCOD during the transformation. A sharp increase in the SCOD level was observed at a lower temperature and lower RT (Fig. 5.2). Similarly a decrease in the SCOD content was observed at higher temperature and high RT (60 minutes).

(II) Discussion

The better destruction of TCOD results obtained under less extreme conditions when using pure oxygen are due not only to the oxidising capability of pure oxygen but also to the SOR condition which provided sufficient oxygen inside the reactor for TCOD oxidation. Increasing the overpressure to 2× SOR, thus providing double the oxygen available for TCOD oxidation, gave no significant improvement in removal efficiency. These results strongly suggest that temperature is the limiting factor in organic matter oxidation.

Unlike Luduvice's (1992) results, some TCOD was destroyed at all retention times (RT) investigated. At low temperature (200°C) an increase in RT was necessary to obtain significant TCOD reduction. The transformation of solid COD into the liquid

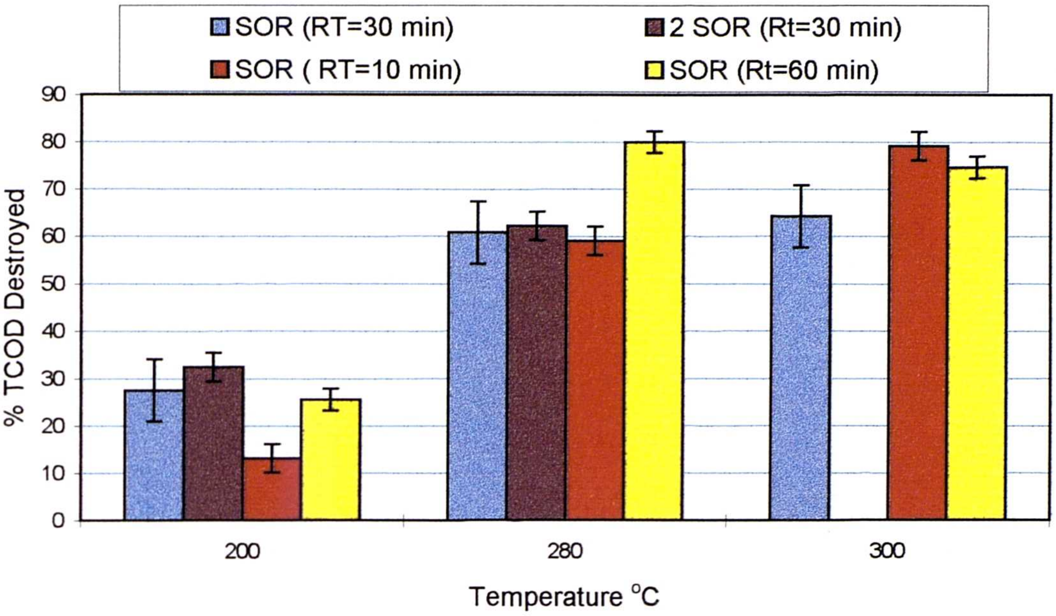


Fig. 5.1: Effect of WO on TCOD of Raw Primary Sludge

Note:
SOR = Oxygen equivalent to TCOD of Sludge
2 × SOR = 2 × Stoichiometric Oxygen Requirement

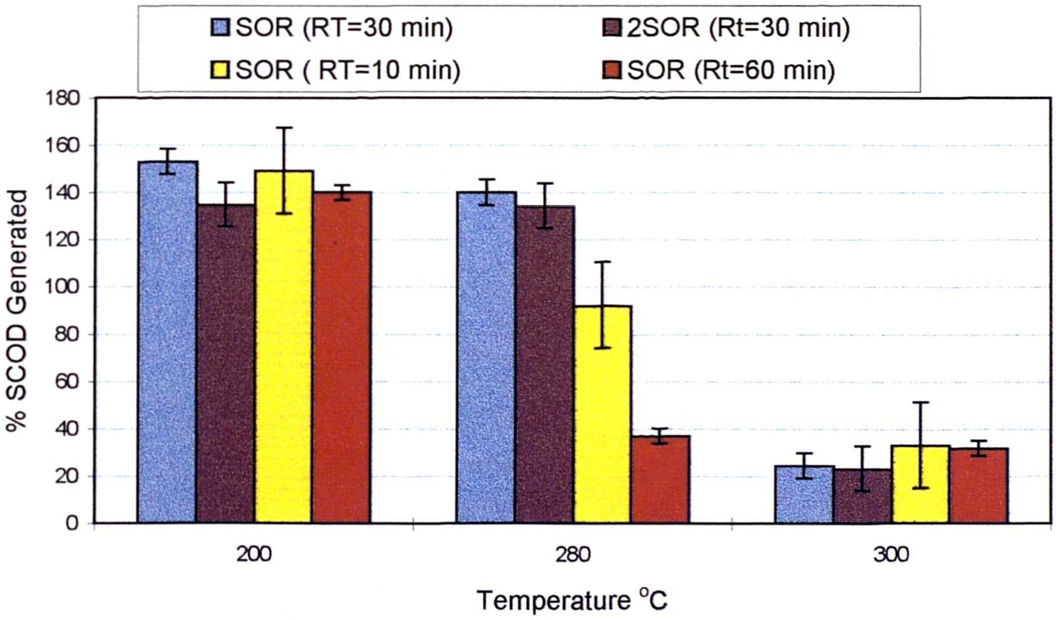


Fig. 5.2: Effect of WO on SCOD Production from Raw Primary Sludge

state provides an indication of the high strength of the liquor which must be treated prior to discharge.

The sludge treated at high temperature, i.e. above 270° C, will produce mostly inert solids which could be readily disposed of into landfill (Shanableh and Tongdhamachart, 1990). One could assume that the environmental threat such as large volume of sludge and pathogens transmission posed by the original sludge has been reduced to the SCOD in the liquor by WO process, which could then be treated by a conventional biological process. When 30% of the TCOD presents itself as SCOD, the overall efficiency of the system was 70% (Luduvice, 1992). In the present study, at 300 C and at SOR, the overall removal efficiency of the process was 92.5%. Relationship between initial solids and transformation products will be discussed later in this chapter. The oxidation model proposed by Li et al., (1992) suggests that the oxidation of organic matter to CO_2 and water occurs either by a direct route or via the formation of more simple intermediate products. The conclusion made by Foussard et al., (1989) and Shanableh and Gloyna, (1993) implied that acetic acid was the main organic compound remaining after highly efficient treatment, and it can consequently be concluded that this acid must be the last intermediate before total oxidation.

The high SCOD at lower temperature was mainly credited to the breakdown of large complex organic compounds into simple, low molecular weight compounds during hydrolysation. As RT and temperature were increased the simple, readily oxidizable organic molecule were oxidised which were the reasons for lower SCODs at high temperature. The destruction of TCOD and the generation of SCOD (Fig. 5.2) at retention times 30 minutes and 60 minutes at SOR were the same, which suggests that 30 minutess RT could be better for sludge under SOR conditions. Using oxygen as an oxidising agent, retention time (RT) could be one of the most important factors from an economic standpoint.

The SCOD generated at lower temperature contains simple low molecular weight compounds, which are usually non-toxic and non-refractory. On the other hand the organic compounds generated at higher temperature and RT transform the simple organic molecules to very refractory non-biodegradable intermediate products (Friedman et al, 1988). The biodegradability of the heat liquor will be discussed in detail later in Chapter 6.

The results have shown that it could be possible to completely destroy a substantial part of the organic matter but if it would be more economical to use the volatile fatty acids in a biological nutrient removal plant then the operating parameters of WO could be adjusted accordingly.

Unlike the Luduvice (1992) results, the solids were observed to be not tar-like when treated at high temperature (300 °C) but were very sandy granules. Furthermore the solids produced during this research contained a level of activated carbon which was successfully used for the removal of colour from a dye wastewater which will also be discussed later in this chapter.

In summary, the effect of WO on the raw primary sludge was that a RT of 30 minutes would be the optimum for TCOD destruction (solids oxidation),and formation of SCOD in the temperature range 200 °C - 300 °C. In addition to the above, the use of pure oxygen created granular solids, which were not greasy, with no odour problems and above all, less over-pressure requirements in the reactor. In contrast to the above the only disadvantage other than the cost of oxygen were health and safety considerations as discussed in the literature review.

5.2.2 TCOD Destruction from WO of Gravity Thickened Activated Sludge

(I) Results

The gravity-thickened activated sludge was collected from Newton Aycliffe wastewater treatment plant (WWTP) prior to their normal practice of adding a cationic polyelectrolyte for the dissolved air flotation (DAF) process. The reason for this was to eliminate the effect of the COD contribution from the polyelectrolyte. Prior to feeding to the WO unit, the sample was further gravity thickened in the laboratory at 4°C. After further decanting the supernatant, the 25 litre container was thoroughly shaken resulting in a uniform sample containing 2.65% TS a TCOD of 26.25 g/l and a SCOD of 0.65 g/l.

The tests reported in Figs. 5.3 and 5.4 were carried out with the objective of knowing as precisely as possible the effects of SOR and pressure under WO conditions at 280 C, and at a RT of 60 minutes. Other than the primary aim of reducing the volume of activated sludge by WO, the reason for selecting activated sludge for efficiency tests was due to its uniform characteristics which could then be used to obtain reliable and consistent results. A total of nine tests were carried out, of which three were conducted at half of the stoichiometric oxygen requirement and a pressure of 1 MPa, three tests were conducted at stoichiometric oxygen requirement which gave a pressure of 2 MPa and the remainder used at half stoichiometric oxygen requirement and a pressure 4.5 MPa. Fig. 5.4 clearly shows the effects of the SOR on the destruction of TCOD and generation of SCOD. TCOD destruction in the first and third (Fig. 5.3) set of experiments were the same although the pressure in the first and third set were 1 MPa and 4.5 MPa respectively.

Results in Figs. 5.5 and 5.6 show the effects of WO on the COD of the activated sludge. The effect of temperature is very evident on the TCOD destruction at 10 minutes and 30 minutes RT. The effect of temperature on the destruction of TCOD is similar to that of the raw primary sludge. Four different temperatures were used to determine the pattern and destruction of TCOD and formation of SCOD. Results shown in Fig. 5.5 show destruction of TCOD at all temperatures and no unexpected increase in TCOD. A TCOD destruction of 80% was observed at 300°C and RT of 30 minutes. The transformation of solids COD (TCOD) into SCOD at a particular temperature and pressure depend upon the time of oxidation. At 10 minutes and 30 minutes RT (200 C), the generation of SCOD was 900% and 400% respectively.

Initially, less than 3% of the total organic matter was in the soluble form, but after heat treatment this figure increased substantially. At 200°C, 30% and 15% of the organic matter were solubilized at RTs, of 10 minutes and 30 minutes with an additional 18% and 26% being oxidised. This left 52% and 59% of the original TCOD in an insoluble form respectively. Furthermore, at a temperature of 300°C, 8.6% and 6.9% of the organic matter were solubilized at RTs of 10 minutes and 30 minutes with another 70% and 75% being oxidised. This left only 21% and 18% of the original TCOD in an insoluble form.

(II) Discussion

At SOR conditions there is always sufficient oxygen present in the reactor to oxidize all the organic compounds in WO system, provided sufficient activation energy

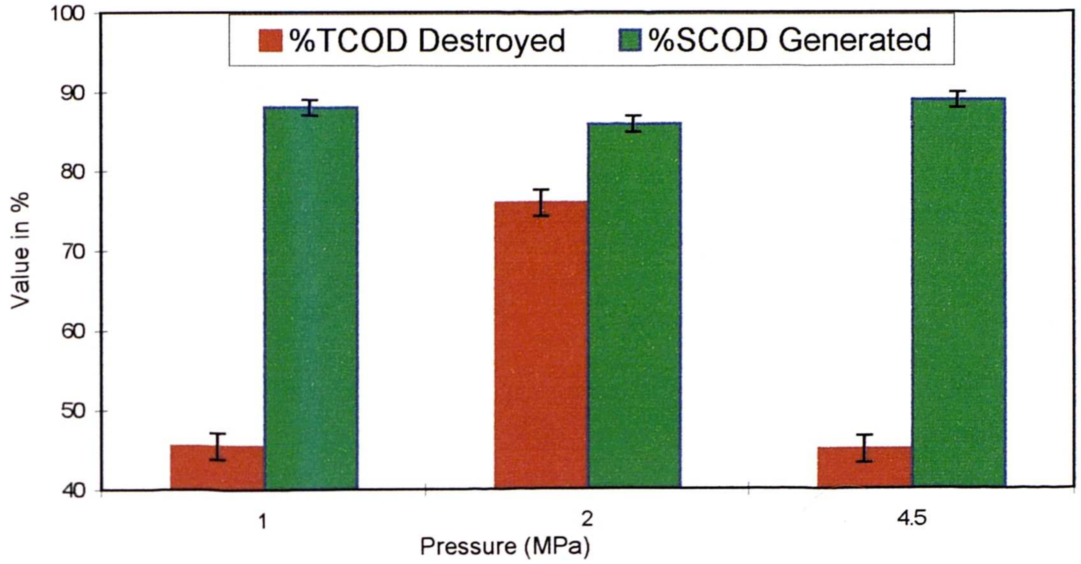


Fig. 5.3: Effect of SOR and Low Overpressure on Activated Sludge

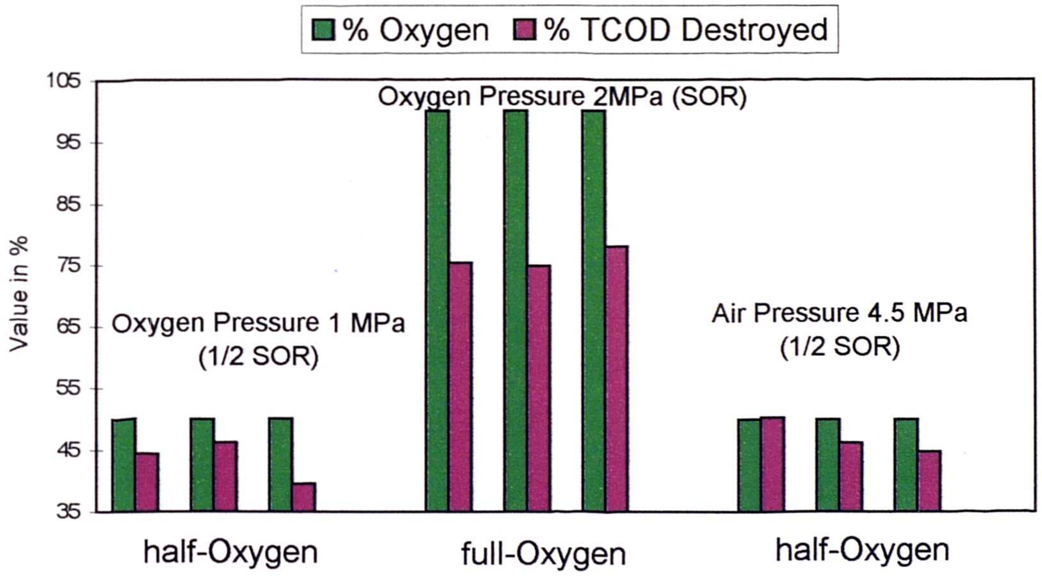


Fig. 5.4: Effect of SOR on COD of Activated Sludge

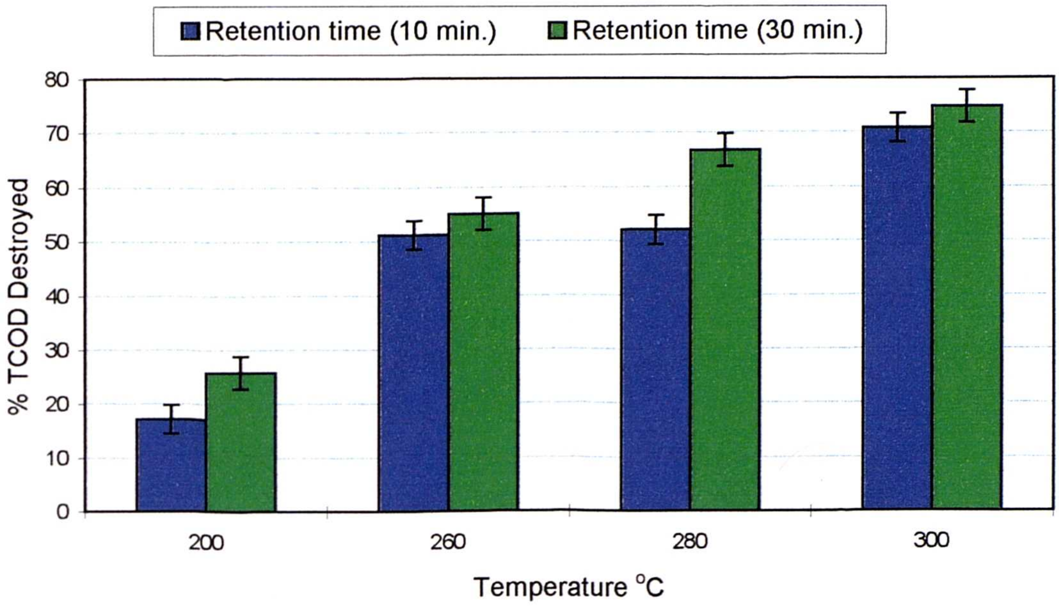


Fig. 5.5: Effect of WO on TCOD of Activated Sludge
Note:
Pressure Equivalent to SOR

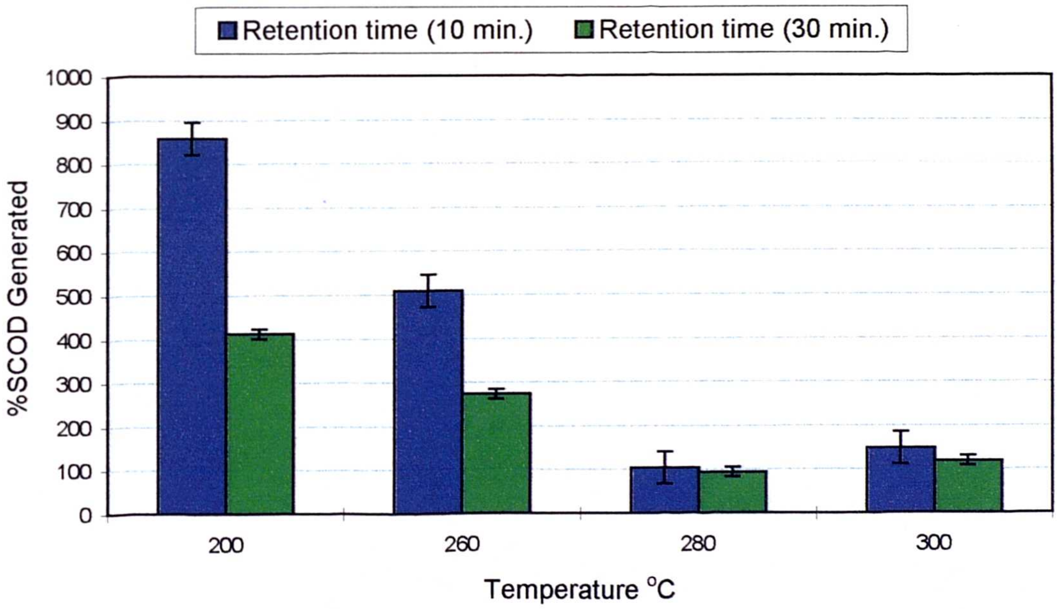


Fig. 5.6: Effect of WO on SCOD of Activated Sludge

is present for chemical oxidation. In Fig. 5.4, although the pressure was different, the amount of oxygen provided for oxidation was the same which was the reason for the same TCOD destruction in both sets. On the other hand the destruction at SOR, which was at a lower pressure than the third set, resulted in greater than 70% TCOD destruction. The generation of SCOD (Figs. 5.3 and 5.4) was almost the same in all three cases but a gradual increase was observed as the pressure was increased. One of the reasons could be that all samples were tested at a similar temperature giving the same rate of generation of SCOD. Figs. 5.3 and 5.4 show the importance of SOR conditions when oxidation of activated sludge is considered.

A TCOD destruction of 80% was observed at 300°C and RT of 30 minutes, on the other hand Luduvice (1992) found only 25% TCOD destruction at a similar temperature and two hours RT. The significant difference in TCOD destruction between the two results was partially due to the SOR condition and to some extent due to the use of pure oxygen. The effect of the latter (pure oxygen) was in agreement with the results of theUSEPA in which it was found that the use of pure oxygen in a WO unit increased the plant sludge handling capacity by six times due to greater oxidation of organic matters (USEPA report 600/2-87/022). At sub-critical temperatures (below 300°C), TCOD destruction greater than 80% was unlikely, because a very high proportion of the SCOD was due to acetic acid which is very resistant to chemical oxidation at sub-critical conditions.

As stated earlier, activated sludge consists mostly of a uniform matrix of bacteria which could be readily hydrolysed at a subcritical temperature. The consequent release of organic matter from the cells accounts for the increase in SCOD. At the initial low RT, contact between the SCOD and oxygen was short therefore less oxidation of SCOD was observed, which in turn was one of the main reasons for the very high SCOD produced at the lower RT. As the RT was increased further, oxidation of the SCOD into CO_2 and H_2O resulted, along with the production of VFAs and other organic compounds. The relatively constant values obtained for SCOD generated at 280°C and 300°C leads to the conclusion that after only 30 minutes most of the soluble organic compounds remaining in solution are recalcitrant products such as acetic acid and other organic acids.

It is clear from Fig. 5.6 that maximum SCOD can be generated at lower temperatures, which would be desirable for the treatment of other wastewaters as in advanced biological nutrient removals plants which are considered to rely on VFAs for the removal of phosphorus (Noone, 1995). The generation of SCOD is mostly dependent upon the VTS in the influents solids of activated sludge. The relation of influent VTS and the transformation of end products in the liquor will be further discussed later in this chapter.

Luduvice's (1992) results showed similar residual solids TCOD of 27%. There is a small difference in results of insoluble COD between Luduvice (1992) and the current research indicating that the insoluble COD in the liquor is mainly temperature dependent. As in Luduvice's (1992) results, 50% of the TCOD was accounted for by SCOD. The reason for this high concentration of COD in the liquor was the oxygen deficiency in the case of Luduvice (1992), on the other hand in the present study 82% of the solids COD (TCOD) were solubilized, of which 75% was oxidized and 7% of the TCOD accounted for SCOD in the liquor, justifying the importance of SOR in the oxidation of organic matter.

The above resluts also confirm the pattern of sludge oxidation in which the organic sludge is oxidised i.e before complete or partial oxidation the solids must pass through a liquid state and then to the corresponding compounds (CO_2 etc.)

No catalyst was used for the raw primary sludge nor for the thickened activated sludge. The need for a catalyst should be decided on a case to case basis. Depending on the concentration of the catalyst used a substantial increase in the metal concentration in residual ash was reported (Chowdhury, 1974, Luduvice, 1992). The increase in metal concentration may pose a problem for residual solids disposal. Maximum concentration limits of heavy metals in landfill and other outlets would feasibly justify omitting the use of catalyst in the WO of biological sludges.

5.2.3 COD Destruction from WO of Detergent Wastewaters

The detergent wastewater and finished detergent used were provided by Unilever Research plc. In the past, Unilever's strategy was to concentrate the detergent wastewaters arising from spillage, plant washing and other similar activities and then convert this into powdered detergent products. Due to the low market value for powdered detergents Unilever are now considering disposing of these wastewaters to sewer. Unilever Research plc has been investigating a range of suitable technologies for such detergent wastewater treatment and at present their primary aim is to minimise the detergent concentration in order to facilitate further biological treatment. Active detergent (AD) removal by conventional treatment processes is very small and it has been found that concentrations in the range of 4 to 5 mg/l interfere with flocculation in sedimentation tanks (Nichole and Koepp, 1961).

The experiments were designed to test detergent destruction efficiency, under various temperature, pressure and oxygen conditions. Tests were run for six different types of detergent. Out of the six, four were the raw original product, and two were the finished product (Persil and Comfort). The experimental conditions and type of detergent are given in Table 5.1. The primary emphasis was on establishing the destruction rate for the cationic and anionic surface-active agents under different operating conditions, and at active detergent (AD) concentration of 2 % to 30 %.

For all six types of detergent, of which two were cationic and four were anionic, different concentrations of active detergent in each sample were tested at different temperature, pressure and retention time, with pure oxygen being used throughout the investigation.

The main research objective of this joint collaboration of Unilever and Newcastle University was to carry out an initial review at laboratory scale of the application of WO for the treatment and disposal of liquid detergent effluents.

The specific objedctives were:

i) to determine typical active detergent (AD) and COD removal over a range of reaction conditions and to test the use of catalysts at low temperature and at short residence time, and

ii) to explore the minimum reaction condition giving sufficient AD removal to enable subsequent biological treatment of the treated liquor.

The target was to have sufficient data to justify establishing a comprehensive research programme in this area.

The project was designed to assess the effective destruction of detergent (AD)

Table 5.1 WO Experimental Conditions for Detregent

Detergent Type	Parameter	Value
a) Zeolite, Anionic, Mol. Wt. 468.75	AD concentration (%)	0.5, 4.5, 6, 12, 30
	Temperature (°C)	200, 280
	Retention time (minutes)	60, 120
	O_2(%Stoichiometric demand)	< 50, 50, 100
	Pressure (MPa)	3.5, 6, 8
	Type of catalyst	$CuSO_4MnO_2MnSO_4$
b) (Linear alkyl sulphonate), Anionic, Mol. Wt. 362	AD concentration (%)	2, 5
	Temperature (°C)	160, 200, 240, 280
	Retention time (minutes)	15, 30, 60
	O_2(%Stoichiometric demand)	100, 200
c) LES (Linear ethyle sulphonate), Annonic, Mol. Wt. 446.5	AD concentration (%)	2, 5
	Temperature (°C)	200, 280
	Retention time (minutes)	60
	O_2(%Stoichiometric demand)	50, 100
d) Persil, Anionic, Mol. Wt. 362	AD concentration (°o)	4.5, 15, 30
	Temperature (°C)	200, 280
	Retention time (minutes)	60
	O_2(%Stoichiometric demand)	50, 100
e) HEQ, Cationic, Mol. Wt. 678	AD concentration (%)	2, 5,
	Temperature (°C)	200, 280
	Retention time (minutes)	30, 60
	O_2(%Stoichiometric demand)	50, 100
f) Comfort, Cationic, Mol. Wt. 678	AD concentration (%)	1.63, 2, 5, 10.84
	Temperature (°C)	200, 280
	Retention time (minutes)	30, 60
	O_2(%Stoichiometric demand)	50, 100

and the chemical oxygen demand (COD) under less severe conditions i.e. low temperature, pressure and retention time and also to determine the behaviour of the detergents under different conditions. Collection of kinetic data for a reasonably low cost WAO unit for the wastewaters (Table 5.1) was also one of the targets set for this study.

The characteristics of the six different detergents are given in Table 5.2. All the values given in Table 5.2 are equivalent to 1% active detergent concentration.

Table 5.2. Characteristics of Diluted Detergents Used in Study

Parameter	Zeolite	LAS	LES	Persil	HEQ	Comfort
AD (mg/l)	10000	10000	10000	10000	10000	10000
Active agent	Anionic (HDL)	Anionic (LAS)	Anionic (LES)	Anionic (LES+LAS)	Cationic (HEQ)	Cationic (HEQ)
TCOD (mg/l)	35400	21440	17600	27900	27120	225090

Note: All the above values are in mg/l and given for a 1 % detergent (Source: Holbrook, 1995)

(a) Zeolite or HDL (Heavy Duty Liquid)

(I) Results

This is one of the heavy duty liquids used in the manufacture of different anionic detergents. The molecular weight of HDL most commonly known as zeolite was 468.75. Due to its very sticky nature it was necessary to carry out some tests for its optimum concentration which could be utilised for better active detergent

(AD)/COD destruction. Two sets of tests were carried out, of which half were conducted at 3.5 MPa pressure and the other sets were conducted at 5 MPa pressure. Fig. 5.7 shows %AD and %COD reduction at two different pressure and AD concentrations. At 200°C, 60 minutes RT the result was a COD and AD reduction of 50% and 95% respectively.

WO of up to 30 % Zeolite concentration was investigated at 280°C and 1 MPa pressure. A unique phenomenon was observed during test runs at 200°C for all samples of 4.5 % active detergent concentration and higher and at 6 MPa pressure. Due to instantaneous oxidation in the reactor, the safety disc burst. The pressure at the time of this sudden explosion of the safety disc was 25 MPa and the temperature was greater than 310°C.

To improve the overall performance of the process the use of a catalyst was initiated to try to achieve a high degree of oxidation of detergent wastewater. Tests were carried out at 280°C to determine the effect of catalysts on the destruction of active detergent (AD) and COD and to produce sufficient data to suggest tests at lower temperature and also to determine the most effective catalyst. The other reasons for selecting the higher temperature was the effect of the catalyst on COD destruction and shorter retention times compared to those at lower temperatures.

Three different types of catalyst were used; MnO_2, $MnSO_4$ and $CuSO_4$. Fig. 5.8 shows that no significant destruction of active detergent and COD was observed for MnO_2 and $MnSO_4$ catalysts since the COD of the sample actually increased. On the other hand, the $CuSO_4$ catalyst achieved AD and COD destructions of 70% and 55% respectively.

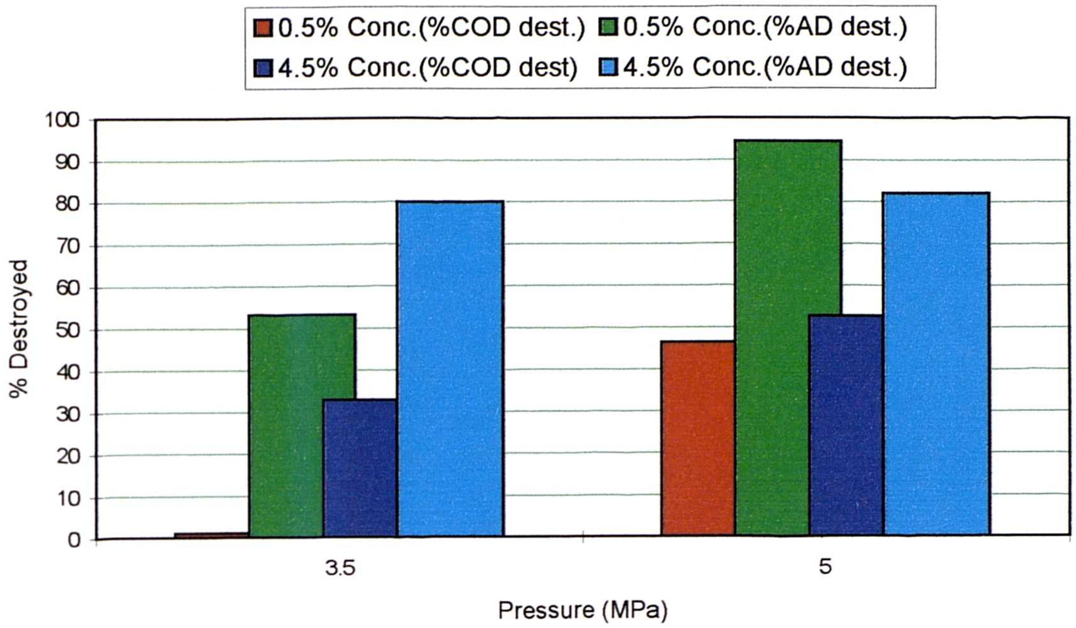


Fig. 5.7: COD and Active Detergent (AD) Destruction at Different Overpressures

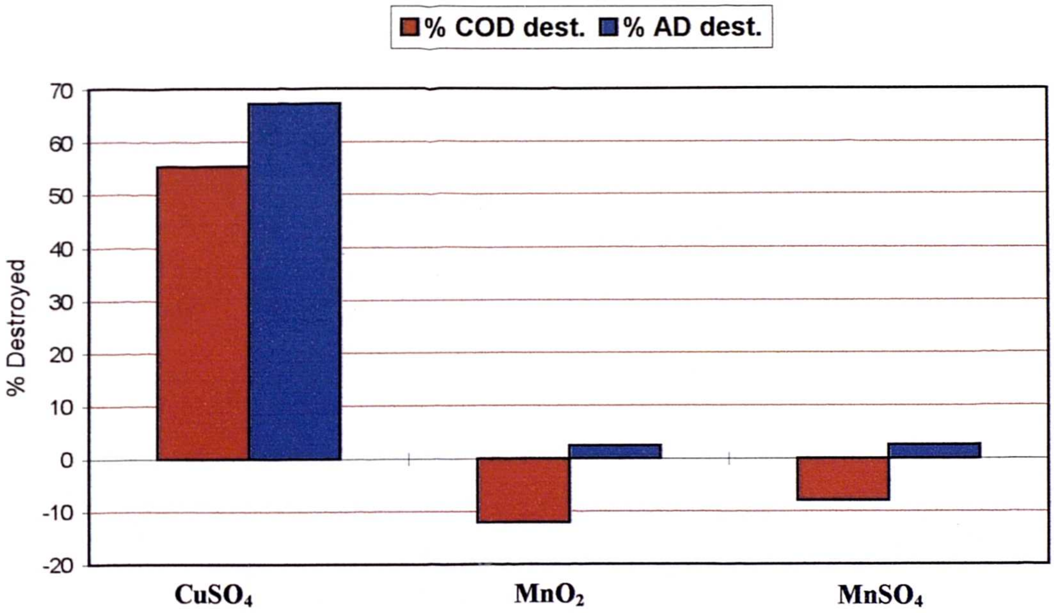


Fig. 5.8: Effect of Different Catalysts on Catalysed WO Performance (HDL)

Note:

Active Detergent Concentration = 6%

Retention Time = 10 minutes

Catalysts Concentration Used: 500 mg/l

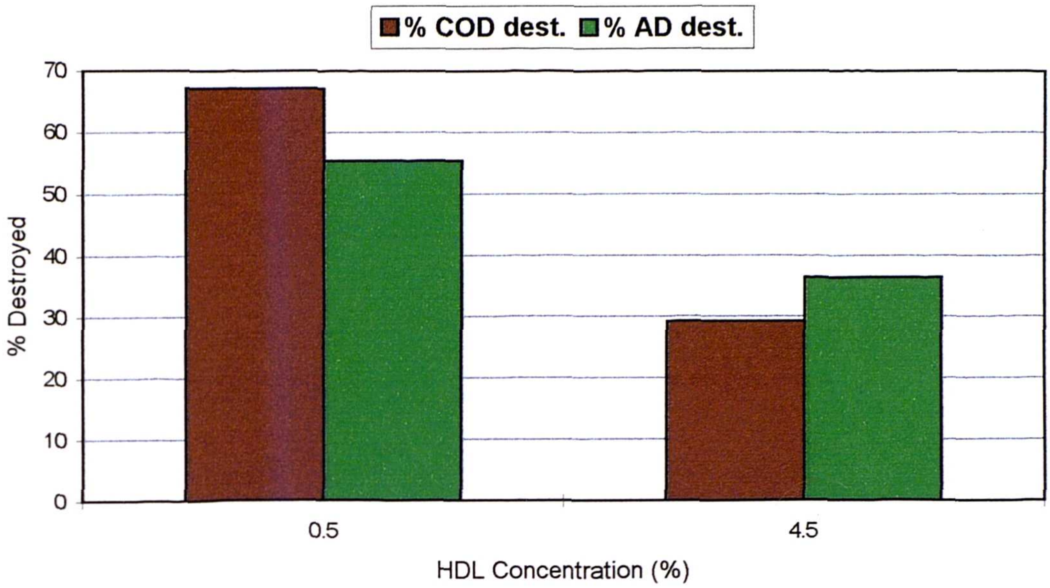


Fig. 5.9: COD Destruction at Different Detergent Concentration
Note:
Catalyst used: $CuSO_4$
Retention time: 10 minutes

(II) Discussion

It has been found from the experimental results that the concentration of the detergent (Zeolite) plays an important role in the WO environment. In general as the concentration of Zeolite was increased, the removal of active detergent and COD decreased. The maximum reduction in active detergent and COD was achieved at 4.5 % Zeolite concentration.

At 200°C the sudden increase in pressure and temperature could have resulted from the high dielectric constant of water. This was also reported by Griffith and Gloyna (1994). At 200°C the viscosity of water molecules is at a minimum and the thermal conductivity at a maximum in the temperature range 0°C to 700°C. It is believed that at low temperature (200°C) the breakage of the detergent molecules might have released large amounts of instantaneous heat energy. This release of heat energy was so sudden that it made it difficult to control the conditions of constant temperature and pressure.

The reason for the lower destruction of active detergent (AD)/COD at high HDL concentrations is probably due to the lack of sufficient oxygen for oxidation and secondly due to its very sticky nature, since mixing could not provide sufficient contact between oxygen and the detergent. This leads to the conclusion that highly concentrated organic compounds will require a long RT, as observed by Luduvice (1992).

In the past the effects of catalysts have been studied in WO systems but non were used in the treatment of detergent wastewater. The use of catalysts has been widely reported in the literature to reduce oxidation temperature and thereby decrease energy costs (Chowdhury, 1974; Chang, 1990; Frisch and Gloyna, 1992). The reason for the increase in COD by using MnO_2 and $MnSO_4$ catalysts might be the solubilization of complex detergent molecules into more simple organic compounds. The effect of $CuSO_4$ on the concentration of detergent was also studied (Fig. 5.9). Typical results show that high active detergent and COD removal at low concentration and low active detergent and COD destruction at high concentrations were achieved. These results suggest that at low active detergent concentrations a low RT, and at high active detergent concentration a long RT would be required for active detergent and COD destruction. A combination of catalyst as recommended by Chang, (1990) should be tested at low temperature to observe any beneficial effects on the overall efficiency.

The results show that at high temperature, manganese catalyst systems could not improve the overall destruction of organic matter of the detergent although pure catalysts were tested in the experiments. The use of catalyst would also increase the metal concentration of the residual ash, depending on the concentration of catalyst used, which may ultimately result in difficulties in disposing of the heat treated ash. It appears that, while treating zeolite at a high temperature, the use of MnO_2 and $MnSO_4$ should be restricted as their use fails to being any significant change in the overall destruction efficiency.

(b) LAS (Linear Alkyl Benzene Sulphonate)

(I) Results

The molecular weight of this anionic detergent was 362 and its maximum active detergent concentration was 5%. The dependence of the oxidation rate on the oxygen partial pressure, retention time and temperature were studied. Typical results are shown in Figs. 5.10 and 5.11. For each temperature the oxygen partial pressure was 2MPa. The active detergent removal at the lower temperature (160°C) was 70% and beyond 200 C the active detergent removal was almost constant at all temperatures tested. The effect of RT on active detergent removal at 200°C was 80% at 15 minutes and 99% at 60 minutes, on the other hand, at 280°C there was no difference in results at different retention times.

(II) Discussion

It can be concluded from the above results that if active detergent destruction is the primary aim of the treatment, 200°C is the optimum temperature to produce

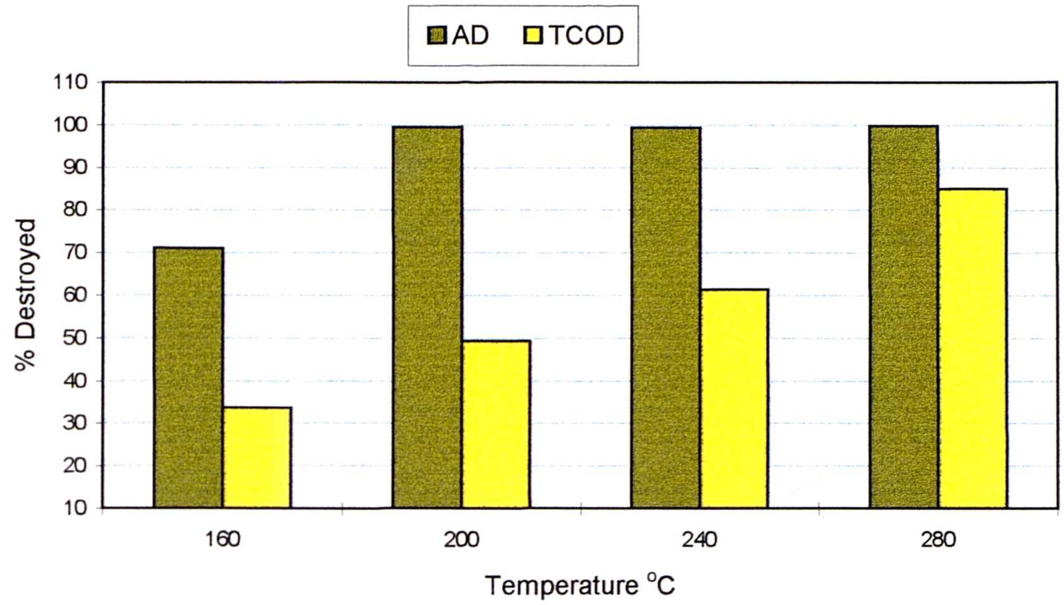


Fig. 5.10: Effect of WO Temperature on Active Detergent (AD) and COD of LAS
Note:
Oxygen Overpressure: 2MPa
Retention time: 60 minutes
Feed COD: 107 g/l

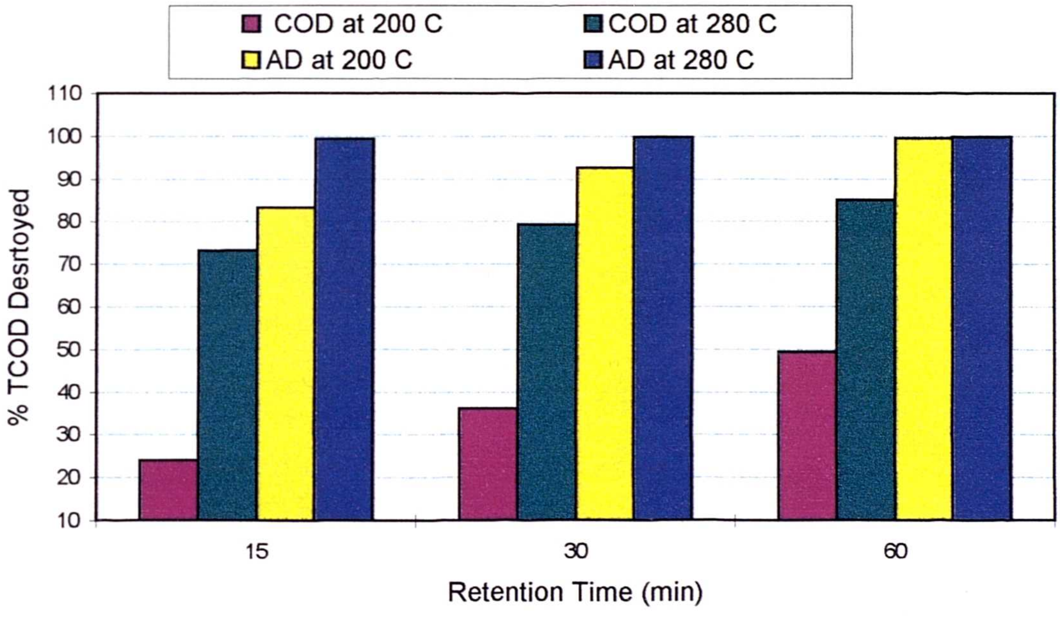


Fig. 5.11: Effect of WO RT on Active Detergent (AD) and COD of LAS
Note:
Oxygen Overpressure: 2 MPa

sufficient destruction of the active detergent for LASs. It was expected that as active detergent destruction proceeded, this would lead to the destruction of COD accordingly, but due to the formation of the generated COD it can be assumed from the results that initial COD was not destroyed. As discussed earlier in Sections 5.2.1 and 5.2.2, similarly, as the initial COD due to active detergent was destroyed, the remaining COD in the liquor was generated (Fig. 5.10). At the higher temperature (280 C), the destruction of active detergent and COD were both very high.

The COD destruction followed the same pattern: at lower temperature the destruction increased with increasing RT, and at the high temperature, no such significant difference in results was observed (Fig. 5.11). The operating parameters of WO (temperature, pressure and retention time) for the destruction of active detergent and COD could be reduced to lower values, if diluted samples (<1%) could be used. It may be concluded from the above results that for the destruction of active detergent, 200 C and 30 minute RT would be optimum process parameters to destroy sufficient active detergent for further treatment by any biological treatment processes.

(c) **LES** (Sodium Lauryl Ether Sulphate)

(I) Results

This is an anionic surfactant used in modern detergent manufacture. The calculated molecular weight was 446.5 and its maximum active detergent concentration was 5%. It has similar properties to LAS with a COD of 88g/l. The difference being its usefullness for dish washing while LAS possesses more favourable cleaning properties for textile.

COD and active detergent destruction at 200° C and 280° C are the same and are above 85% and 99% respectively (Fig. 5.12), which suggests that 200° C is the most appropriate temperature for the destruction of organic detergent molecules. No significant difference in destruction efficiency was noted at different LES concentrations (Fig. 5.13).

(II) Discussion

The destruction of active detergent is similar to that of LAS, with the only difference between the LAS and LES being that in the case of LES greater than 86% COD was destroyed even at the lower temperature (200° C). On the other hand similar COD destruction for LAS was observed at 280° C. The reason for this is that LES has 45°o less initial COD, which indicates that the smaller and weaker molecules of LES after breakdown generated less COD. If COD destruction is desirable, a long RT will not favour further COD destruction because 100% of the final VFAs were acetic acid. Acetic acid destruction below 300° C is most unlikely to occur. In the past, research was conducted by Immamora (1982), as reported by Chang (1990), on the destruction of acetic acid, using combinations of catalysts, but their results suggest no appreciable destruction of acetic acid below 300° C.

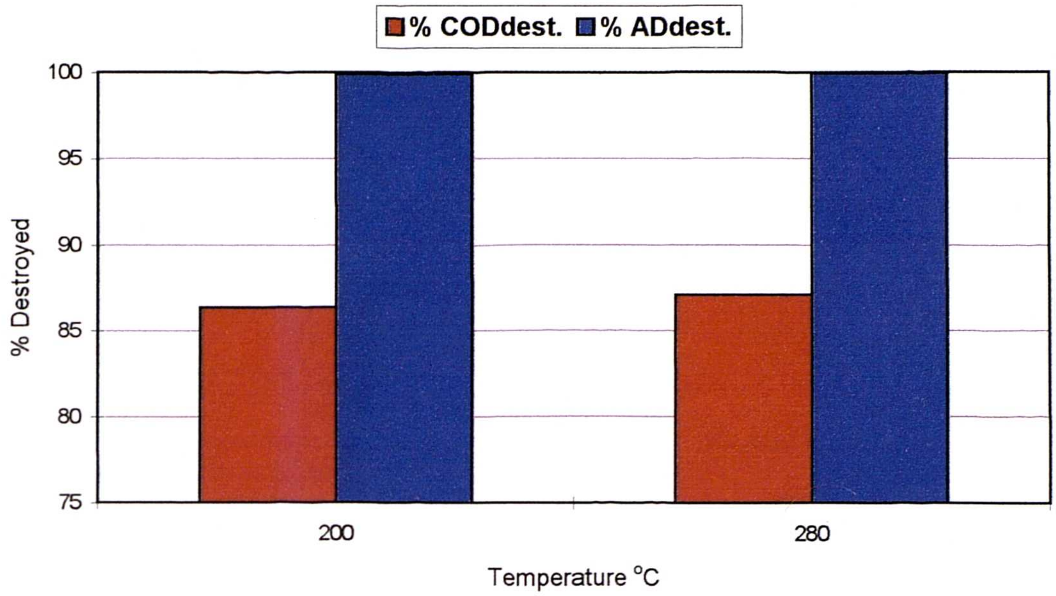


Fig. 5.12: Effect of WO Temperature on Active Detergent (AD) and COD of LES
Note:
Detergent Concentration (AD): 5%
Oxygen Overpressure: 2mpa
Feed COD: 88 g/l

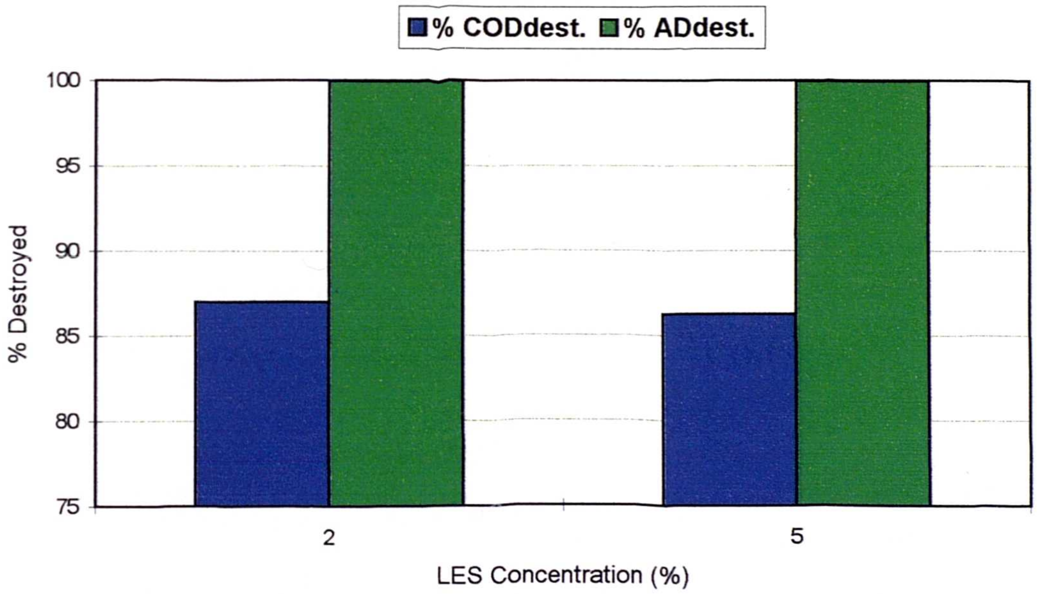


Fig. 5.13: Effect of Concentration on Active Detergent (AD) and COD of LES
Note:
Oxygen Overpressure: 2MPa
Retention time: 60 minutes

(d) Persil Dish Washing Liquid

(I) Results

Persil is the trade name of one of Unilevers' dish washing liquid detergents. This is mainly an anionic detergent, having a molecular weight of 362 and is made from a combination of LAS and LES (>90%) along with other organic and inorganic compounds, such as ethyl alcohol, mercury (a type of perfume) citric acid, tartrazine yellow E102, duasyn acid blue AE02, LMEA, LAPB.

The COD of the Persil supplied was 837 g/l, with an active detergent concentration of 300 g/l. As most of the Persil consists of LES molecules, which were highly oxidizable as shown in Figs. 5.12 and 5.13, it was assumed that a high concentration of Persil could be used. The assumption proved accurate and active detergent destruction occured at all concentrations of Persil and at considerably lower partial pressure of oxygen (Figs. 5.14 and 5.15). At 2MPa pressure the COD destruction was 45% at 30% Persil concentration and above 95% at 4.5% Persil concentration.

At 15% active detergent concentration treated at 280°C, the active detergent removal of anionic surface-active detergent was 100% but unexpectedly some cationic detergent molecules appeared. While using pure Persil which was 30% active detergent concentration, the treated sample of Persil was clearly divided into two layers, the upper layer of pure oil texture and the lower layer containing detergent suspended in a water medium. The COD of both layers was determined separately. Results show that an oxidation of 41% of COD was reached for the top oil layer with the COD content increasing to 26% with a decrease of COD in the bottom layer of 91%. This brought the COD level of the top layer from 837 gram/l to 1126 gram/l, a net COD generation of 26% and the COD level of the bottom layer from 837 gram/l to 79 gram/l, i.e a net decrease of 91%.

(II) Discussion

The above results clearly indicate that Persil molecules can easily be broken down under less severe operating conditions. The destruction of active detergent was mainly temperature dependent. On the other hand, the destruction of COD was dependent on both temperature and oxygen partial pressure.

The COD destruction was 45% at 30% Persil concentration and above 95% at 4.5°o Persil concentration, suggesting the need for the presence of sufficient oxygen inside the reactor for oxidation. This statement bears little weight, from a stoichiometric point of view, because at any temperature, the corresponding oxygen partial pressure does not satisfy the oxygen demand of the Persil molecules as estimated from the COD requirement of the sample due to limited reactor pressue (13.1MPa). One of the reasons which could explain this uncertainty is that Persil detergent molecules are weak and may be broken down into simpler smaller organic molecules without the need for oxygen. This argument can be explained by the fact that when biological sludges were treated at a high temperature without oxygen, hydrolysation of sludge solids occured. Detergent molecules have followed a similar pattern resulting in less active detergent concentration in the effluent.

The similarity in results (Fig. 5.15) at high and low temperature is due to more

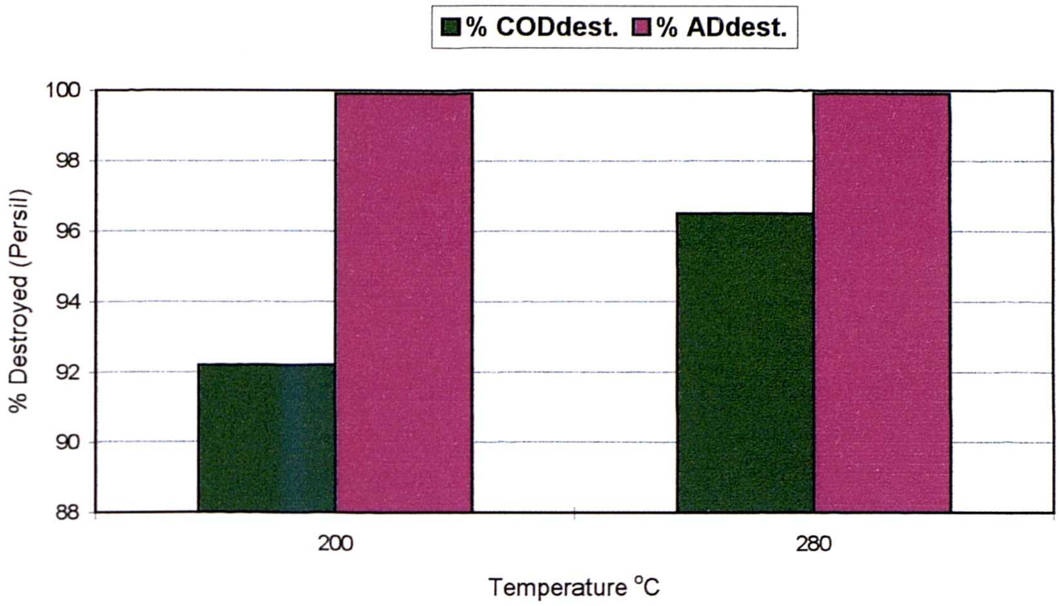


Fig. 5.14: Effect of WO Temperature On Active Detergent (AD) and COD of Persil

Note:
Oxygen Overpressure: 2MPa
Retention time: 60 minutes
Persil Concentration: 6%
Feed COD: 126 g/l

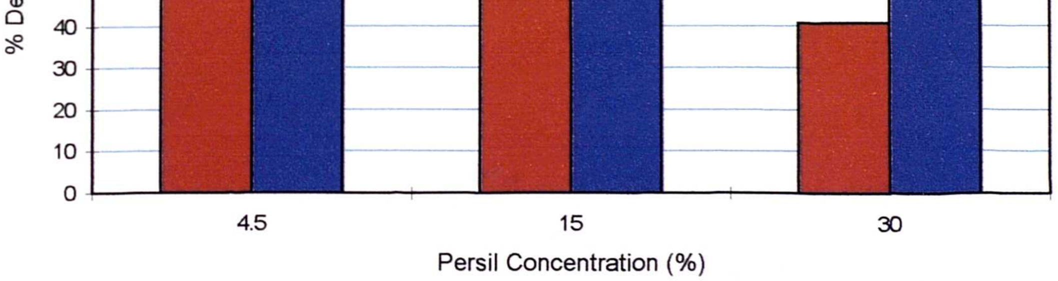


Fig. 5.15: Effect of Concentration on Active Detetergent and COD of Persil

Note:
Oxygen Overpressure: 2MPa
Retention time: 60 minutes
WO Temperature: 280°C
Feed COD: 126 g/l - 837 g/l

oxygen being available at the lower temperature, but the oxygen concentration was still less than the stoichiometric requirements of the sample at the lower temperature, (due to a limited reactor pressure of 13.1 MPa). This suggests the validity of both arguments which in turn also implies, as discussed in the previous sections that at lower temperature, pressure plays an important role in organic matter destruction.

The increase in COD (top oil layer) was probably due to an increase in the breakdown rate of the large detergent molecules into more complex molecules which impart a higher COD than the original molecules. The formation of high COD can be explained from the results of Luduvice (1992) who while treating organic sludges found a substantial increase in TCOD.

As discussed earlier, the formation of two separate zones (oil and water) might be due to an oxygen starved system. One of the outcomes of these results could be the recovery and utilisation of the oil into the manufacture of other similar products.

(e) **HEQ** (Hamburg Ester Quaternary Ammonium Surfactant)

(I) Results

This is a cationic surfactant most commonly used in the manufacture of Comfort fabric conditioner. Its molecular weight is 530, the maximum active detergent concentration was 5% and had a COD of 135.6 g/l.

Results show (Fig. 5.16) that high organic matter destruction at both lower and higher concentration of HEQ, i.e. 100% active detergent and 85% COD destruction. Although a significant destruction of COD and total destruction of cationic detergent

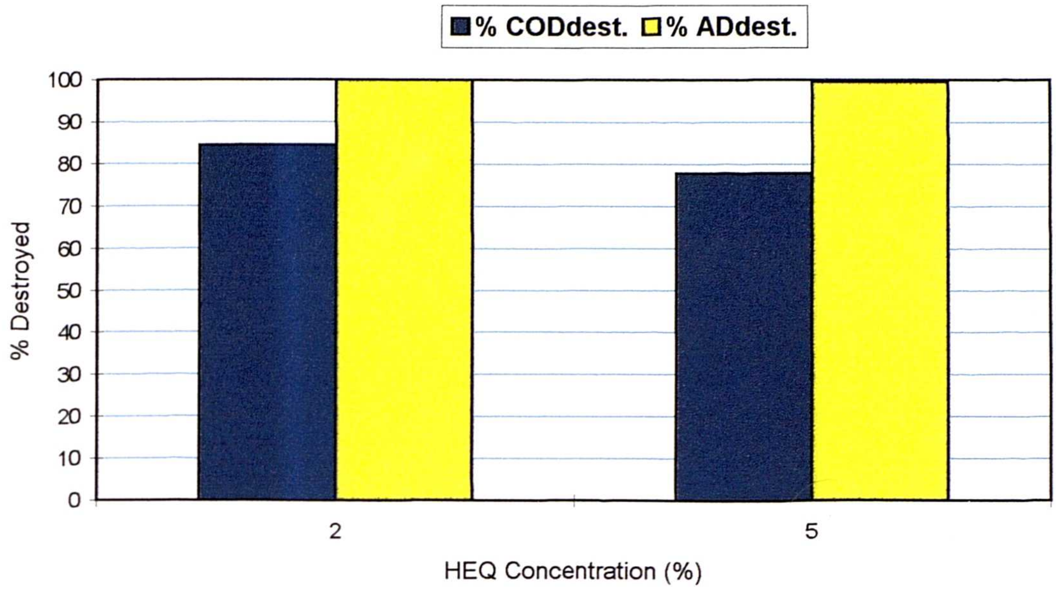


Fig. 5.16: Effect of WO on Active Detergent and COD of HEQ Concentration
Note:
Oxygen Overpressure: 2MPa
Retention time: 60 minutes
WO Temperature: 280°C

was achieved, the remaining COD of the liquor was 30 g/l, which could be readily treated by any conventional treatment process. The most significant aspect of these results is that only 1 MPa overpressure was used, which was well below the stoichiometric requirement of the sample.

(II) Discussion

The exact path of the reaction for HEQ is not known but it could be explained as being similar to the HDL results. As the cationic molecules were very reactive, the first breakage of the cationic detergent molecules could have given rise to the formation of some highly reactive radicals which act as a catalyst in the system. This would aid in the oxidation reaction and subsequently reduce the demand for oxygen from outside sources.

100% of the VFAs of heat treated liquor was in the form of acetic acid and the high COD liquor suggested that an anaerobic process would be the best option provided there were no other anaerobic inhibitor compounds present. Preliminary tests on HEQ were carried out to investigate the behaviour of cationic detergent during destruction. Results suggest that a cationic surfactant could be readily oxidised even at the lower operating conditions.

(f) Comfort Fabric Softner

(I) Results

Comfort is the trade name of a cationic surfactant, used as a fabric softener. Cationic surfactant quality depends on the molecular structure of the surfactant i.e. chain length and type of alkyl substitute, time of reaction, temperature, pH and the presence of other surfactant or builder etc.

This is mainly a cationic detergent having a molecular weight of 678 and is made from Hamburg Ester Quat. (HEQ) along with other organic and inorganic compounds such as builder, perfume, and colour to enhance its aesthetic value. The COD of the Comfort supplied was 2.44 kg/l, with an active detergent concentration of 101 gram/l .

Two different temperatures were used to evaluate the organic matter destruction (Figs. 5.17 and 5.18). Results show that active detergent destruction is nearly similar at all concentrations and temperatures. The COD destruction was mainly temperature dependent, with a better removal at higher temperature than lower

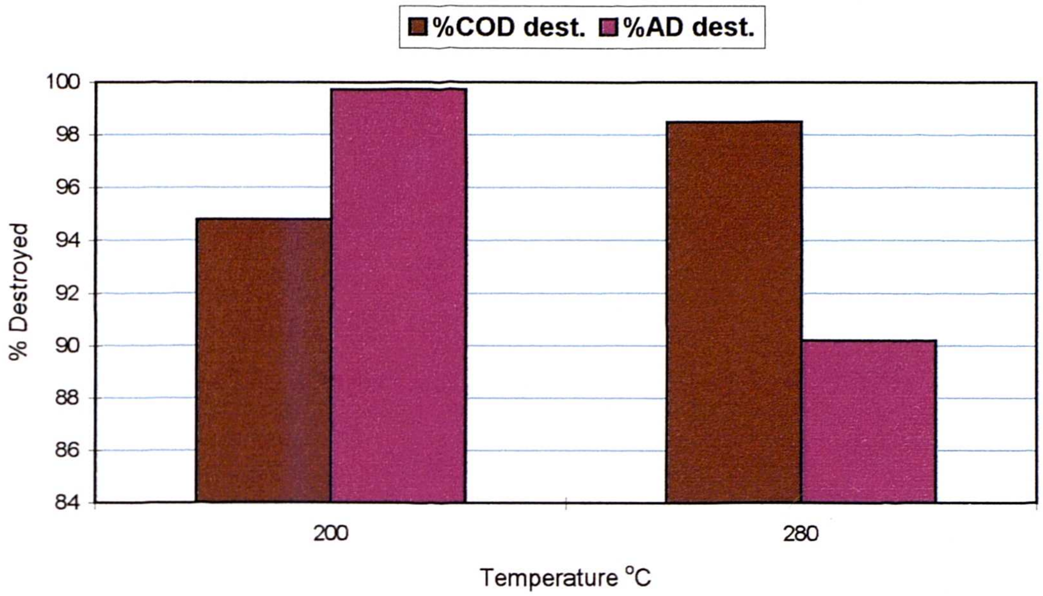


Fig. 5.17: Effect of WO temperature on Active Detergent andCOD of Comfort
Note:
Oxygen Overpressure: 2MPa
Retention time: 60 minutes
Detergent Concentration: 1.63%
Feed COD: 367 g/l

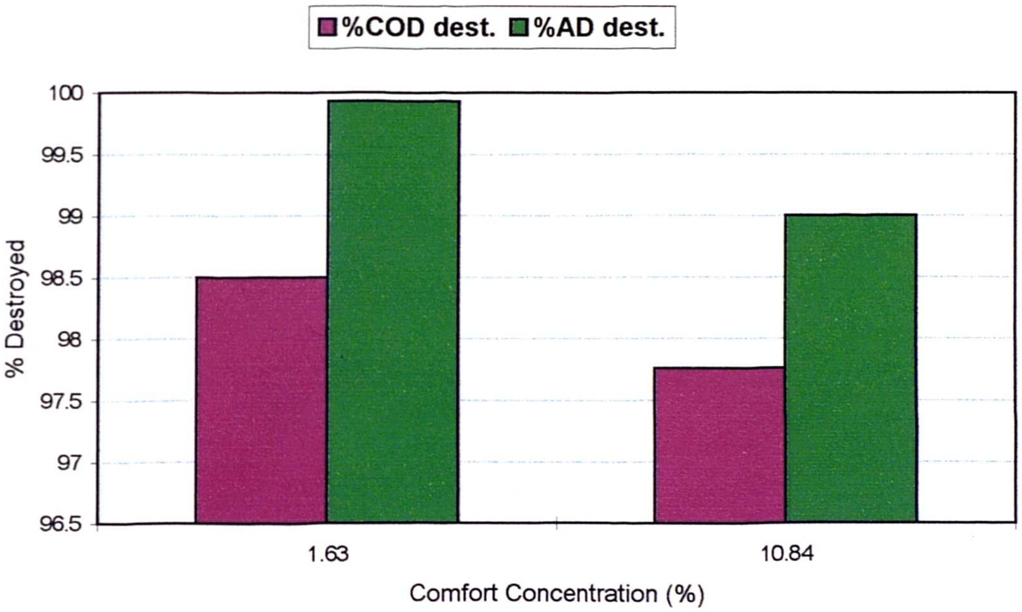


Fig. 5.18: Effect of WO on Active Detergent and COD of Comfort Concentration
Oxygen Overpressure: 2MPa
Retention time: 60 minutes
WO Temperature: 280°C
Feed COD: 367 g/l - 2440 g/l

temperature. The COD destruction indicates that, unlike anionic detergent, the cationic detergents were highly resistant to temperature. There was 98% COD destruction of the sample having a COD of 2.44 kg/l, although the oxygen present inside the reactor for the sample was not more than 15 g/l, which was clearly insufficient for the level of oxidation.

(II) Discussion

From the above results it can be concluded that the cationic molecules used in Comfort fabric softener can easily be broken down at lower temperatures and retention time. The exact reason for this much higher oxidation is not known but may be explained on the reasoning given in previous Section.

According to the oxidation model proposed by Li et al., (1991) the majority of the organic matter oxidises in a reaction process formed by two parallel systems and total oxidation into carbon dioxide and water occurs either by a direct route or via the formation of more simple intermediate products. At low temperature significant oxidation was observed and changes in the organic content were probably due to hydrolysation.

5.2.4 TCOD Destruction from WO of Paracetamol Wastewater

(I) Results

Paracetamol (acetaminophen) is an analgesic and used as a pain killer. The wastewater from the Paracetamol plant at Sterling Organics at Dudley, England contains of acetaminophen and intermediates such as para-amino phenol (PAP) and other by-products of sulphates. The sulphate quantity determined by the barium chloride method was 5 to 7 g/l and the TCOD of the Paracetamol was 60 to 90 g/l. The colour of the raw wastewater was dark black.

Since 1977, Sterling Organics had dumped all the wastewater in the North Sea but due to the strict environmental legislation in UK, such dumping was stopped and a WAO plant was installed in August 1992. The unit was designed and constructed by Zimpro Envi. Inc. USA.

Sterling Organics investigated different biological and non-biological treatment options for their recalcitrant wastewater, but could not arrive at a definite solution. Both aerobic and anaerobic methods were tried but no effective anaerobic method could be found to treat a waste stream with very high concentration of phenol and SO_4. The presence of 5 to 7 g/l of SO_4, inhibited the aerobic process.

Both landfilling and incineration of the effluent were ruled out because of high capital and operating costs. In addition, landfill had the potential for continuing future liability. Purely chemical treatment methods i.e fixation, solvent extraction and co-solvent precipitation could not completly remove all of the contaminants from the wastewater. Purely physical processes such as reverse osmosis and ultrasonic treatment generated organic tar and inorganic salts that fouled the treatment equipment and were also ruled out. WAO overcame the limitations of purely, physical , chemical or biological processes (Zimpro Envi. Inc. Rothschild, Wis., 1993).

Fifty litres of untreated and one litre of treated samples of paracetamol wastewater were collected for treatment and analysis. Tests were carried out with the objective of knowing as precisly as possible the similarities in destruction efficiences between full-scale WAO and laboratory bench-scale WO unit under similar conditions.

A series of tests was undertaken to evaluate the effects of WO on the destruction of paracetamol wastewater and the transformation of inorganic compounds. Typical results of organic matter destruction are shown in Fig. 5.19. The effect of temperature is very evident on COD destruction at 60 minute retention time. The destruction of COD follows a similar pattern to those discussed earlier in this chapter: a low COD destruction at low temperature and a high COD destruction at high temperature. A COD destruction of 45% and 99% being observed at 200 °C and 300 C respectively. Destruction of COD beyond 260°C was almost remain the same for 280 C and 300°C for the laboratory- scale WO unit.

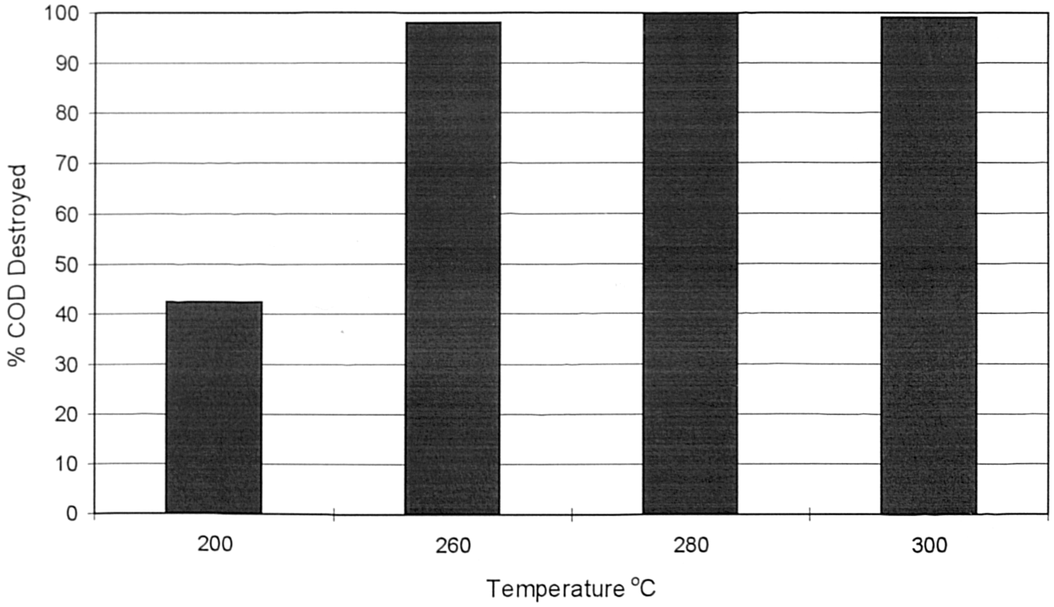


Fig. 5.19: Effect of Wet Oxidation on COD of Paracetamol Wastewater
Note:
Oxygen Overpressure: 2 - 5MPa
Retention time: 60 minutes
Feed COD: 80000 mg/l

(I) Discussion

One of the aims for selecting the above industrial wastewaster was to compare the results from the full-scale continuous flow wet air oxidation plant at Sterling Organic's and the laboratory batch-scale wet oxidation reactor, to evaluate and find justification for installing a continuous flow wet oxidation laboratory-scale reactor. By comparing the results from both processes no justification has been found for installation of continuous flow wet oxidation laboratory-scale reactor.

Sterling Organics operate the WAO plant at $260^\circ C$, one hour RT and a flow rate of 60 l/minute. Under the above operating conditions a destruction of 96% COD has been achieved. On the other hand at laboratory-scale under similar conditions 99% COD destruction was achieved. The reason for this better efficiency in laboratory-scale WO unit could be due to the longer heating-up and cool-down time.

5.3 SOLIDS DESTRUCTION BY WO

In wastewater treatment, sludge management and disposal are often the most difficult and expensive operations. Sludge treatment generally consists of dewatering and destruction of sludge solids before ultimate disposal of any residue. Throughout this research, total solids (TS) and volatile total solids (VTS) were the parameters chosen for monitoring the destruction of solids during WO. VTS is the most important parameter of sludge solids, and is used to estimate the organic content. If VTS is destroyed, then the residual solids will be considered inert. Most of the transformations which take place during WO of liquors come from the initial VTS. A kinetic model of activated sludge destruction and transformation will be discussed later in this chapter.

All percentage destruction of solids under WO were calculated using the equations in Appendix A (1.2A). A knowledge of the changes in VTS and TCOD during WO of sludges and wastewater provides a good indication of the transformations which are taking place and the nature of the residual material.

Sludge solids are solubilized through the hydrolysis of organic material in a WO environment. Pure oxygen as the oxidising agent, increases the oxidation process of both the soluble and insoluble organic matter. Pure organic wastewaters, such as those from the production of detergents contains nearly equal quantities of VTS and TS.

If the wastewater or sludge consists of purely organic matter such as in the detergent wastewater, the relation between COD and the organic matter is linear. The destruction of AD implies the destruction of organic matter. In the case of biological sludge solids, the COD : TS ratio and the VTS : TS ratio are good indicators of the oxidizable organic matter present in the sludge solids. A higher COD : TS and VTS : TS ratio before WO treatment and reduced value of the above ratio at the end of treatment are indications of higher organic matter removal and less inert ash for disposal.

5.3.1 Solids Destruction from WO of Raw Primary Sludge

(I) Results

It was decided to use a constant solids concentration throughout this study in order to achieve results that could be compared under different operating conditions.

The ratio of COD : TS for the first batch of sludge collected from the Howdon wastewater treatment plant (which has primary treatment only) was found to be 0.93. The subsequent samples were either thickened or had tap water added. One of the reasons for selecting diluted sample of sludge was to increase its handling characteristics. Samples having more than 5% solids required more time for loading and unloading due to the need to open the reactor lid each time compared to feeding and removal of low solids (< 5%) samples through the feed and outlet ports.

The effect of SOR, retention time (RT) and temperature on the destruction of TS and VTS are shown in Figs. 5.20 and 5.21 respectively. TS destruction in the range of 20% to 80% was achieved. Fig. 5.20 shows that the destruction of TS appears to be independent of the SOR but was highly dependent on temperature and RT.

Volatile solids destruction followed a pattern similar to that for TS. The significant aspect concerning VTS destruction was that it took place at low temperature and high partial pressure. At 200 °C, 60% of VTS were destroyed, with a 30% TS destruction being observed (Figs. 5.20 and 5.21). Destruction of VTS at other temperatures was slightly greater than the corresponding TS destruction.

The overall destruction of TS and VTS at 300 °C is shown in Fig. 5.22. One of the advantages in using pure oxygen was the improvement in filterability (CST) which will be discussed later in this chapter. The composition of the residual solids was changed significantly, and in such a way as to enable the dried powder form to be used for colour removal from textile waste.

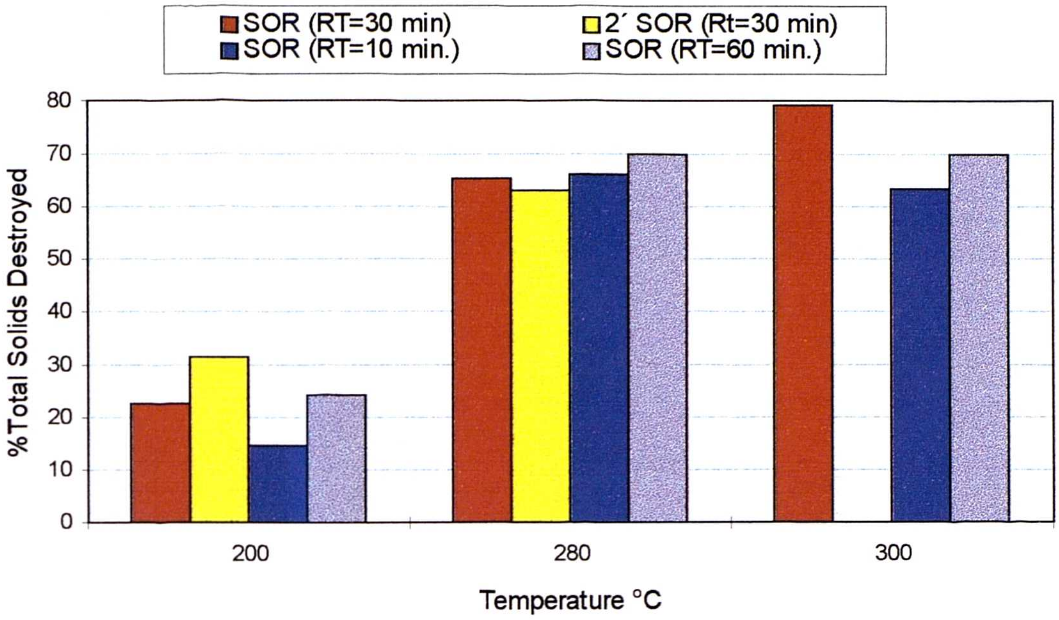


Fig. 5.20: Effect of WO Temperature on Total Solids of Raw Primary Sludge

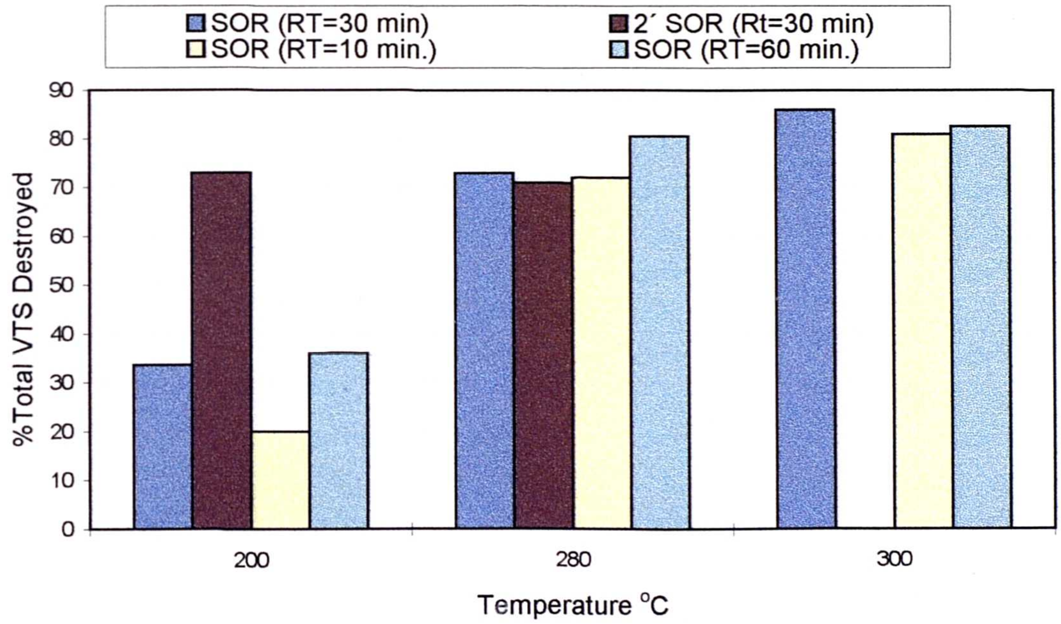


Fig. 5.21: Effect of WO Temperature on VTS of Raw Primary Sludge

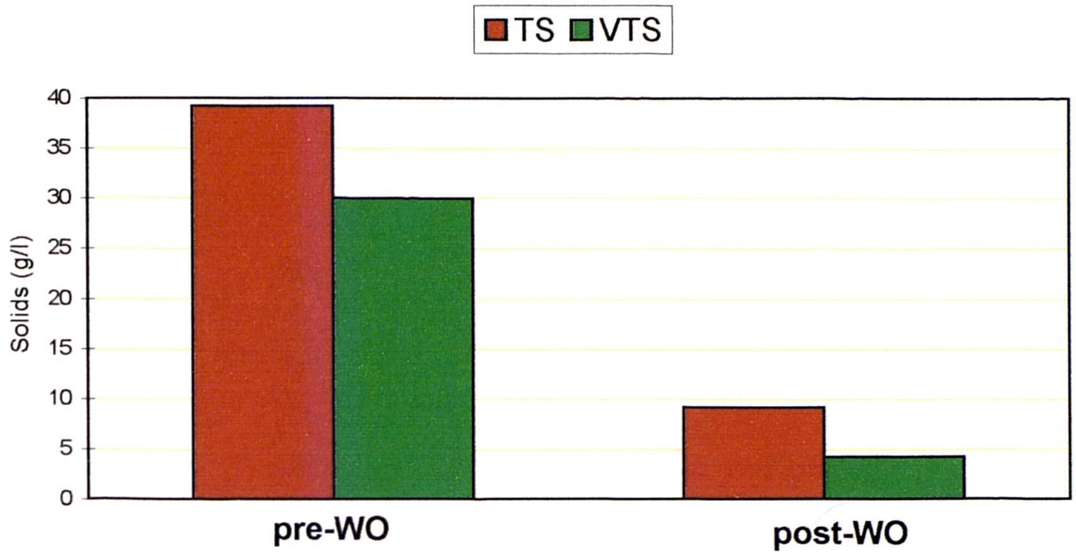


Fig. 5.22: Effect of Wet Oxidation on Solids of Raw Primary Sludge
Note:

Temperature: 300 ° C
Retention time: 60 min.
Oxygen overpressure: 2 Mpa

(II) Discussion

In this study TS destruction was achieved due to thermal decomposition and hydrolysis before the injection of oxygen while further TS destruction was achieved through solubilization of TS followed by subsequent oxidation of the solubilized organics. The TS destruction followed a similar pattern to that reported by Luduvice (1992), despite the fact that air was used in his investigations. This suggests that if TS destruction is the only objective then there is no need to use pure oxygen.

The greater destruction of VTS at 200 ° C could be attributed to high partial pressure and could be explained on the basis of the physical and chemical behaviour of the water vapour. At 200 ° C and high pressure the viscosity of the water molecules is a minimum while its thermal conductivity becomes maximum, which aids thermal decomposition, and solubilization in turn followed by oxidation accounted for a greater removal of VTS. At 300°C, 80% VTS destruction was observed but this does not justify the use of pure oxygen if only solids destruction is required.

5.3.2 Solids Destruction from WO of Gravity Thickened Activated Sludge

(I) Results

The TS and VTS of the thickened activated sludge used in the present study were found to be 2.65% and 2.1% respectively while the average TS : COD ratio of the sludge was 1. The destruction of TS was studied under stoichiometric oxygen requirement (SOR) conditions. The destruction of the activated sludge was found to be significantly influenced by temperature and by retention time.

Due to operating at SOR conditions, the destruction of activated sludge was observed at all temperatures and RTs. At the lower temperature of 200°C, TS destruction was 20% compared to 65% at 300 C. The effect of RT at lower temperatures is more significant than at higher temperature.

The destruction of TS in activated sludge (Fig. 5.23) was observed to be lower than that obtained for raw primary sludge. VTS destruction compared to TS was comparatively high (Fig. 5.24). At 200°C, 40% VTS, and at 300°C nearly 90% VTS destruction were observed. The organic concentration of activated sludge was represented by a VTS : TS ratio of 0.8 and a non-SCOD : TS ratio of 1.04. After heat treatment, the VTS : TS ratio was significantly reduced (Figs. 5.23 and 5.24). A general view of TS and VTS destruction is given in Fig. 5.25.

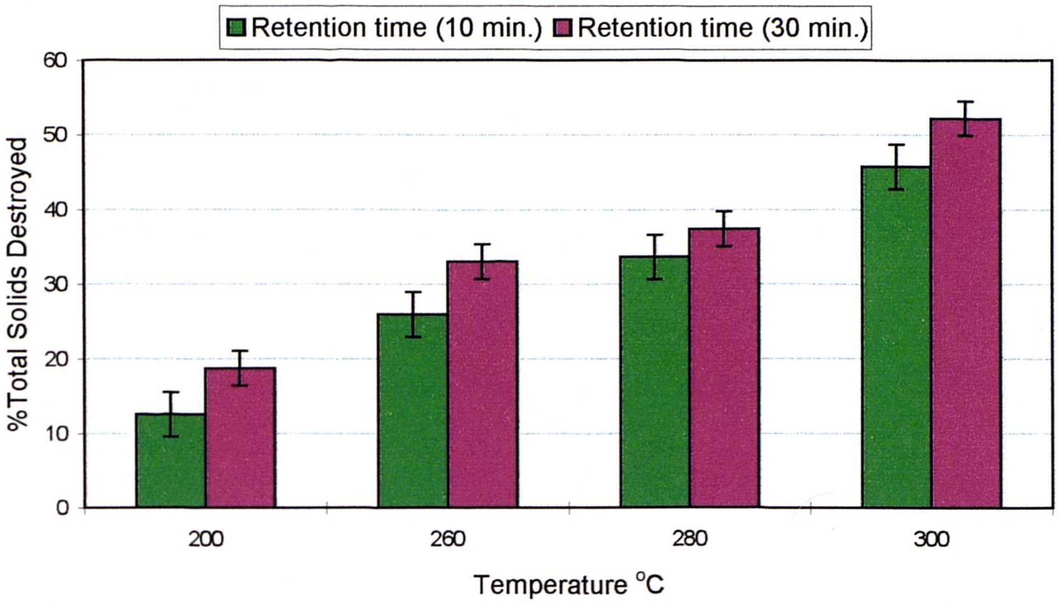


Fig. 5.23: Total Solids Destruction of Activated Sludge During WO

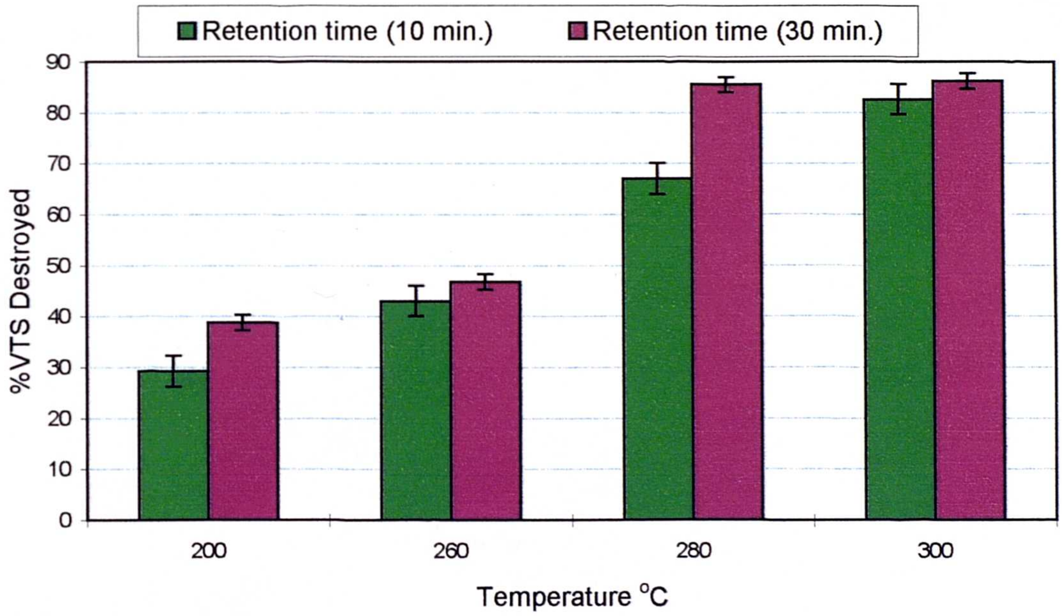


Fig. 5.24: Volatile Total Solids Destruction of Activated Sludge During WO

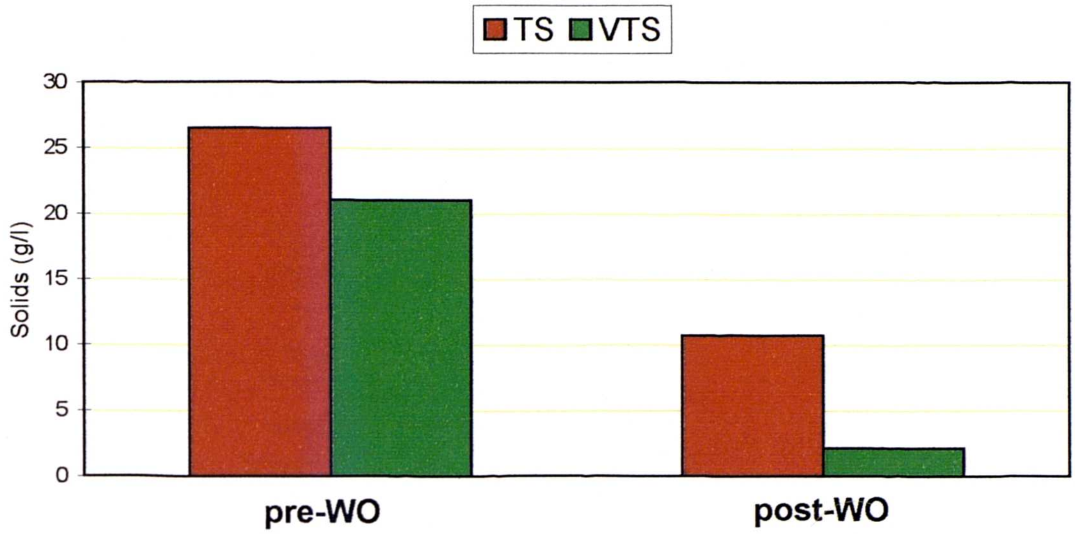


Fig. 5.25: Solids Destruction of Activated Sludge During WO
Note:
Temperature: 300 °C
Retention time: 30 min.

(II) Discussion

The destruction of TS in activated sludge as shown by the above resluts was observed to be lower than that obtained for raw primary sludge. The reason for this may be due to some organic molecules being highly resistant to WO and may also be because of more inert material in activated sludge. The destruction of TS was much higher than that observed by Luduvice (1992), even at the lower RT of 30 minutes (Fig. 5.23). The reason for this could be the SOR and the high oxidative capacity of pure oxygen. A combination of high pressure and low temperature could give high TS destruction. At low temperature, RT plays an important role in TS destruction.

Unlike the results obtained by Luduvice (1992), who concentrated on an oxygen deficient system, (due to limit on reactor pressure) the sludge treated at the higher temperatures was shown to have better filterability than those treated at lower temperature, and furthermore the residual solids at the higher temperature (> 260 °C) experiments did not result in a "sticky" residue.

5.3.3 Solids Destruction from WO of Detergent Wastewater

(I) Results

Detergent solids were mostly due to detergent molecules in addition to some colour and other builders which contributed towards both the TS and VTS. The initial high organic matter concentration of the detergent is given by a VTS : TS ratio of 0.85 to 1 and an AD:TS ratio of 1, which would mean that $AD \cong TS \cong VTS$. The COD AD ratio varies from one detergent to another being 0.04- 0.4 in the present study.

The effect of heat treatment or WO on the relationship of AD:TS and VTS : TS was very significant with an average reduction of 99% of TS being observed. The solids destruction of the detergent was very high but there was no significant reduction of COD. Due to the high ratio of VTS to TS, the detergent wastewater resulted in a much greater response to WO treatment and a very high solids destruction was achieved at all temperatures (Fig. 5.26).

(II) Discussion

The solids destruction of the detergent as given above was very high but there was no significant reduction of COD. The reason for this high COD after heat treatment (WO) could be due to the conversion of the original active detergent (AD)

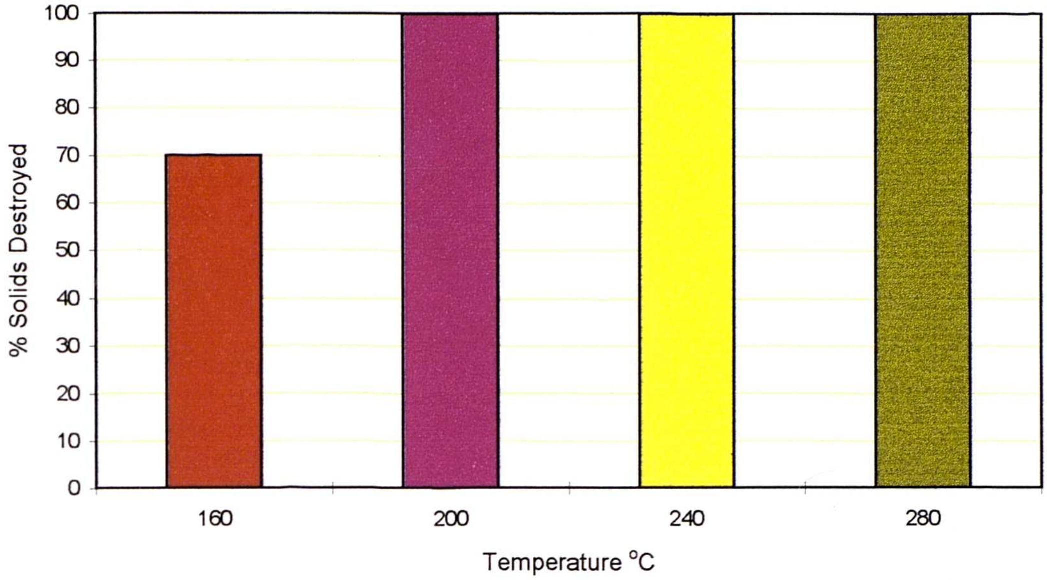


Fig. 5.26: Solids destruction of Detergent wastewater

molecules to other simpler organic molecules. There was a significant destruction of the initial solids at $200^{\circ}C$, while at $160^{\circ}C$ solids destruction was still as high as 70%. The destruction of the solids was mostly due to thermal decomposition and to a lesser extent by oxidation of the solubilized organics, because the oxygen provided did not satisfy the stoichiometric requirement of the organic matter in the samples. This indicates that most detergent solids would be very easy to destroy due to their weak molecular structures and to their high VTS and TS ratio (0.85 to 1).

5.3.4 Solids Destruction from WO of Paracetamol Wastewater

(I) Results

The solids destruction of this wastewater was not a real matter of concern but due to the nature of the WO liquor, it is necessary to point out some significant points concerning this liquor. Fig. 5.27 shows the effect of temperature on the percentage crystal formation from paracetamol liquor after cooling to ambient temperature. The results show that crystallisation is directly proportional to temperature. At high temperature a greater volume was occupied by crystals which would be difficult to handle. The organic portion of the paracetamol wastewater was destroyed by WO but the formation of inorganic compounds could make the liquor unsuitable for disposal to sewer.

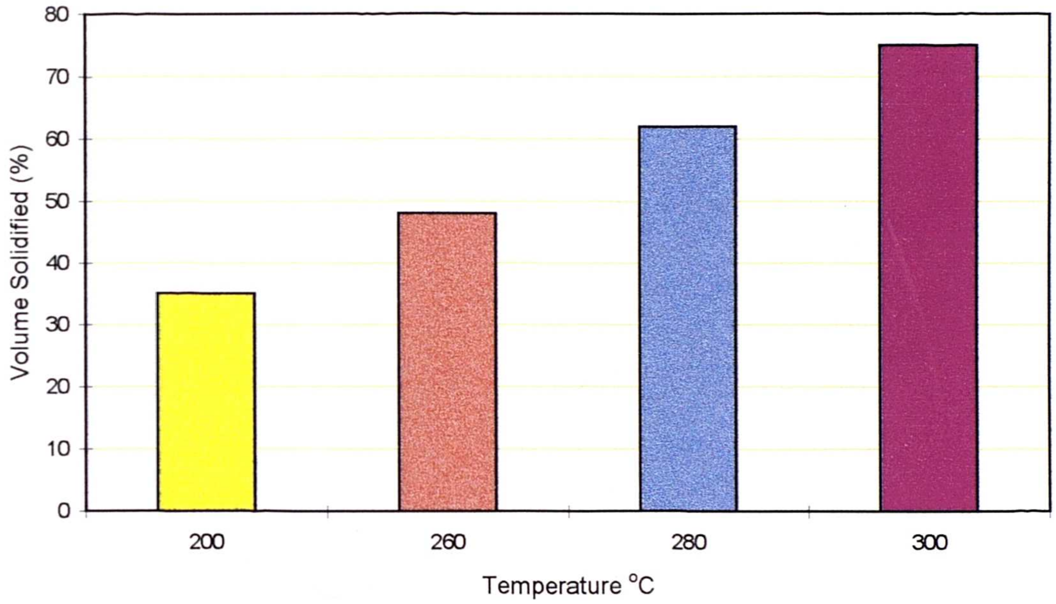


Fig. 5.27: Solids Formation of Paracetamol During WO

(II) Discussion

Although the initial TS of the paracetamol wastewater was less than 1% and was mostly due to inorganic salts. After heat treatment, the characteristics of the liquor was found to be unique. Due to the presence of inorganic salts, the liquor became crystalline at ambient temperature. The present study suggested that the crystallisation of the liquor was mainly temperature dependent; i.e., liquor treated at low temperature produced less liquor containing crystals than that treated at higher temperature. For the wastewater to be in an aqueous phase the liquor needed to be at least at $45\,^{\circ}C$.

Due to the presence of inorganic crystals the disposal of paracetamol liquor would not be easy at ambient temperature due to potential problems of pumping. The liquor produced, which was not very high in organic matter, was further treated by a high rate biological treatment process (JLR) and will be discussed in detail in Chapter 6.

5.4 WET OXIDATION LIQUOR CHARACTERISTICS

In line with the main objectives of this research, i.e. the treatment of liquors produced by WO, and which will be discussed in the second part of the chapter, it was necessary to consider the liquor characteristics in terms of pH, settleability, filterability and VFA concentration in order to evaluate its further treatment by biological systems. From a disposal point of view this is essential because wastes treated by WO clearly need further treatment for the removal of the soluble organics prior to discharge.

The production and transformation of ammonia were also important aspects of sludge and wastewater destruction. The production of ammonia was greater at higher temperature and pH changes followed a similar pattern. The pH of the liquor was observed to be affected by the production and transformation of both VFA and ammonia.

Settleability and filterability were determined using an Imhoff cone and capillary suction time (CST) respectively. The settled solids collected from the bottom of the Imhoff cone were used for CST determination in order to standardise the results obtained from the CST test. As discussed earlier, the main objective of the WO process for sludge treatment was to make the sludge more filterable since solid-liquid separation is usually the main aim of sludge conditioning. On the other hand, if WO is soley used for the destruction of toxic organic compounds, settlebilituy and filterability are not important parameters.

With respect to the potential for biological treatment of WO liquors, their strength was assesed using VFAs and COD, with acetic acid being the major contributor. These parameters are an indication of the residual organic matter in the WO liquor which could not be readily oxidized under sub-critical conditions. Acetic acid is usually the final product prior to complete oxidation into CO_2 and H_2O. Other than the VFAs, ammonia and formaldehyde were also of interest and were occasionally measured.

Any liquor with a high COD and a high concentration of acetic acid and in the absence of other contaminants could potentially be treated by an anaerobic process. Aerobic treatment would be suitable if organic contaminants such as formaldehyde etc, are present in the wastewater.

5.4.1 Liquors from WO of Raw Primary Sludge

(I) Results

The effects of temperature on the relationship of ammonia and pH are presented in Figs. 5.28 and 5.29. As the WO temperature increased both ammonia and pH of the liquors increased. The pH observed at 200 °C was generally in the range of 4 and 5.5, but was between 5 and 8 at 300 °C (Figs. 5.28).

Retention time (Fig. 5.28) also had a significant effect on the pH of the WO liquor. As the retention time was increased, due both to the oxidation of VFAs and the release of ammonia, the pH of the liquor was increased. The production of volatile fatty acids (VFA) at different temperatures is shown in Fig. 5.30. Very high VFAs were observed at lower temperature but due to the oxidation of VFA at high temperature, the VFA molecules were oxidised to a simpler form of organic acids, such as acetic acid, resulting in an overall decreased concentration of VFAs (Fig. 5.31).

Acetic acid contributed between 30% to 90% of the effluent VFAs when the TCOD removals were in the range of 10-80%. The formation of formaldehyde was not very significant, being 0.1 mg/l and 10 mg/l at 200 °C and 300 °C respectively. Due to the presence of sufficient oxygen inside the reactor, there were no noticeable odour observed.

The settling characteristics of the oxidised residues were measured using an Imhoff cone and are shown in Fig. 5.32. At an influent TS concentration of 3.92%, the solids in the effluent settled to an average volume of 85 ml/l in two hours. The colour of the residual ash darkened with an increase in temperature. An increase in temperature also improved the filterability (CST) as shown in Fig. 5.33.

The colour of the treated liquor was also temperature dependent. Liquor treated at low temperature had a dark brown colour, while those treated at high temperature were greenish-yellow in colour (Fig. 5.34). It was also noted that an increase in WO temperature decreased the tubidity.

(II) Discussion

The pH, VFA and ammonia production, acetic acids and settleability all depend upon the temperature of the WO system as shown in the above results. The pH was increased with the increase in process temperature on the other hand the production of VFA was maximum at lower temperature and gradually decreased with RT and temperature. Production of acetic acid was greater at high temperature and lower at lower temperature. The increase in concentration of acetic acid with increase in temperature may be explained by fact that others VFAs, such as valaric, propionic and butyric acids converted into more simple compounds such as acetic acid. Ammonia could be removed from the liquor by air stripping, which require raising the pH of the effluent to 10.

At temperature greater than 280°C there was a significant change in the effluent mixed liquor. It acquired a black colour, mostly due to the presence of the heavy, readily settleable, activated carbon like solids while the supernatant retained a yellowish/urine colour. The high CST results at lower temperatures may have been due to the partial oxidation of sludge, resulting in its fluffy nature which in turn hinders the seepage of liquid from the residual settled solids. A reduction in volume of sludge

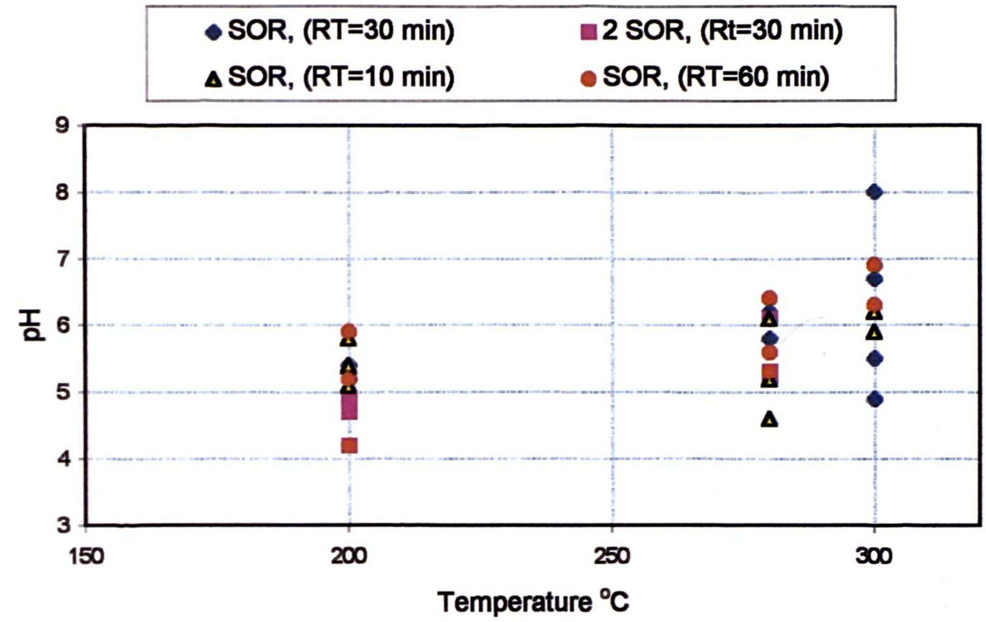


Fig. 5.28: The Effect of WO Temperature on pH of Raw Primary Sludge

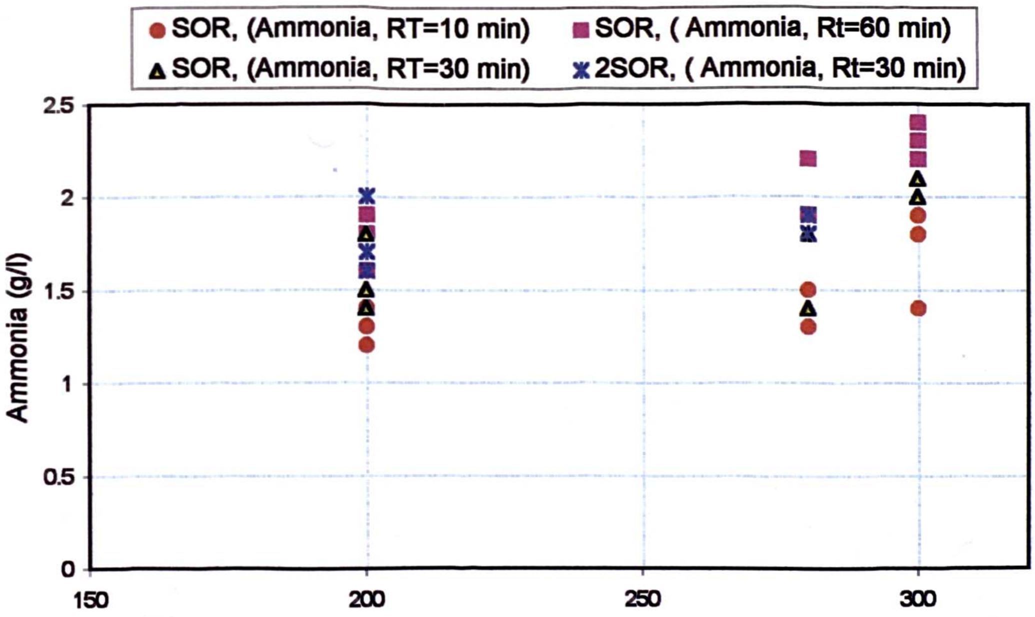


Fig. 5.29: The Effect of WO Temperature on Ammonia of Raw Primary Sludge

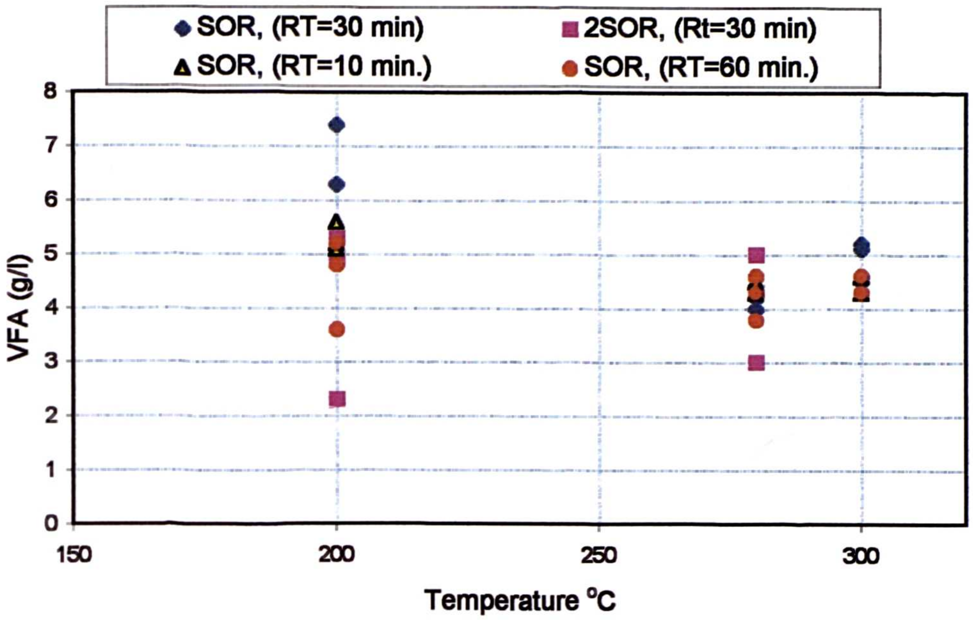


Fig. 5.30: Effect of WO Temperature on the VFA Concentration of Raw Primary Sludge

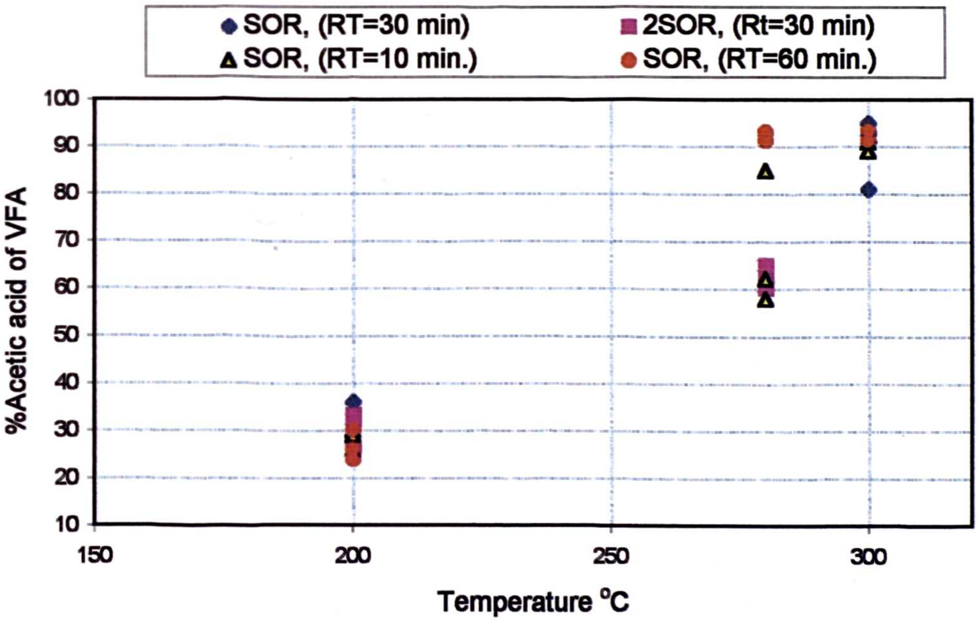


Fig. 5.31: Effect of WO Temperature on the Acetic acid Concentration of Raw Primary Sludge

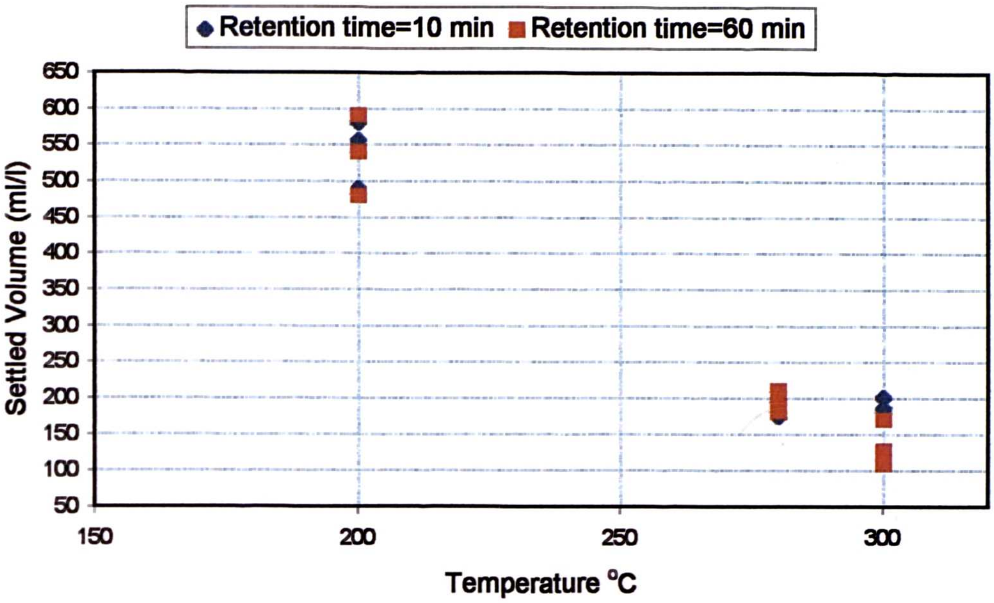


Fig. 5.32: Effect of WO Temperature on the Settleability of Raw Primary Sludge

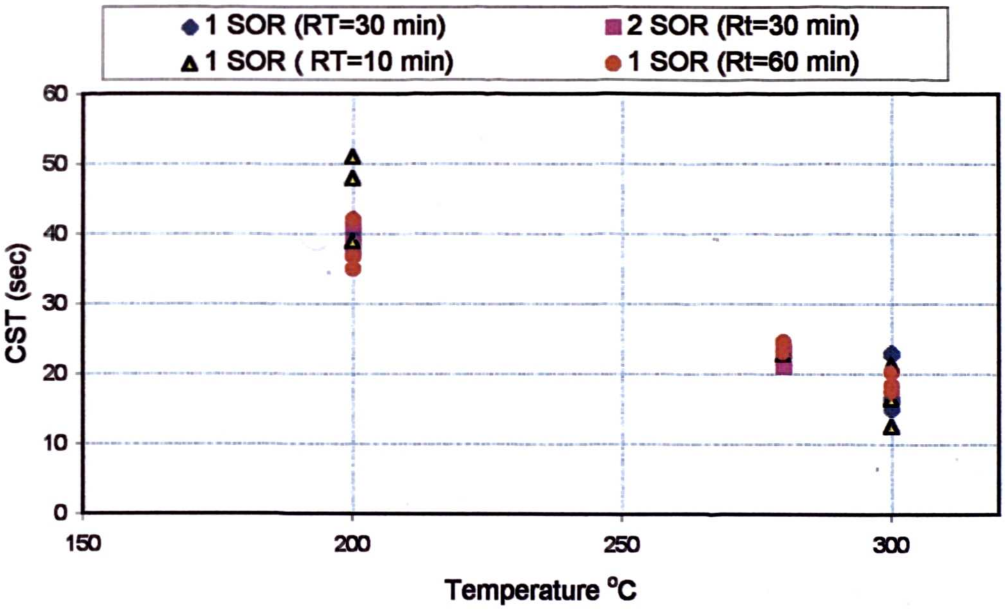


Fig. 5.33: Effect of WO on the CST of Raw Primary Sludge

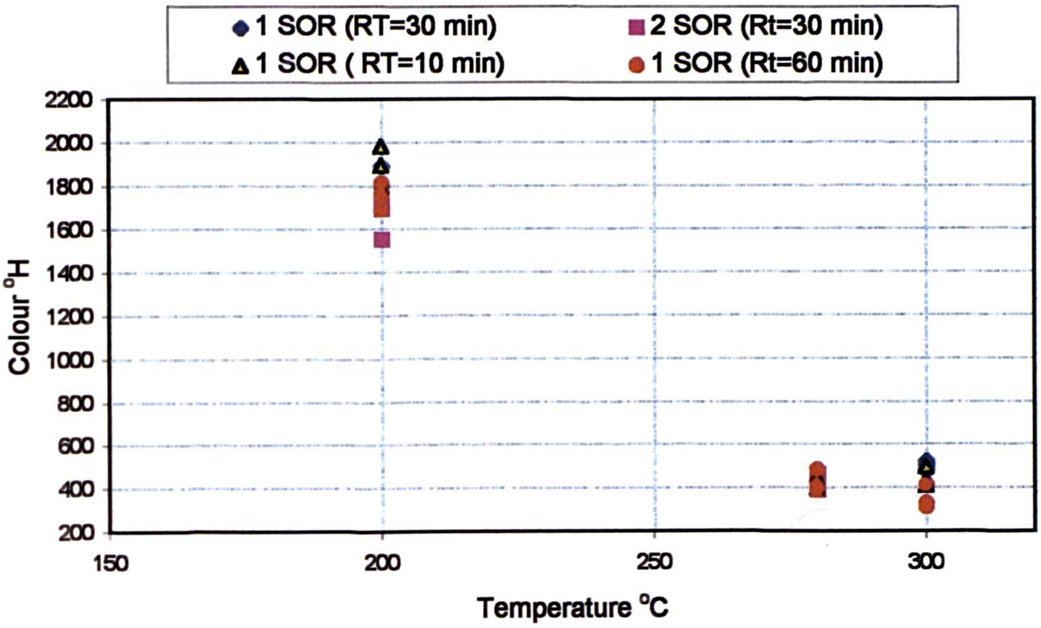


Fig. 5.34: Effect of WO Temperature on the Colour Concentration of Raw Primary Sludge

greater than 90% was obtained at high temperatures, which could have been increased even further by dewatering the residual solids. The residual solids after dewatering by any suitable means could be used for the removal of colour from dye wastewater. The residual solids formed during WO treatment at low temperatures could be readily handled and safely disposed of to a landfill.

5.4.2 Liquors from WO of Thickened Activated Sludge

(I) Results

The pH and ammonia concentration of the effluent liquor were influenced by the process temperature, Figs. 5.35 and 5.36. At low temperature, the pH range was 5.9 to 4.5 due to production of VFAs and increased to neutral (7) with increasing temperature (260°C) due to oxidation of VFAs. Further oxidation beyond 260°C, increased the production of acetic acid which may be one of the reason for low pH at higher temperature. At low and high temperature the formation of ammonia was small but found to be maximum at 260°C. The overall effect of retention time on pH and ammonia was not very significant but its effect on pH and ammonia was pronounced at 260°C.

The average formation of volatile fatty acids at all temperatures followed a similar pattern to that in Section 5.4.1. In general temperature had a significant effect on the destruction of volatile fatty acids (Fig. 5.37). The formation of acetic acid was greatly influenced by the process temperature, Fig. 5.38. At the low temperature its contribution to the volatile fatty acids was less than 20% and greatly increased to around 90% at high temperature (300°C). The data in Fig. 5.37 indicate that at 200 C and 300°C the volatile fatty acids concentration increased to 4000 mg/l and 2000 mg/l respectively from an initial value of 58 mg/l.

The CST values obtained for the liquors represent a substantial increase in filterability (Fig. 5.39). The initial CST of the raw thickened activated sludge prior to WO was 870 seconds but was reduced to 42 seconds and 6 seconds at 200°C and 300°C respectively. Under similar pressure and retention time the CST was temperature dependent, with a high CST value found at low temperature and a low CST at high temperature. The CST results followed the TCOD destruction pattern, at high TCOD destruction the CST was less and vice versa.

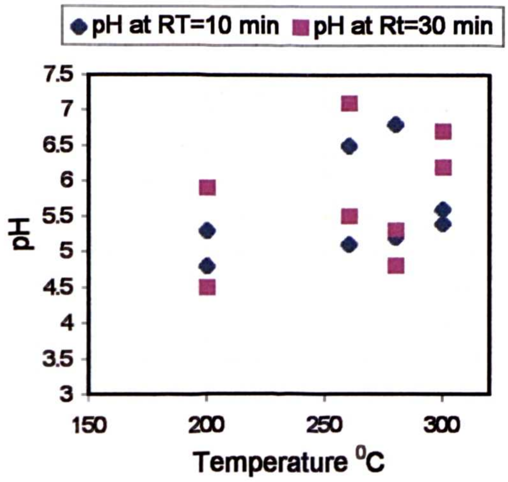


Fig. 5.35: Effect of WO Temperature on pH of Activated Sludge

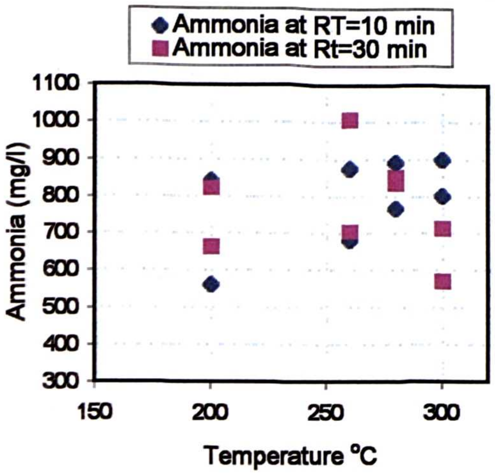


Fig. 5.36: Effect of WO Temperature on Ammonia of Activated Sludge

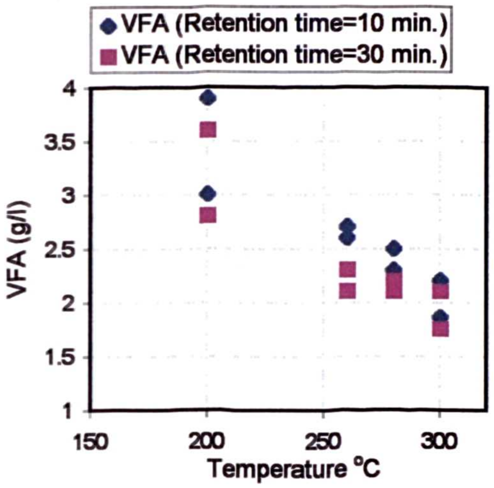


Fig. 5.37: Effect of WO Temperature on VFA of Activated Sludge

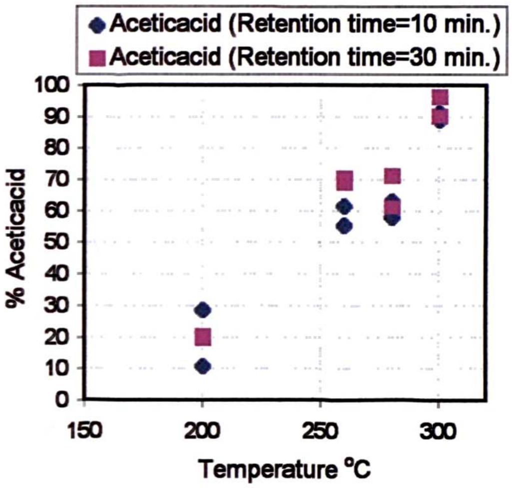


Fig. 5.38: Effect of WO Temperature on Aceticacid of Activated Sludge

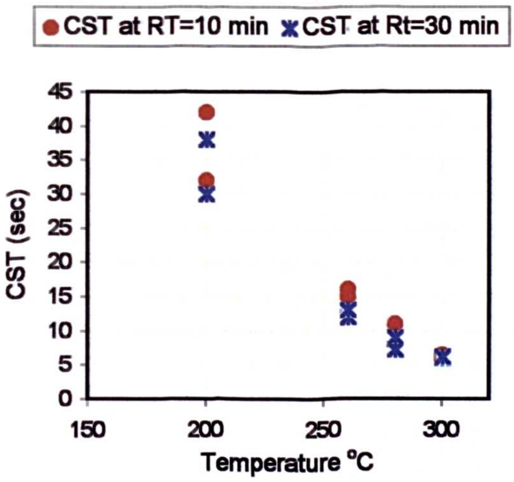


Fig. 5.39: Effect of WO Temperature on CST of Activated Sludge

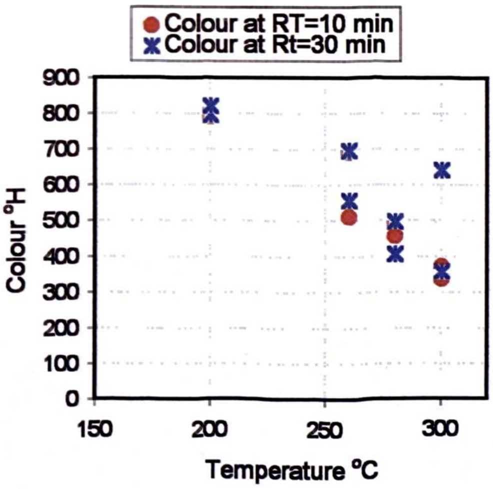


Fig. 5.40: Effect of WO Temperature on Colour of Activated Sludge

The colour was greatly affected by temperature but less by retention time (Fig. 5.40). The colour of the effluent liquor from the low temperature treatment was dark brown while the liquor treated at high temperature was dark yellow in colour. The residual decanted solids after settling from the low temperature range was a brown clay colour and that from the high temperature generation had black colour.

The generation of formaldehyde in the range of 0.5 mg/l to 17 mg/l was observed. Its generation was temperature dependent, being greater at low temperature and less at high temperature. The formaldehyde results were greatly affected by the colour of the heat liquors.

(II) Discussion

The formation and destruction of volatile fatty acids are important aspects of the treatment of wastewater and sludges. It may be explained that during solubilization and hydrolysis, volatile fatty acid formation was at a peak, and a considerable decrease in volatile fatty acids occured after the oxidation of low molecular weight organic acids other than acetic. In Luduvice's (1992) results, which were obtained at less than SOR, the production of volatile fatty acids was greatly reduced with increased temperature, an average reduction of 50% (VFAs) being observed at 300°C compared to that at 200°C.

The CST results observed in this research are no better than Luduvice's (1992) results despite the use of pure oxygen and operating at the SOR. The reason for the difference in CST results in both cases may be the difference in the standardisation of the method adopted for the CST tests. From the above results it is clear that heat treatment effects the reduction of CST. It is probably the packing together of live microbes during filtration which contributes to the high CST values. Heat treatment, by destroying their structural integrity, prevents them packing together in a manner which impedes filtration. The other components of the sludges and their differing microbial populations give each type of sludge a different CST value.

The residual decanted solids after settling from the low temperature range was a brown clay colour and that from the high temperature generation had black colour. The reason for the clay colour could be incomplete burning at low temperature and for the black colour of residual ash may have been the presence of a activated carbon.

Due to the presence of sufficient oxygen for oxidation inside the reactor the effluent liquor did not produce an offensive odour as was found by Luduvice (1992). The liquor treated at a low temperature had some odour but was not very offensive.

The generation of formaldehyde in the range of 0.5 mg/l to 17 mg/l was observed. Its generation was temperature dependent, being greater at low temperature and less at high temperature. The formaldehyde results were greatly affected by the colour of the heat liquors.

5.4.2 (i) Reaction in WO of Thickened Activated Sludge

(I) Results

(a) Introduction

The main purpose of this section was to identify an empirical model of the reactions which take place during the WO process and to obtain fundamental information for optimising treatment of the mixed effluent liquor. As discussed in Section 5.1, in thermal decomposition the sludge component is broken down into a soluble form which increases the concentration of contaminants in the effluent liquor and which may require further biological treatment before discharge due to the presence of a high concentration of SCOD.

As most of the solids in the influent sludge either solubilize or undergo a chemical change thus remaining in the effluent liquor, it is necessary to know how much the volatile total solids in the influent could affect the end products in the effluent. This could then provide information as to the most suitable biological treatment of the resultant liquor.

b) Data Analysis

The experimental conditions are presented in Table 5.3. Measurements of volatile fatty acids and formaldehyde in the liquor showed that these two compounds represent 85% - 99% of the SCOD. Figs. 5.41 - 5.45 show the relationship between SCOD, ammonia acetic acid and volatile total solids at four different temperature. This data may also be represented by Equations 5.1 - 5.4, which in turn may be combined into Equation 5.5.

Table 5.4 shows the correlation coefficient of the independent variables, demonstrating that VTS and SCOD are most closely related. Consequently, measuring the VTS of the activated sludge should be sufficient to determine the operating conditions for the WO reactor (from the graphs) in order to optimise the overall treatment scheme, including both WO and biological post- treatment.

Table 5.3 Experimental Conditions

Run No	INFLUENT VTS (mg/l)	Temperature ^{0}C	Retention time (min.)	Pressure (MPa)
1 (n =3)	1206	200	60	2.5
2 (n =3)	2412	200	60	2.5
3 (n =3)	4825	200	60	2.5
4 (n =3)	9650	200	60	2.5
5 (n =3)	19300	200	60	2.5
6 (n =3)	38600	200	60	2.5
7 (n =3)	1855	260, 280, 300	60	2.5
8 (n =3)	3710	260, 280, 300	60	2.5
9 (n =3)	6970	260, 280, 300	60	2.5
10 (n =3)	7425	260, 280, 300	60	2.5
11 (n =3)	14856	260, 280, 300	60	2.5
12 (n =3)	26300	260, 280, 300	60	2.5

$$\mathrm{VTS} = 0.7(\mathrm{SCOD})^{0.91}(\mathrm{NH_3})^{0.54}(\mathrm{aa})^{-0.22} \quad (5.1)$$

(aa = acetic acid, $R^2 = 0.99$, Temperature = 200^{0}C)

$$\mathrm{VTS} = 46.7(\mathrm{SCOD})^{2.62}(\mathrm{NH_3})^{2.6}(\mathrm{aa})^{-0.03} \quad (5.2)$$

(aa = acetic acid, $R^2 = 0.98$, Temperature = 260^{0}C)

$$\mathrm{VTS} = 6.6(\mathrm{SCOD})^{0.54}(\mathrm{NH_3})^{0.07}(\mathrm{aa})^{0.37} \quad (5.3)$$

(aa = acetic acid, $R^2 = 0.98$, Temperature = 280^{0}C)

$$\mathrm{VTS} = 0.8(\mathrm{SCOD})^{0.82}(\mathrm{NH_3})^{-0.73}(\mathrm{aa})^{1.02} \quad (5.4)$$

(aa = acetic acid, $R^2 = 0.98$, Temperature = 300^{0}C)

$$\mathrm{VTS} = 3.85(\mathrm{SCOD})^{0.42}(\mathrm{NH_3})^{0.21}(\mathrm{aa})^{0.47} \quad (5.5)$$

(aa = acetic acid, $R^2 = 0.98$)

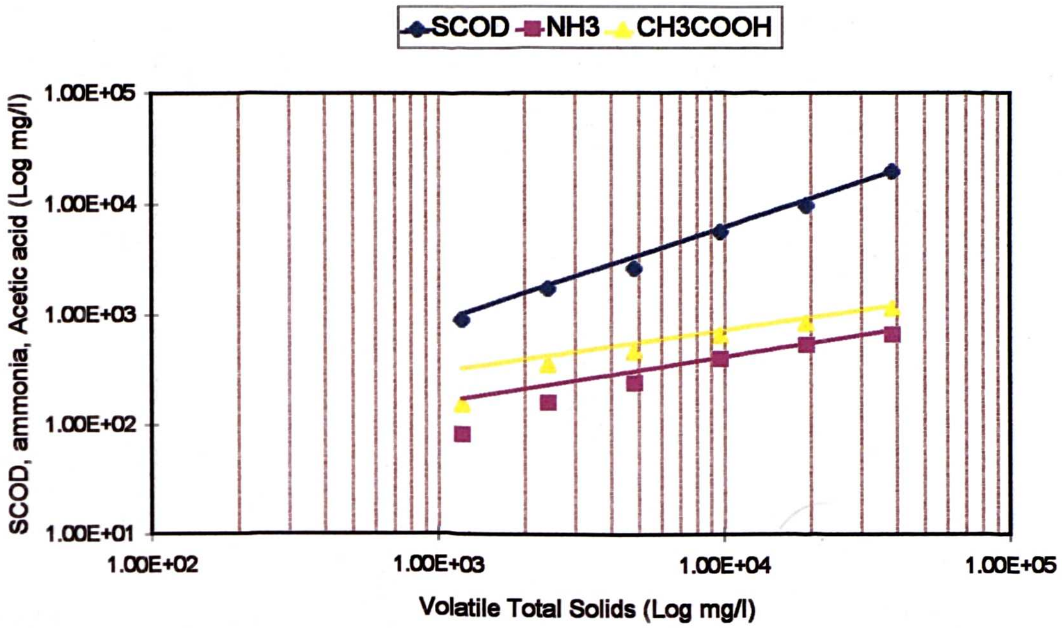


Fig. 5.41 VTS Transformation at 200°C
Oxygen overpressure: 2.5 MPa
Retention time 60 min.

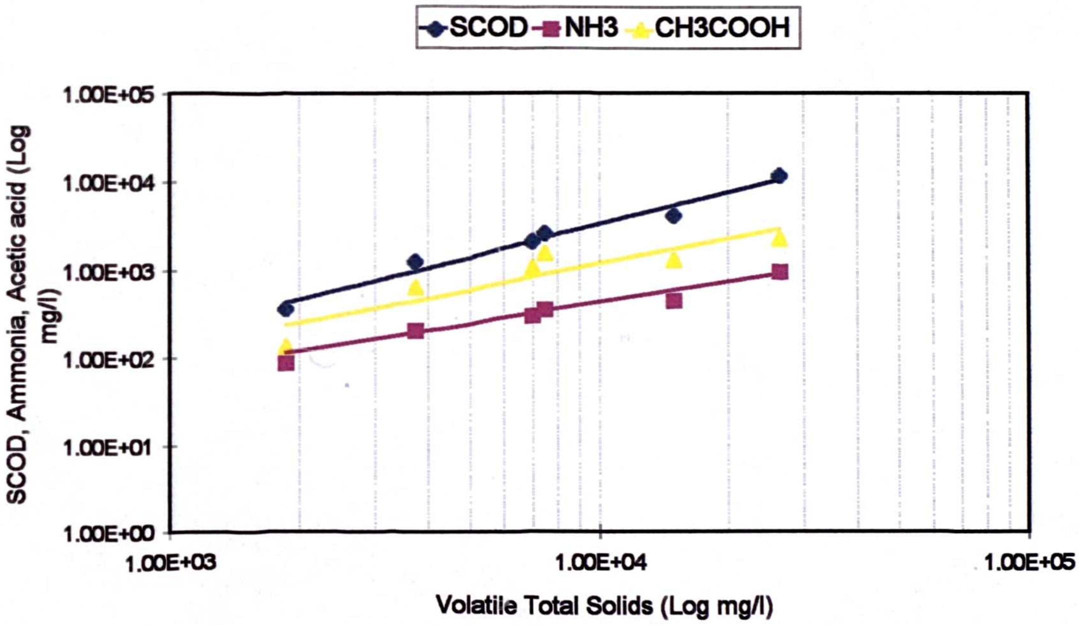


Fig. 5.42 VTS Transformation at 260°C
Note:
Oxygen overpressure: 2.5 MPa
Retention time 60 min.

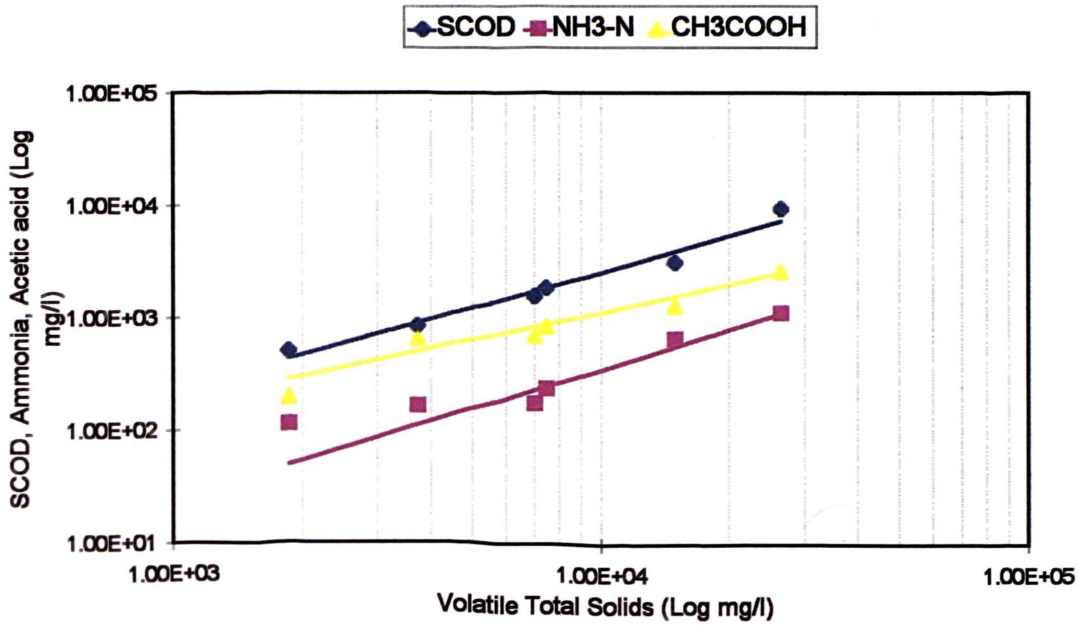


Fig. 5.43 VTS Transformation at 280°C

Note:

Oxygen overpressure: 2.5 MPa

Retention time 60 min.

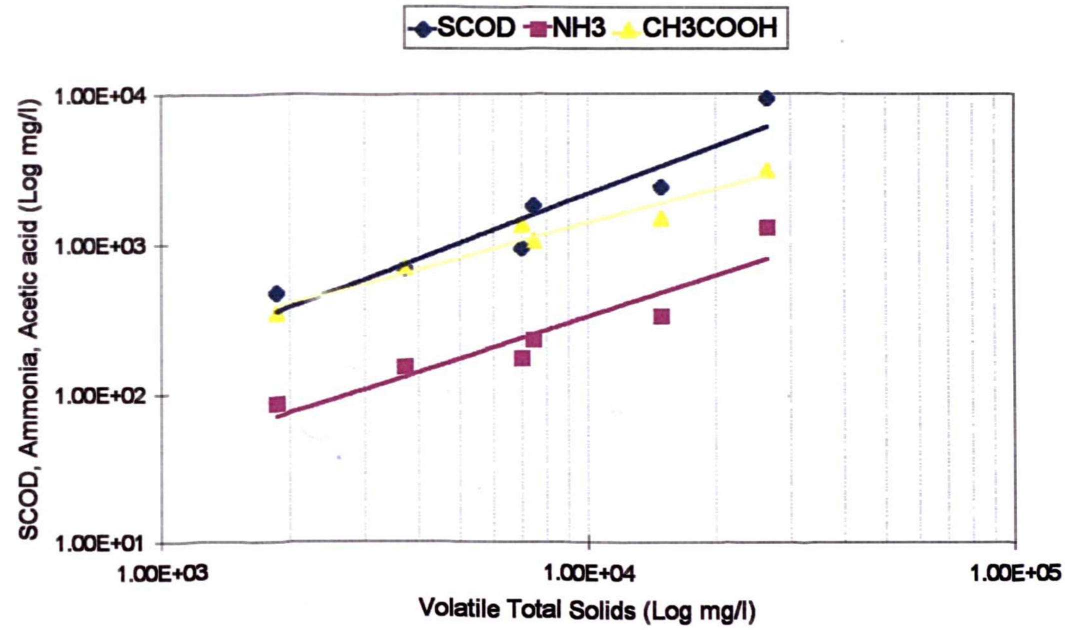


Fig. 5.44 VTS Transformation at 300°C

Note:

Oxygen overpressure: 2.5 MPa

Retention time 60 min.

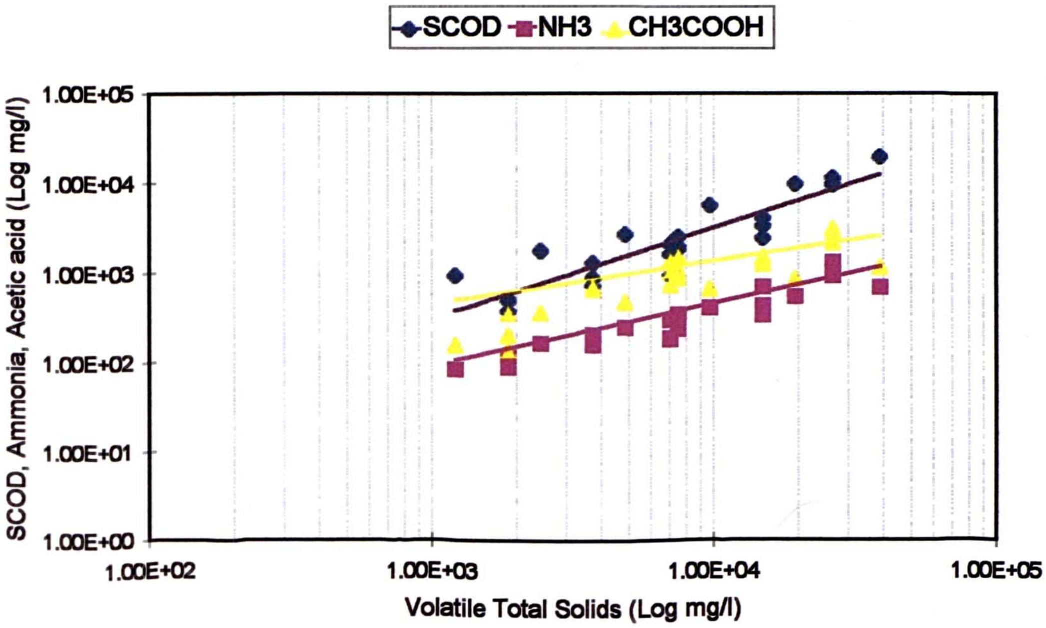


Fig. 5.45 VTS Transformation at 200°C, 260°C, 280°C and 300°C

Note:

Oxygen overpressure: 2.5 MPa

Retention time 60 min.

Table 5.4 Analysis of Correlation Coefficients

Parameter	SCOD	Ammonia	Acetic acid
1- Correlation coeff. at 200°C	0.99	0.97	0.94
2- Correlation coeff. at 260°C	0.97	0.96	0.80
3- Correlation coeff. at 280°C	0.97	0.90	0.95
4- Correlation coeff. at 300°C	0.90	0.88	0.95
5- Combined Correlation coeff.	0.90	0.72	0.30

(II) Discussion

The lysis of the cell walls during heat treatment releases the cell's contents. The higher the temperature and longer the holding time, the more cells will be ruptured, and more soluble COD, ammonia will release from it. Also some proteins which are insoluble are broken down into their more soluble constituent amino acids, and this would increase with longer times and higher temperature. Non-microbial organic matter would also partly or fully be solubilised which will add up to the final transformed product. It appears that, at temperatures above 200^0C, little further cellular destruction occurs, but chemical reactions continue, producing material which is precipitated thus resulting in a lower dissolved solids content. It is thought that these reactions are similar to those which produce the coloured chemicals so characteristic of heat treatment liquors.

Because activated sludge consists of a wide range of complex compounds, including proteins, lipids, and fats, its constituents are very difficult to represent by a simple expression. However, in order to design the post-WO biological treatment process, some simple analytical parameters must be used. The parameters selected for the evaluation were VTS, NH_3, SCOD, and acetic acid formaldehyde. Once the combination of these parameters had been optimised it would then be possible to operate the WO system under the best conditions for feed stock to a biological treatment process.

As discussed earlier these state variables were selected on the basis of its further treatment. In any wastewater treatment process, the above parameters would be sufficient to enable the selection of appropriate biological treatment. In the absence of other contaminants it could be sufficient to design a wastewater treatment facilities for the heat liquor.

A general presentation of transformation and the mass balance condition of the transformation are shown in Fig. 5.46. It is clear from the general presentation of the kinetic data that SCOD presents almost all the organic matter in the liquor which comes through transformation in soluble form. It is possible using mass balance to estimate the amount of organic matter which accounted for SCOD in the liquor.

SCOD > VFA + HCHO

SCOD : VFA + HCHO ratio

1 : 0.85-0.99

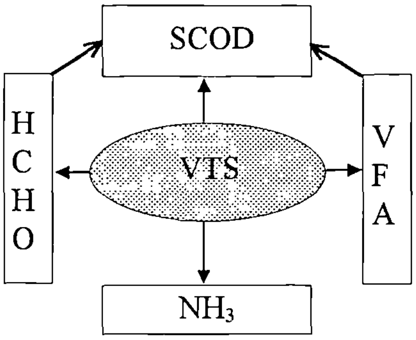


Fig. 5.46 Influent VTS Transformation Path

The theoretical COD of acetic acid was determined from the volatile fatty acids results and the theoretical formaldehyde COD was calculated from the formaldehyde results. The COD due to volatile fatty acids and formaldehyde was always less than SCOD, because SCOD present all the COD of the organic matter in the soluble form. It was found that the difference between the two COD was not very much, an indication that other organic matter like carbazole, ketone etc. are present in only very small concentrations. If high concentrations of other organic compounds had been in the liquor, then there would have been big gap between the COD due to volatile fatty acid plus formaldehyde and SCOD of the liquor. In short the ratio between the two was in the range of 0.85-0.99 (1 to 15%) suggesting low concentration of other organic compounds in the liquor.

The concentration of low molecular weight volatile fatty acids in the effluent liquor was selected due to its importance in the selection of in future treatment process for the heat treated liquor. As stated earlier, that acetic acid is very resistant to further

WO treatment under sub-critical condition, but is readily degradable by both aerobic and anaerobic biological systems. Due to the above reason, acetic acid, was chosen for kinetic data, instead of volatile fatty acids.

5.4.3 Liquors from WO of Detergent Wastewater

The effect of WO on different detergent wastewaters varied. The characteristics of the liquors were different from each other but not significantly. Unlike in the case of the biological sludges, the pH of most of the detergent wastewater liquors was reduced significantly at all temperature ranges. Some liquors showed an increase in pH at high temperature and some exhibited a reduction in pH as the temperature was increased. In the temperature range tested, the pH of the effluent varied between 1.2 and 10.5. The formation of ammonia also followed the same pattern i.e. its concentration was lower at low temperature and increased as the temperature increased. As for the previous sludges the effluent liquor volatile fatty acids were also dependent on the process temperature being high at the lower temperature and low at a high temperature.

It was generally noted that settleability of all types of detergent wastewater was greatly improved and the remaining detergent and residual decanted solids settled very quickly, leaving the supernatant liquor crystal clear.

(a) Liquors from WO of Zeolite or HDL (heavy duty liquid)

(I) Results

The pH of the liquor from WO of HDL followed a similar pattern to that observed for biological sludges. It was very acidic for the low temperature oxidation and nearly neutral for the high temperature oxidation. The formation of ammonia followed a similar pattern at different temperatures. At 280°C the formation of ammonia was 300 mg/l and was less than 50 mg/l at 200°C. Acetic acid accounted for the majority of the volatile fatty acids present in the effluent liquor (Appendix-B). At 200 C for the same AD concentration, the volatile fatty acid formation was 50% more than at 280°C. The minimum and maximum generation of volatile fatty acids at 200 C and 280°C were 85% and 100% respectively.

The concentration of AD in the wastewater had a direct effect on the pH of the effluent liquor. As the concentration in the influent was increased, the pH of the effluent liquor also increased. The pH of the WO effluent liquor was greatly increased while using a catalyst, i.e. the pH of the liquors without the catalyst was 6 and that using the catalyst was10.5.

(II) Discussion

At a low temperature the pH was more acidic due to the quantity of volatile fatty acids generated and the reduced generation of ammonia whereas at high temperature the reduction in volatile fatty acids and the production of ammonia “counter balanced” the volatile fatty acids resulting in a net increase in pH. The reason for increased pH when using a catalyst may have been due to the increased oxidation of organic matter, which could have increased the concentration of ammonia in the effluent liquor, which in turn would have increased the pH.

(b) Liquors from WO of LAS (linear alkyl benzene sulphonate)

(I) Results

The influence of WO temperature and retention time on pH was found to be relatively small, as shown in Figs. 5.47 and 5.48. Contrary to the results from the previous sections, the pH decreased as the temperature increased. An average of 30 mg/l ammonia was observed at 160°C but no ammonia was noted at higher temperature oxidation. Throughout the tests the effluent pH remained between 2 and 3 at any given temperature or retention time.

The effect of retention time on pH at the lower temperature was significant compared to that at the higher temperature (Fig. 5.48). The production of volatile fatty acids (VFA) at different temperatures is shown in Figs. 5.49. Lower VFAs were observed at the higher temperature. Production of acetic acid significantly increased as the process temperature was increased (Fig. 5.50).

(II) Discussion

The influence of WO treatment on the pH of LAS was characterized by a small decrease in the pH of the effluent liquor. Neither temperature nor retention time, were of any significant influence in the pH of the WO effluent. The absence of ammonia

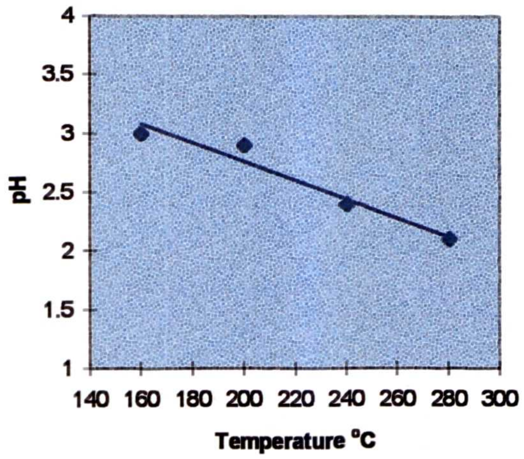


Fig. 5.47: Effect of WO Temperature on pH (LAS)

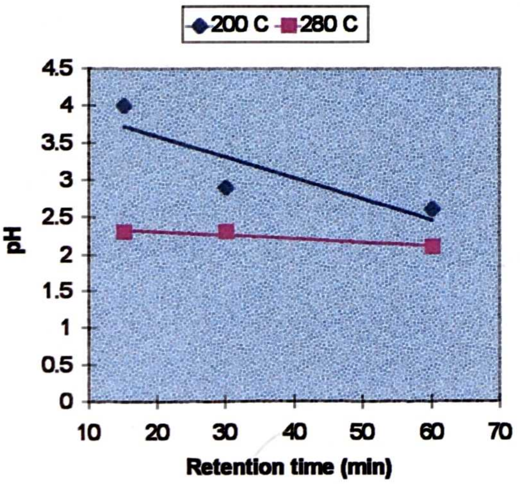


Fig. 5.48: Effect of WO RT on pH of LAS

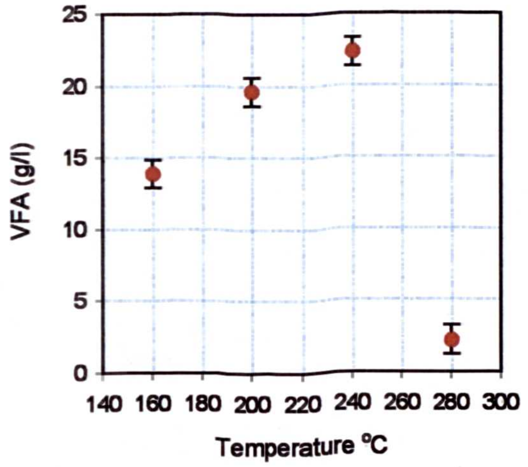


Fig. 5.49 Effect of WO Temperature on VFA of LAS

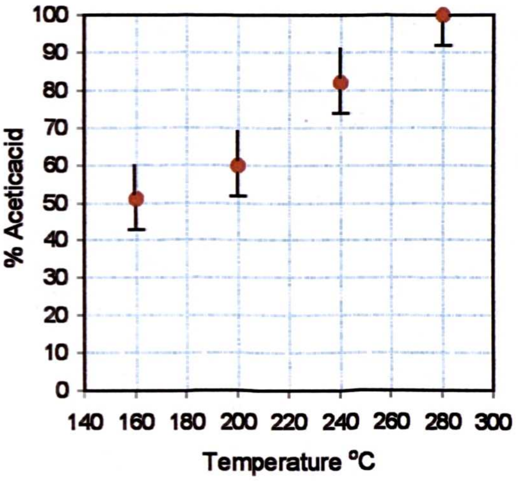


Fig 5.50: Effect of WO Temperature on Aceticacid Concentration of LAS

could have been the reason for the decrease in pH which in turn counter balanced the volatile fatty acids in the liquor. Lower VFAs were observed at the higher temperature due to their oxidation. The production of acetic acid was increased with the increase in process temperature may be due to conversion of low molecular volatile fatty acids other than acetic acid into acetic acid. In the absence of toxic organic compounds, such as formaldehyde, the resultant liquor could potentially be more readily treated by a subsequent biological process.

(c) Liquors from WO of LES (sodium lauryl ether sulphate)

(I) Results

LES is similar in composition to LAS and similar WO liquor characteristics were observed at different temperatures and concentrations. The pH of the liquor was reduced with increased temperature (Appendix-B). The formation of ammonia was almost negligible and may have been one of the reasons for the low pH at all temperatures. The pH of the effluent liquor was highly acidic and was always less than 2.2. At 200°C, 41% of the volatile fatty acids was accounted for by acetic acid whereas 100% of the VFAs was acetic acid at 280°C (Appendix-B).

(II) Discussion

Acetic acid is believed to be the last intermediate product before total oxidation of the organic matter during WO. This explains the significant increase in volatile fatty acids, especially acetic acid, observed in the supernatant of the effluent liquor. It can be concluded from the acetic acid results that complete hydrolysation of the detergent molecules has taken place, and no further oxidation can be possible due to the production of 100% acetic acid, will not oxidise at sub-critical temperature.

(d) Liquors from WO of Persil Dishwashing Liquid

(I) Results

The Persil detergent responded very significantly to WO treatment, even at a very high concentration. The pH of the effluent liquor reduced as the WO temperature increased (Appendix-B). As the feed Persil concentration increased the pH and ammonia concentration in the resultant liquor increased slightly (Appendix-B). The difference in pH between the liquor treated at 200°C and 280°C was small although the concentration of ammonia in the higher temperature liquor was 2.8 g/l, even though the pH had decreased, indicating the presence of a very high concentration of volatile fatty acids. The effluent pH remained between 1.8 and 2.1 at any given temperature or retention time.

The generation of volatile fatty acids followed a similar pattern to the wet oxidation of the previous detergent (LES). The acetic acid concentration was very low at all temperatures and accounted for an average of 99% of the volatile fatty acids. At 30° o Persil concentration the formation of oil made the determination of VFAs difficult (Appendix-B). The pH of the effluent liquor was unaffected by the influent AD concentration.

(II) Discussion

The pH of the effluent liquors from Persil dish washing liquid treated by WO was not considerably influenced by the process temperature. At lower temperatures it reduces sharply to values close to 2 and slowly decreased to around 1 with increasing temperature. This pattern for pH may also be explained by the increase, with temperature in ammonia formation in the effluent, which counterbalances the production of VFA and increase pH was not in the effluent and hence instead of increasing in pH a decrease in pH was observed.

The reduction in concentration of acetic acid in the may be explained by the lack of sufficient oxygen to oxidise the other fatty acids, such as propionic, valaric and butyric and even oil molecules into more simple compounds such as acetic acid. If sufficient oxygen had been available such hydrolysation products would certainly be oxidised into acetic acid maintaining a constant proportion or possibly increasing it.

(e) Liquors from WO of HEQ (Hamburg Ester Quaternary Ammonium Surfactant.)

(I) Results

The pH of the effluent mixed liquor, (pH< 2), was very low. The formation of ammonia was not very significant and the pH of the effluent liquor was further decreased as the concentration of the influent HEQ was increased. A similar pattern was observed for the ammonia concentration.

As expected, the generation of volatile fatty acids was low at a low influent concentration and high at a high influent concentration of HEQ. At high temperature 100% of the volatile fatty acid was acetic acid (Appendix-B).

(II) Discussion

The pH of the effluent liquors from HEQ treated by WO was considerably influenced by the process temperature. At high temperature it reduced sharply to values close to 1.7. Acetic acid was by far the main volatile fatty acid formed. When warm the odour released by the effluent liquor was considerably less offensive than that released by activated sludge and raw primary sludge with practically no odour present after an hour.

(f) Liquors from WO of Comfort (fabric softener)

(I) Results

The pH of the effluent liquor followed a similar pattern to that in the raw primary and activated sludge. It was highly acidic at low WO temperature due to presence of volatile fatty acid and decreased as the temperature increased. At a low influent Comfort concentration, high pH liquors were produced due to the low generation of VFAs while at a high influent concentration the pH of the resultant liquor was low, indicating the formation of more acids in the heat liquor (Appendix-B).

(II) Discussion

Contrary to the results from the other detergents studied, acetic acid did not account for the majority of the volatile fatty acids present in the effluent liquor from 10.84% Comfort. This time valaric acid was by far the main organic acid present, with its concentration increasing with process temperature at the expense of acetic acid. Valaric acid accounted for more than 87% of the VFA concentration in the final effluent. This increase in valaric acid concentration, which was found in WO effluents, may be explained by the high fat/oil generation, present in the Comfort detergent.

5.4.4 Liquors from WO of Paracetamol Wastewater

(I) Results

The pH of the liquor from the WO of paracetamol wastewater Fig. 5.51 was largely dependent on the temperature of the WO process. At the low temperature the effluent pH was reduced to 3.5, and it gradually decreased with an increase in process temperature, to values as low as 1.8.

The generation of volatile fatty acids was not very significant, it followed a similar pattern to the studies on detergent and sludges, i.e. it decreased with temperature (Fig. 5.52). At 280°C a minimum concentration of volatile fatty acids was recorded, possibly due to insufficient oxygen at 300°C, in turn due to the limited reactor pressure. Due to a shortage of expensive and weak safety discs an attempt was usually made to apply less overpressure at 300°C to minimise unnecessary bursting of the safety discs.

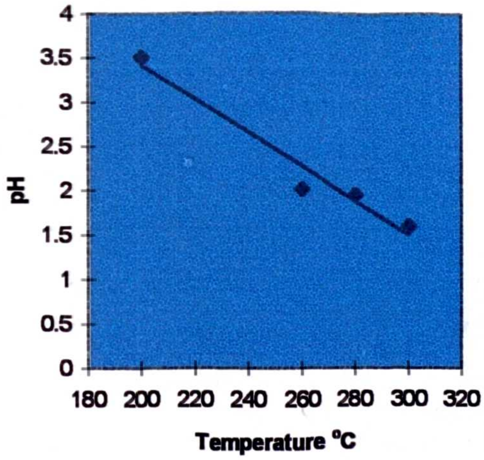


Fig. 5.51: Effect of WO Temperature on pH of Paracetamol

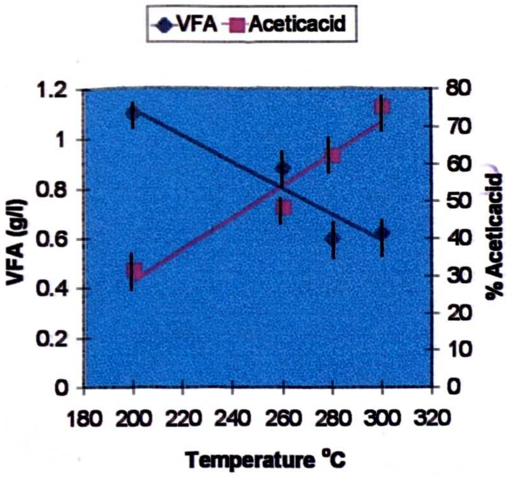


Fig. 5.52: Effect of WO Temperature on VFA of Paracetamol

The acetic acid contribution towards the volatile fatty acids was also temperature dependent, increasing with temperature. At 200 °C, 35% of the volatile fatty acids was acetic acid while at 300 °C its proportion was 75%. By breaking down the contaminants and by-product in the effluents, WO also removed the majority of the colour, changing from black to a light yellow. The inorganic concentration of the effluent liquor was very high, with sulphate contributing more than 5000 mg/l to the effluent mixed liquor.

(II) Discussion

The low effluent pH compared to that of the raw paracetamol wastewater (pH 10.5) indicates that the paracetamol wastewater had a low buffering capacity. Due to this low buffering capacity, the formation of ammonia was not sufficient to shift the pH towards an alkaline value. The VFA concentration in the effluent liquor was also dependent on the process temperature. The effluent liquor collected from Sterling Organics treated at 260 °C was used to investigate biotreatment which will be discussed in detail in Chapter 6.

5.5 POSSIBLE USE OF WO ASH

(I) Results

In order to evaluate a potential use of the residual WO solids it was decided to investigate their application for colour removal from a textile-dye wastewater. A dry powder was produced from primary and activated sludge solids after WO. This was achieved by settling the sludges, centrifuging, and drying them at 104 ° C before mixing in approximately equal proportion. The composition of the textile-dye wastewater is given in Appendix A (Table 2A). The wastewater contained a concentration of 1000 mg/l of dye and the treatment "target" required by a U.K Water Co. was 0.35 absorbency at 500 nm. One litre of textile-dye wastewater was treated with 70 grams of dried WO sludge for 5 minutes. This resulted in a liquor with 0.1 absorbance at 500 nm indicating a high removal efficiency by the WO sludge.

The same textile-dye wastewater was also treated with an activated carbon. It was found that 2.6 grams of activated carbon was required for one litre of textile- dye wastewater in order to achieve the "target" thus demonstrating that dried WO sludge may have adsorption properties similar to that of activated carbon.

(II) Discussion

The above results show that the ideal working condition, when organic matter destruction/transformation is the main concern, depends on what type of effluent liquor/residual solids one is expecting to deal with. If low molecular weight volatile organic acids as a precursor for the production of biogas/biological phosphorus removals is of interest then the retention time and temperature become the main variables. When organic matter destruction is the main objective then a combination of high temperature and long retention time is recommended. This will produce a relatively strong effluent liquor with high concentration of acetic acid and the residual solids may containing some activated carbon which could be successfully used for the removal of other nasty organic compounds such as colour from dye wastewater as shown in the above result.

5.6 SUMMARY

The effect of the Wet Oxidation process on the selected wastewater and sludges, described in this chapter has been evaluated. Specifically the effect of WO on (i) the oxidation of organic compounds, (ii) destruction of solids, and (iii) the characteristics of the final effluent liquor was evaluated. It is important to note, that complete oxidation of organic matters was not observed in the present study due to reactor limited pressure and temperature.

Retention time (RT) and temperature quite clearly affect the liquor strength. As the reactor needs certain time to reach to specified working temperature, therefore the sludge and wastewater undergo a long period of heat treatment under anaerobic conditions where the temperature is gradually increased from room temperatue to the test operational temperature. The time could last from one to three hours depending on the test temperature. Such long heating-up time would not occur in a continuous flow unit, however, the time spent in heat exchangers could produce similar effects to an in coming stream.

The main conclusion to be drawn from this chapter is that it is not possible, within the temperature range 200 °C or less and retention time of up to 10 minutes, to produce both a weak liquor and a well conditioned or stable sludge and wastewater. The experiments with activated sludge and primary sludge show that temperatures greater than 200°C can produce a weaker liquor but without much further improvement in the filterability. For detergent wastewate and paracetamol wastewaster the destruction of organic matter was mainly temperature dependent i.e., with increase in temperature greater removal of organic matter was observed.

The role of pressure especially at SOR conditions has not been reported in the literature. In the past most of the research in this field were carried out inadequetly. In addition to the above the use of WO residue solids for the removal of colour from dye wastewater was also not found in the literature. Wet Oxidation of detergents used in this reaserch have also not been mentioned previously in the literature.

After 300 tests carried out under severe operating conditions with the pH inside the reactor varying from 1 to 8, depending on the sludge and the process temperature, the internal condition of the reaction vessel was not very good. The reactor vessel showed some evidence of corrosion inside as well as on the out side surface. Severe corrosion to the glands of the reactor was caused by the paracetamol wastewater.

CHAPTER 6

BIOTREATMENT OF WET OXIDATION LIQUORS

6.1 INTRODUCTION

Due to increased public awareness, and increasingly stringent environmental regulations during the past 30 years, many municipal and industrial wastewater treatment plants have constructed a heat treatment process as a part of their wastewater and sludge disposal system. Although WO destroys most of the sludge solids, and makes it readily filterable, the liquor, which usually contains high levels of organic matter, still needs to be treated prior to discharge.

Most of the studies by previous research workers were carried out using liquors obtained from low temperature (150 °C to 220 °C) heat treatment of activated sludge. No work however has so far looked at a range of different WO treated sludges and industrial wastewaters liquors and compared their individual response to aerobic and anaerobic biological treatment. Table 6.1 gives a summary of the different liquors used for the biological treatment studies in this project.

The purpose of this study was to demonstrate the feasibility of reducing the strength of heat treatment liquors to that approximating domestic wastewater i.e. 200-300 mg/l BOD_5. A range of aerobic and anaerobic biological treatment systems was investigated. The details of the equipment and the reasons for selection have already been discussed in Chapter 4.

Soluble COD and biodegradable COD removal were generally used to determine the efficiency of the various treatment processes. The loading rate to the laboratory-scale units was varied to determine at what rate the aerobic and anaerobic processes could treat the liquors, and what effect the loading rate would have on the overall efficiency of the process. Other parameters considered were ammonia removal in the aerobic processes and the inhibition effects of ammonia and formaldehyde in the anaerobic processes.

Table 6.1 WO Liquors Used in Biotreatment Study

Sludge/wastewater used	Aerobic	Anaerobic	WO operating Temperature (°C)
Activated Sludge (AS280 C)	YES	YES	280 °C
Detergent Wastewater	YES	YES	280 °C
Paracetamol Wastewater	YES	NO	260 °C

6.2 ANAEROBIC BIOLOGICAL TREATMENT OF ACTIVATED SLUDGE LIQUOR

6.2.1 Introduction

An up-flow anaerobic filter (UFAF) packed with synthetic media was used for the treatment of liquor from activated sludge which had been treated at 280 °C

(AS280 °C). The UFAF system was selected for this study because high temperature heat treated liquor contains inhibitory substances and has a high COD. As discussed in Chapter 5 Wet Oxidation liquors contain high levels of ammonia and acetic acids. Micro nutrients were added for optimum biological growth, the details of which are given in Appendix C. The ammonia toxicity was minimised by controlling the pH of the influent liquor to 7. The WO effluents were also buffered by using $Ca(OH)_2$ solution. An organic loading rate of 6 kg/m^3. day was rapidly achieved with spoilt beer in the UFAF system although this was later reduced to 4 kg COD/m^3.day for the following 70 days. The results of OLR, HRT and COD removal are given in Table 6.2. The details of acclimatisation and incremental increases in loading rate to the UFAF are given in Chapter 4.

(I) Results

The total continuous anaerobic UFAF process was operated for 450 days. A summary of the results is shown in Table 6.2. Period I which lasted for 70 days at room temperature only gave 29% COD reduction. The initial reduction in COD at the start of experiment shown in Fig. 6.1 was due to the presence of a high proportion of brewery wastewater in the influent and which was readily biodegradable. As the concentration of brewery wastewater was reduced during Period I the efficiency of the UFAF also reduced due to the toxicity effect of the WO liquor on the anaerobic system.

Period II showed the lowest COD removal of all UFAF tests, during this period an average of only 4.4 % COD removal was observed. It can be seen from Table 6.2 (Period III) and Fig. 6.3 that a small decrease in organic loading rate and further acclimatisation led to an increase in COD removal to 29%. As found from mass balance of SCOD and VFA/formaldehyde in Chapter 5, which indicates the presence of toxic and non toxic organic compounds in the above heat liquor could be 1% to 15 %.

Table 6.2. Summary of UFAF Experimental Conditions and Results

Period	Day	OLR (kg SCOD/ m^3.day)	Influent SCOD (mg/l)	Effluent SCOD (mg/l)	% COD removal	HRT (days)	Temp (°C)	Micro nutrient
I	1-70	4	4000	2813	29	1	22	No
II	70-165	1.16	3500	3346	4.4	3	37	No
III	165-245	1	3000	2135	29	3	37	Yes
IV	245-320	0.25	3000	1113	63	12	37	Yes
V*	320-450	0.5	3000	1945	38	6	37	Yes

* Ammonia was removed by boiling prior to UFAF

At this stage it was decided to increase the HRT of the system to 12 days and consequently decrease the organic loading rate to 0.25 kg COD/m^3.day. This resulted in an average of 63.1% COD removal during Period-IV and the increase was due to either long hydraulic retention time (HRT) or dilution of the wastewater.

At this stage an attempt was made to reduce the toxicity of the WO liquor by removing the ammonia from the liquor prior to feeding to the UFAF system by pH adjustment and boiling. The concentration of ammonia in the feed for Period V was in the range of 120 mg/l to 150 mg/l. Generally 40 to 50% of the original volume of the

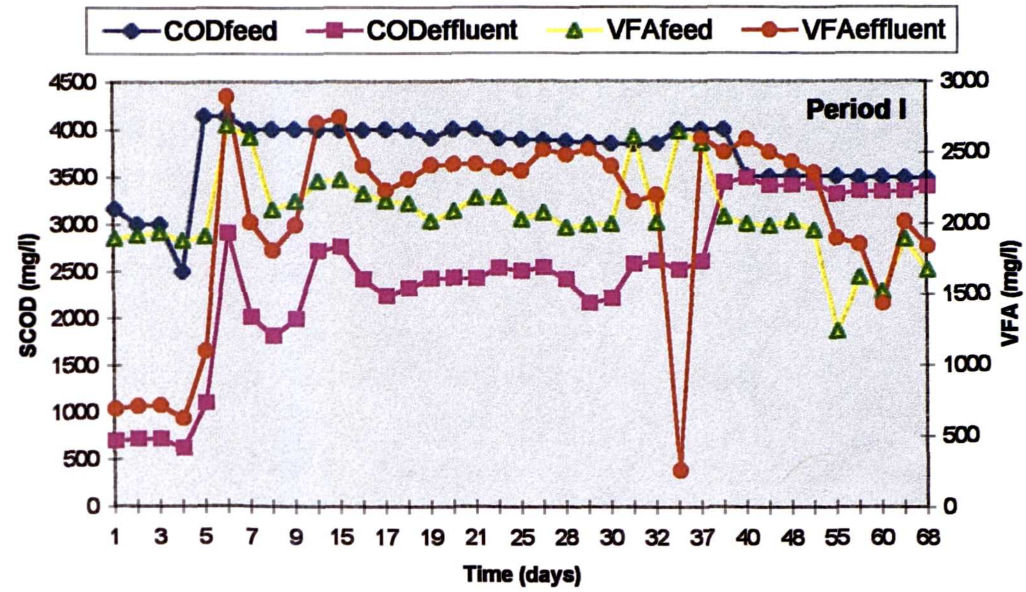


Fig. 6.1 Results from UFAF Days 1-70

Note:

HRT: 1 days

ammonia concentration: 721 mg/l

formaldehyde concentration: 0.1-0.5 mg/l

OLR: 4 - 6 kg/m^3-day

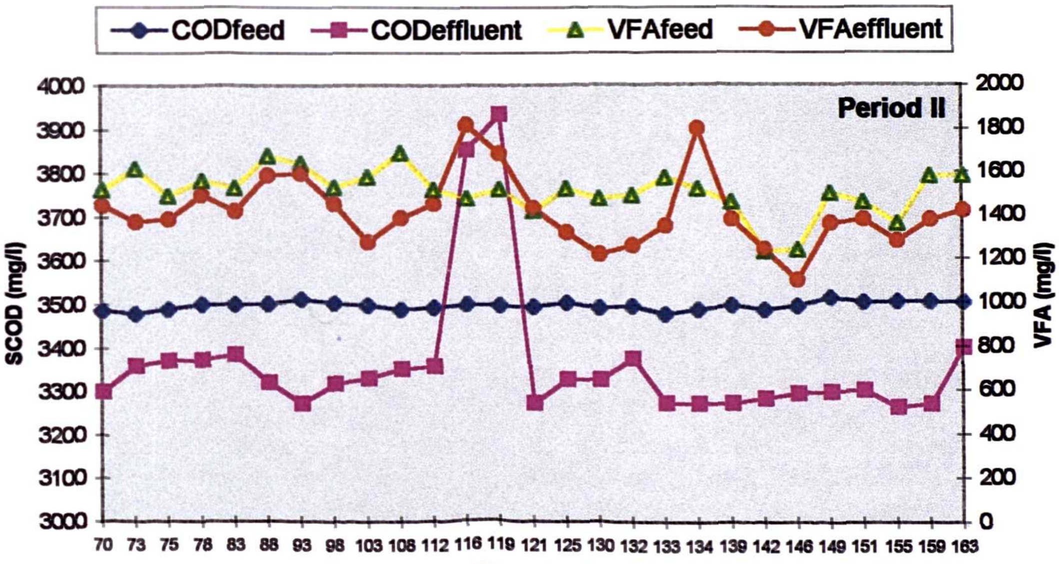


Fig. 6.2 Results from UFAF Days 70-165

Note: HRT: 3 days

ammonia concentration: 721 mg/l

formaldehyde concentration: 0.1-0.5 mg/l

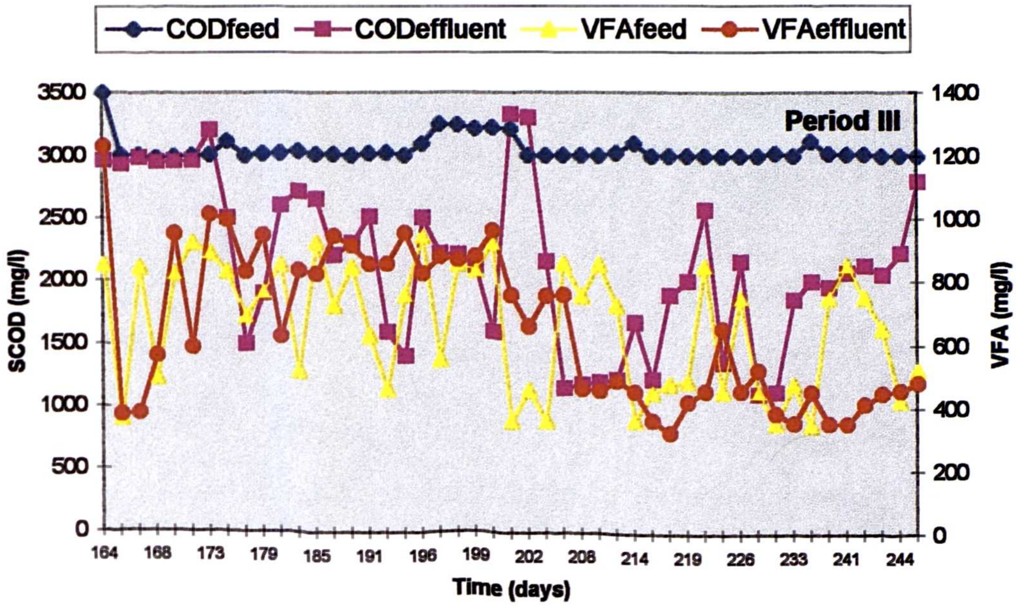


Fig. 6.3 Results from UFAF Days 165-245

Note:
HRT: 3 days
ammonia concentration:721 mg/l
formaldehyde concentration: 0.1-0.5 mg/l

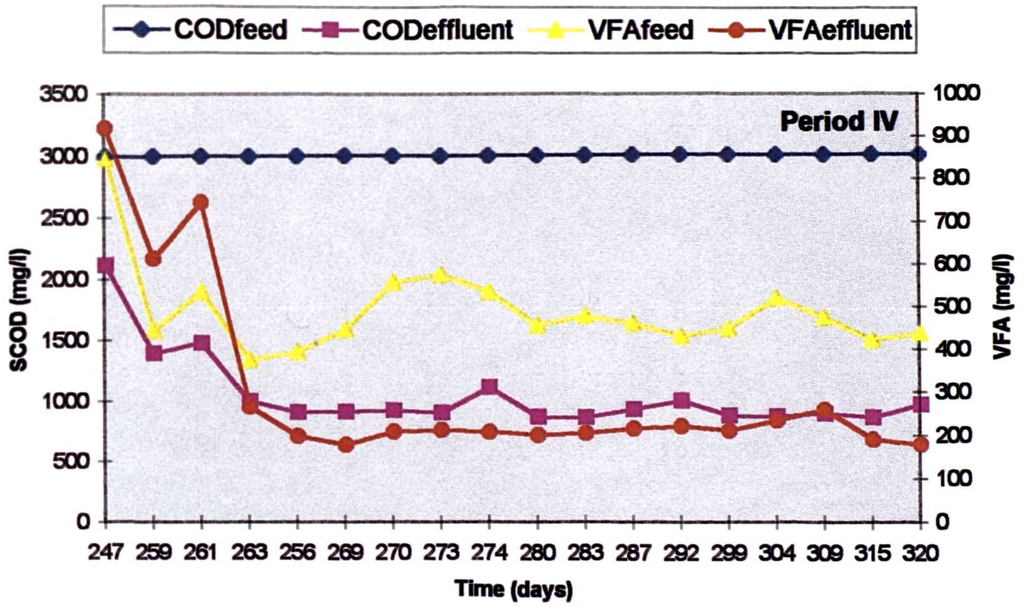


Fig. 6.4 Results from UFAF Days 245-320

Note:
HRT: 12 days
ammonia concentration: 721 mg/l
formaldehyde concentration: 0.1-0.5 mg/l

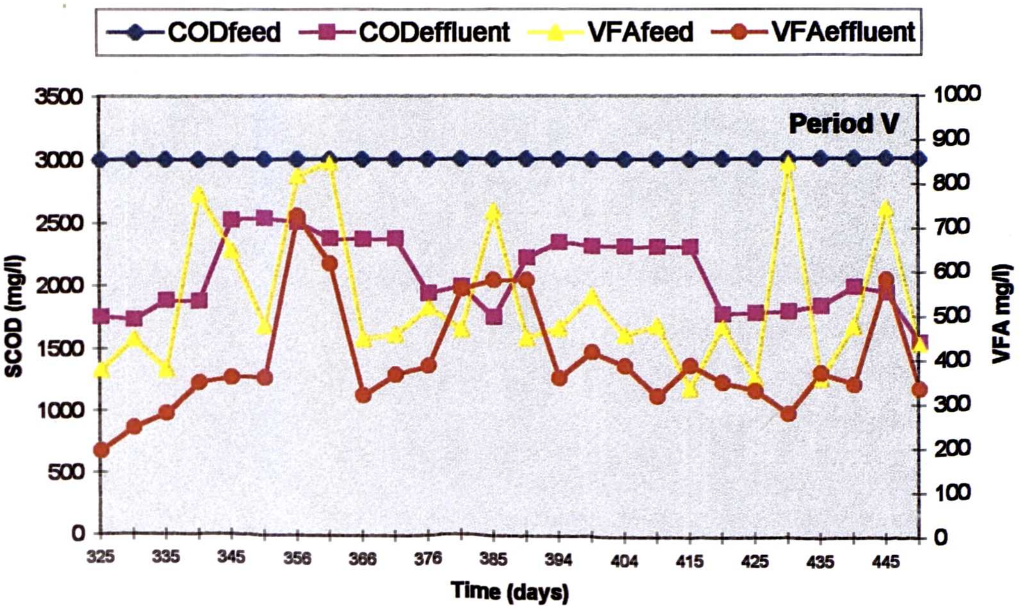


Fig. 6.5 Results from UFAF Days 320-450
Note:
HRT: 6 days
ammonia concentration: 130 mg/l
formaldehyde concentration: 0.1-0.5 mg/l

WO liquor was evaporated to reach such a low ammonia level but the COD concentration was reduced to the original value by adding water. Fig. 6.5 shows that no significant improvement in COD removal took place as a result of ammonia removal.

The concentration of formaldehyde in all feed stocks was not more than 0.2 to 0.5 mg/l. At this concentration it would not have an adverse effects on the anaerobic system.

During Period-I gas production was very steady and rapid. As the proportion of WO liquor to brewery wastewater was increased the production of gas was significantly reduced. The production of gas at the start of Period-I was 2-3 l/day and during Period-II and III reduced to 30 ml/day, of which methane contributed 60-78%.

(II) Discussion

The organic loading to the UFAF was varied to discover at what rate, in terms of kg COD/m^3.day the UFAF could purify the liquor. Other factors of interest were the effect of ammonia and formaldehyde on the anaerobic system.

The main constituent of VFA from WO was acetic acid (60-90 %) followed by n-valeric acid (< 4%), n-butyric acid (<3 %), and propionic acid (<1 %). The reason for selection of ambient temperature during Period I was that it was considered that hydrolysis of organic matters by WO would result in the production of mainly low molecular weight volatile fatty acids, thus making anaerobic treatment relatively straight forward. However this did not work in practice and for the remaining periods the reactor was operated at a constant temperature of 37 °C.

Period II showed the lowest COD removal of all UFAF tests (Fig. 6.2). During this period the brewery wastewater had been completely replaced by WO liquor which showed a considerable toxicity effect on the anaerobic system resulting in a significant increase in VFAs in the effluent. This suggests that the acidogens were active but it was the methanogens which were either affected by the toxic compounds in the liquor or required a larger retention time to degrade the organic matter. The increase in the effluent VFA results from UFAF shown in Fig. 6.4 imply that improved methanogenesis requires a long HRT.

These results confirm the data presented by Speece (1994) who found that the presence of amino-like compounds require a much longer HRT for their degradation under an anaerobic environment. Period I to V can be explained on the basis of Speece and Parkins (1983) observations. "The structural characteristics of compounds also appeared to influence the length of lag period for metabolism by an acetate enriched culture their data suggested that:

1. Non-toxic aliphatic compounds containing carboxyl, ester, or hydroxyl groups were all metabolised readily by acetate cultures. Butyric acid, valeric acid, propanol, propylene glycol, ethyl acetate, and vinyl acetate were all degraded within 4 days.
2. Toxic compounds with carbonyl functional groups or double bonds were all metabolised within a short period of time, although these compounds were usually toxic to unacclimatised acetate cultures. For example, butyraldehyde and sorbic acid required 7 and 10 days for metabolism respectively.
3. Compounds with amino functional groups showed difficulty in metabolism. Aniline, 4-amino-butyric acid and sec-butylamine were not metabolised in this study. 1-amino-2 propanol was the only amino compound metabolised, but it degraded at an extremely slow rate.
4. Compounds with dicarboxylic groups required a longer length of time to be metabolised as compared to compounds with one carboxylic group and the same carbon chain length, for example, succinic acid, adipic acid, and phthalic acid all had longer lag periods as compared to butyric acid, hexanoic acid, and benzoic acid respectively.
5. The position of the functional group also affected the length of lag period for metabolism. In the case of the hydroxyl group, primary butanol required 4

days for metabolism, and secondary butyl alcohol required 14 days while tertiary butyl alcohol was not metabolised in the serum bottles."

Results for Period-V indicates the presence of inhibitory compounds may be present in the liquor, because there was no significant removal of COD observed despite ammonia removal from the feed. Contrary to the conclusions of Friedmann et al., (1987) that "liquor treated at temperatures of 270 °C and above may not be treatable by a continuous anaerobic process due to the presence of formaldehyde" the results here suggest that a continuous anaerobic process would be viable but with at least 12 days HRT to degrade a significant level of organic matter.

The overall results imply that, due to the nature of WO liquor an uneconomical HRT would be required to attain significant treatment. It is also apparent from the above and Speece and Parkins (1983) findings, that the structural characteristics of compounds affect the length of the lag period for metabolism in a UFAF system.

6.3 AEROBIC BIOLOGICAL TREATMENT OF ACTIVATED SLUDGE LIQUOR

6.31. Introduction

Usually activated sludge is more robust and can operate under more severe conditions than anaerobic processes because aerobic bacteria are less sensitive to toxins than anaerobic bacteria. Continuous activated sludge processes have proved to be one of the most efficient and economical biological processes to be used in the water industry throughout the world, both for domestic and industrial wastewater. On this basis an aerobic process was selected for the treatment of AS280 °C. Liquors subjected to high temperatures (280 °C) were initially selected for the aerobic treatment because the inhibitory properties of the liquor have proved not to be very suitable for treatment by anaerobic processes as shown in Section 6.2.

At a paracetamol production factory operated by Sterling Organic Co., an activated sludge plant with an influent COD of 90000 to 120, 000 mg/l, at a two and a half (2.5) days retention time (HRT) and an operating temperature of 37 °C is operating satisfactorily and reduces the COD to 1200 to 2000 mg/l. The wastewater contains organic compounds such as phenol, formaldehyde etc.

The heat treated liquor used in this study was similar to the one used in the previous section (Section 6.2). The operating parameters, for WO such as temperature, pressure and retention time, for the preparation of the liquor for aerobic biological treatment was almost identical to the previous liquor of Section 6.2.

(I) Results

Table 6.3. shows the results from the activated sludge investigation into the treatment of liquor from AS280 °C. Several features are of special interest. It can be seen from Fig. 6.6 that there is a little difference between the process efficiency at the two loading rates investigated during Periods-I and II. Although the OLR was fairly high (4 - 6 kg COD/m^3.day), the reactor performed well under these loading rates. A maximum removal of SCOD was 66 %, with 86 % biodegradable COD (BCOD) removal being achieved. Period-III shows that by recirculation of the effluents 100%

BCOD could be removed but only 76.5 of the COD. Although BCOD could be completely removed by recycling, the residual COD implies that 23.5% was inert.

Table 6.3 Summary of Results for Activated Sludge Liquor (AS280 °C)

Period	Days	OLR (kg COD /m^3 .day	COD removal (%)	BCOD removal (%)	NH_3-N removal (%)	HRT (hours)
I	1-10	6	66	85.3	59	12
II	10-41	4	65.5	86	57	12
III	41-51	--	76.5	100	96	240

Note: During Period III, effluent from aerobic reactor was completely recycled

The pH and nutrient levels were monitored throughout the test periods. During Period-III, the effluent from the MAS system was recycled to remove all the biodegradable COD from the liquor, for the determination of inert COD. On the final day (the 10th day of recycling) the BOD_5 was 0 to 4 mg/l. A value of 470 mg/l COD appeared on 4th day of the recycling and remained reasonably constant upto the end of 10th day of recycling.

Table 6.3 shows that less than 60% ammonia removal was obtained for both loading rates and Fig. 6.7 shows that the concentration in the effluent was always greater than 120 mg/l, which inturn would cause a high BOD load on a receiving water. It appears from the nitrate results in the foot note to Fig. 6.7 that the removal of

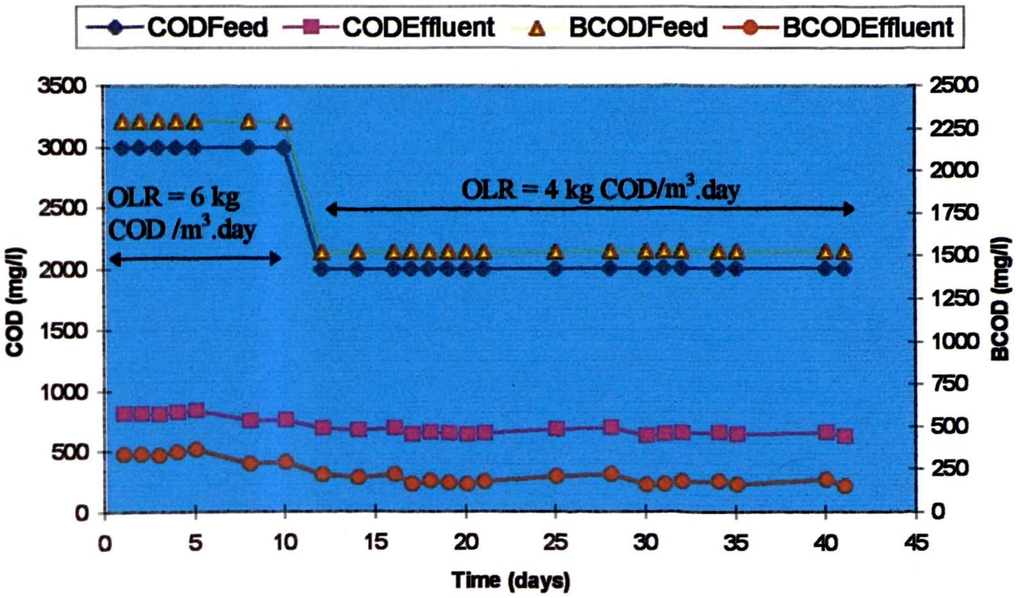


Fig. 6.6. Feed- Effluent Characteristic of Continuos Activated Sludge Process

Note:
HRT: 12 (hours)
MLSS: 2000 mg/l
HCHO: 0.2-0.5 mg/l

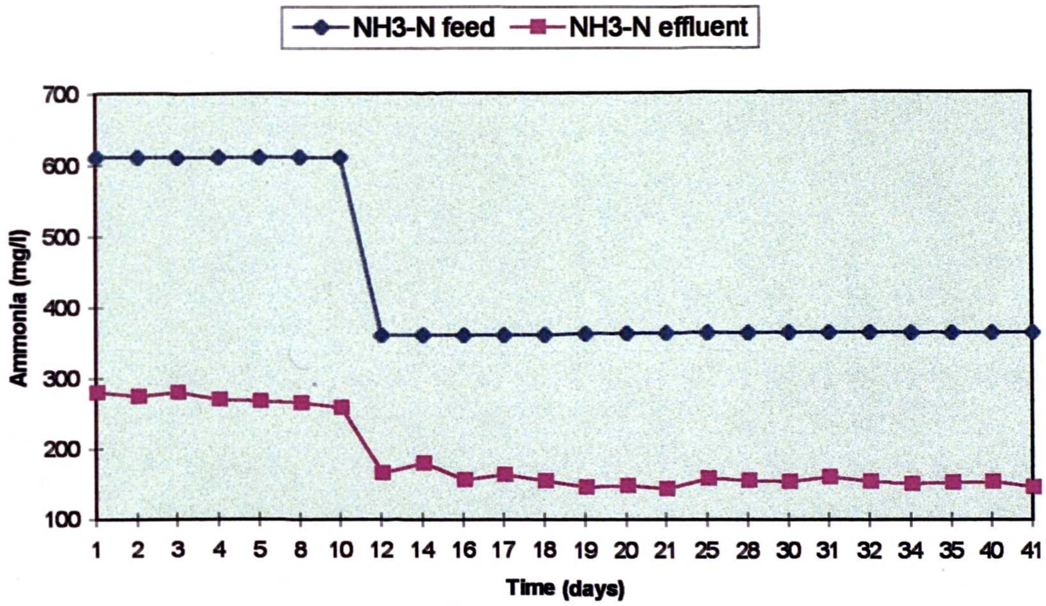


Fig. 6.7 Ammonia Concentration Days 1-41

Note:
Feed NH_3: 600-721 mg/l
Feed NO_3: 3-6 mg/l
Effluent NO_3: 3-6 mg/l

ammonia was probably due to air stripping except for that required for metabolism. The concentration of nitrate in both the feed and effluent was similar, being in range of 3 to 6 mg/l, i.e no nitrification had taken place in the activated sludge process.

The SVI of the activated sludge at both loading rates was in the range of 50-80 indicating a better potential solids/liquor separation for the process. The sludge age analysed at both loading rates was 4.5 day. The cell growth coefficient for the process under both loading rates was nearly the same i.e. 0.2.

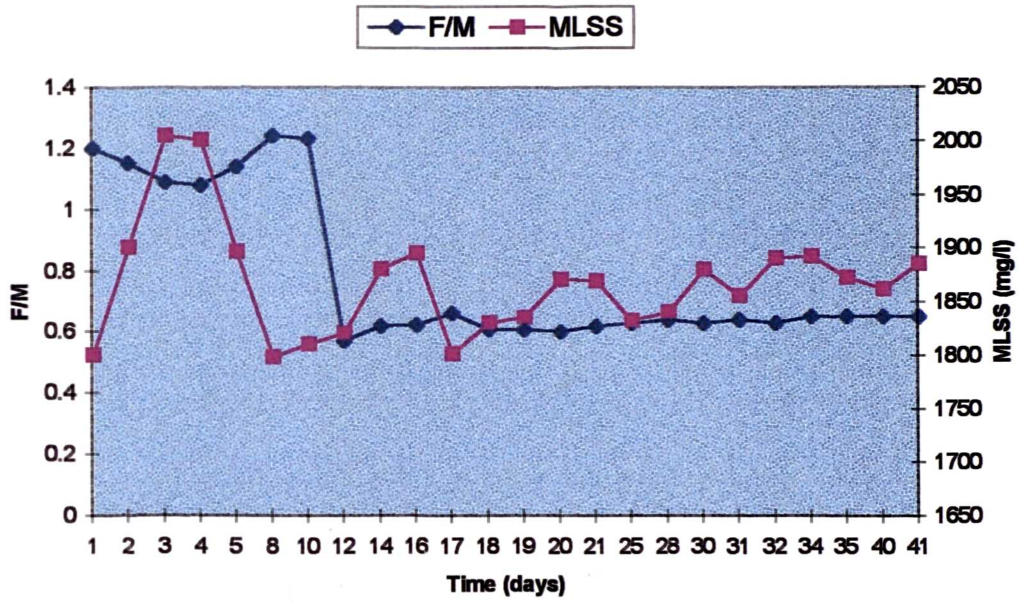


Fig. 6.8 MLSS-F/M Ratio Results Days 1-41
Cell growth coefficient: 0.2
sludge age: 5 days
SVI: 50-80

A visual observation of the effluent was made although no laboratory data were taken to measure the colour and turbidity of the effluent liquor. At both loading rates the colour of the feed, which was clear, greenish- yellow, changed to a clay colour and also became slightly turbid. Under all conditions the feed pH to the membrane activated sludge process (MAS) was 7 and the effluent pH was in range of 8-9.

Throughout the 41 day period the reactor gave a uniform removal of COD, BCOD and ammonia. The average MLSS and F/M of the reactor were approximately 2000 mg/l and 0.6 respectively (Fig. 6.8). The SS of the effluents were less than 15 mg/l.

(II) Discussion

The BCOD was determined as in the procedure suggested by Germirli et al., (1991) for the determination of inert COD of an industrial wastewater. The BCOD in this study represent the ultimate BOD of the liquor. After knowing the inert COD of the liquor the BCOD were then calculated from the initial COD values of the liquor (Appendix-C).

The value of 23.5% inert COD, although apparently very high compares favourably with values of 8%, 12%, and 24% inert COD as reported by Erickson (1972), Everett (1971), and Heyda et al. (1980) respectively for liquors produced under similar conditions.

The high removal of BCOD can be explained on the basis of the BOD rate constant k value. Erickson (1972) has reported k=0.4/day, for WAO liquor. which indicates that oxygen uptake by the aerobic bacteria was very high compared to domestic sewage which is generally reported as 0.1/day. Wastewater having a k=0.1/day means that 20.6% of the ultimate BOD would be exerted on day one and 0.4/day would mean that 85% of the BCOD would be exerted on day one. From the results (Fig. 6.6) it appears that a very high uptake of oxygen has been observed in these experiment, which nearly match the findings of Erickson (1972).

It appears from the results that the organic compounds in the liquor which inhibited the anaerobic process could be more readily degraded by the activated sludge process. Alcohols, phenols, ester, aldehyde, amino acids, cyanides or nitriles, compounds containing the vinyl group, surfactant and allied structure and many other toxic compounds which may be present in WO liquor have been reported to be easily degraded or assimilated by the activated sludge process (Ludzack and Ettinger, 1959).

The cell growth coefficient value indicates that the amount of feed COD converted to sludge was low (20%) compared to that for domestic sewage which is usually considered to be 50 to 80%. The value 0.2 (kg VTS/kg COD removed) may be due to the high inert COD in the feed and also due to the very low suspended solids in the feed or due to different microbial population.

The sludge age analysed was 4.5 days which may be one reason for the low SVI of the process. Examination of flocs by electron microscopy reported by Gray (1989) has shown that "granular and amorphous materials are present in activated sludge, and that fine cellulose fibrils are formed. Young flocs contain actively growing and dividing heterotrophic bacteria with a high rate of metabolism. Older flocs, in contrast, have a lower proportion of viable cells, being composed mainly of dead cells surrounded by a viable bacterial layer. Although the majority of these cells are no linger viable they retain active enzyme systems. Older flocs have a reduced rate of metabolism but as they are physically larger they settle far more readily than younger flocs." Activated sludge having sludge age of between 3 to 4 days has good settling properties. However, at sludge age greater than 6 days or between 0.5 to 3 days, there is a reduction in settleability.

The average MLSS and F/M of the reactor were approximately 2000 mg/l and 0.6 respectively (Fig. 6.8), which is an acceptable value for activated sludge (Metcalf and Eddy, 1991). Finally the data demonstrates that an aerobic treatment process can provide consistent COD removal for WO effluents despite the high OLR value and the presence of inhibitory substances especially those toxins which inhibited the anaerobic system.

6.4 ANAEROBIC BIOLOGICAL TREATMENT OF DETERGENT LIQUOR

6.4.1 Introduction

Much research has been carried out on the biotreatability of detergent wastewater by both aerobic and anaerobic processes but no report has been found in the literature regarding the biological treatment of liquor produced from the WO of detergents. The presence of detergents in wastewater will inevitably create problems such as oxygen transfer the possible transmission of pathogens, and removal of biomass, by the wind blown foam layer (Kulandai et al., 1984).

Under EU Directives 73/404/EEC, 73/405/EEC and 82/242/EEC, all member states forbid the sale and use of anionic, cationic, non-ionic and ampholytic detergents where the average level of biodegradability of the surfactants is less than 90%.

Relaxations were, however, permitted in 1982. The Directives also provide for methods of testing for biodegradability (Garbutt, 1995).

(I) Results

The treatment of detergent wastewater in high concentrations is very difficult by any conventional treatment process. As discussed in Chapter 5, Unilever plc were considering any treatment process which could be used to reduce the effect of their highly concentrated detergent wastewaters.

In this research project a UFAF was operated under two different modes. In the first run only LAS liquor was used as feedstock to the UFAF. Initial acclimiatizaion of the reactor was carried out by using a brewery wastewater. In the second run a combination of all six liquors was used as the feed to the UFAF. The experimental work for the detergent liquor was carried out for 110 days (Figs. 6.9 and 6.10). pH adjustment, buffering of the feed, and nutrient adjustment, have all been carried out according to, and similar to, the previous process AS280 °C liquor (Section 6.2). The experimental conditions and results are shown in Table 6.4.

Table. 6.4 UFAF Continuous Flow Performance Characteristics at 37 °C

Detergent Type	Days	OLR (kg/m^3 .day)	Influent SCOD (mg/l)	Effluent BCOD (mg/l)	COD removal (%)	HRT (days)	AD removal (%)
LAS	1-50	2.53	15200	7500	51	6	49
Mixed WO Liquors	50-110	2.32	13920	10360	25	6	45

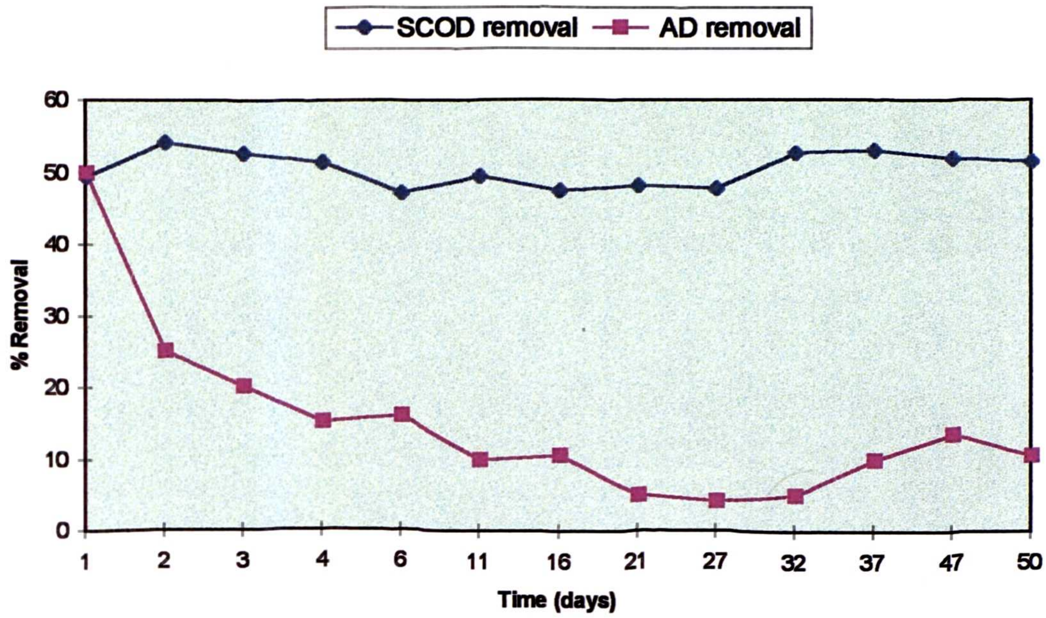


Fig. 6.9 UFAF Continuos Flow AD/SCOD Removal at 37 °C (LAS liquor)

Note:OLR: 2.53 kg COD/m^3.day

Feed COD: 15200 mg/l, Feed active detergent (AD): 200 mg/l

HRT: 6 days

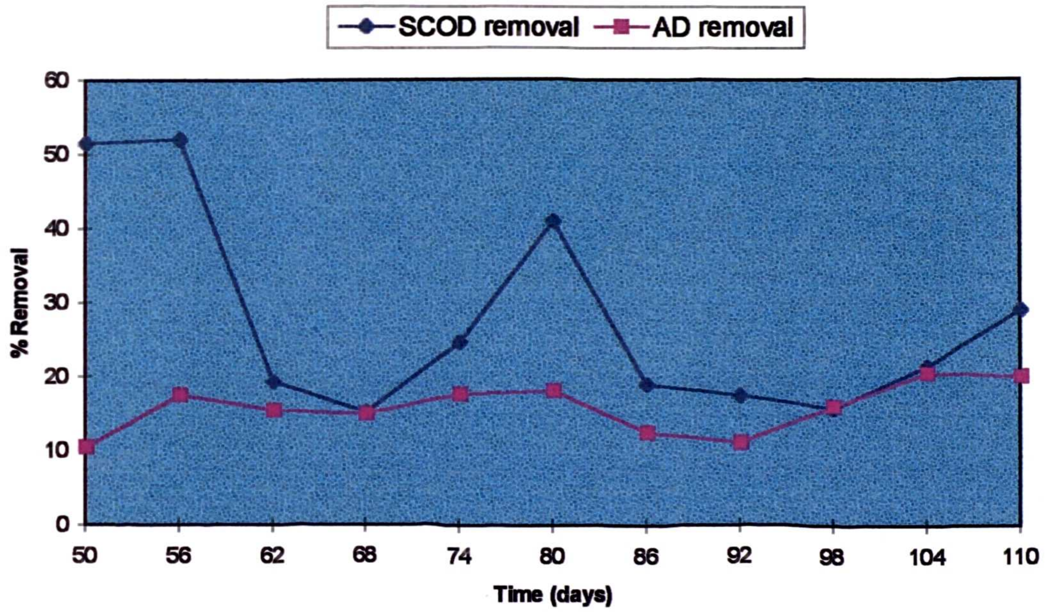


Fig.6.10 UFAF Continuos Flow AD/SCOD Removal at 37 °C (Mixed WO liquor)

Note:OLR: 2.32 kg COD/m^3.day, Feed COD: 13920 mg/l

Feed AD: 200 mg/l

HRT: 6 days

It was not possible to perform separate tests on six different detergents using UFAF. A mixed WO liquor of all six types of detergent as discussed previously, was prepared in order to make a combined feed stock for its further biological treatment by UFAF. The net COD of the mixed WO liquor was 20 g/l which was then diluted accordingly by adding tap water.

At the start, the UFAF which was already being feed on WO AS280 °C liquor, was diluted with beer, the production of gas sharply increased from nearly zero to 850-1250 ml/day within three days. The acclimatisation period of the UFAF receiving detergent liquor was completed within a three week period. A constant OLR value, as given in Table 6.4 was decided in order to see if there was any detrimental effect on the anaerobic process.

The UFAF was loaded on the basis of the SCOD, the feed active detergent in both cases was 200 mg/l. Fig. 6.9 shows that an average destruction of detergent liquor (LAS), SCOD and active detergent (AD) was 51% and 10% respectively. The methane content of the gas production in the UFAF ranged from 65-70% and the methane yield ranged from 0.01-0.05 m^3 CH_4/kg of $SCOD_{removed}$. Fig. 6.10 shows that average SCOD and AD removals of 25% and 15% respectively were obtained for the WO mixed liquors.

(II) Discussion

It was also decided for the detergent liquor to operate the UFAF under mesophilic temperature condition since mesophilic digestion was considered to be a more stable process compared to thermophilic digestion, mainly due to the fact that fewer species of bacteria are active at the higher temperatures (Evison, 1993).

Results in Figs. 6.9 and 6.10 indicate the presence of inhibitor organic compounds in the liquor which affect the removal of SCOD from the liquor, or it might not be due to the toxicity on methanogens but on the production of certain types of organic compounds that are relatively difficult to degrade and therefore require more time. The reduction of detergent suggests that the detergent molecules may be degraded by bacteria or chemical reaction or the accumulation of detergent molecules in solids of the anaerobic system resulting in low active detergent concentration in the effluents.

In contrast to the ABS and LAS results reported in the literature, that ABS (Alkylbenzene sulphonates) and LAS are recalcitrant and not possible to be degraded by an anaerobic biological process alone, the LAS (Linear Alkylbenzene sulphonates) results shown above suggest, that it can be degraded by an anaerobic process after WO. These results also suggest that high COD and active detergent removal may be achieved by using 10-15 days HRT or low OLR to the anaerobic system.

6.5 AEROBIC BIOLOGICAL TREATMENT OF DETERGENT LIQUOR

6.5.1 Introduction

As stated in the previous Section 6.4, WO detergent liquors are difficult to treat by anaerobic biological processes. An SBR system was used to determine if the anoxic stage showed any improvement in the removal of detergent and nitrogen from the liquor. In aerobic systems, oxygen is the terminal electron acceptor and is reduced while organic or inorganic electron donors are being oxidised. In the absence of oxygen, other material such as nitrates may become electron acceptors. Nitrate can be used, however, by facultative organisms living under intermediate conditions refered to as anoxic, which are characterised by end products of carbon dioxide, water and nitrogen gas. The above statements can be presented in equation form as given below.

Conceptual Anoxic stage in SBR

$$1\ 8\ CO_2 + 1/8\ HCO_3^- + H^+ + e^- \rightarrow 1/8\ CH_3COO^- + 3/8\ H_2O \qquad (6.1)$$

$$1/8\ HCO_3^- + 1/5\ NO_3^- + 1/5\ H^+ \rightarrow 1/8CO_2 + 1/8HCO_3^- + 1/10N_2\uparrow + 9/40\ H_2O \qquad (6.2)$$

In the case of the SBR (activated sludge process), the effect of detergent is more serious. The vigorous aeration used in the process makes it a foam generator if foaming components, such as detergents are present. Excessive foam is not welcome because it contributes to unsightly conditions in the plant, and when wind blown can be a nuisance to the neighbourhood. Furthermore, it can affect the rate of oxygenation of water, so the efficiency of a given sewage disposal unit will be reduced. The presence of detergent in a river water or stream can lead to a reduction in the rate of reoxygenation from the atmosphere. This will reduce the rate of self-purification of the river and have an unfavourable effect on flora and fauna in streams.

(I) Results

The operating parameter and results of the SBR treatment of detergent liquors are given in Table 6.5. The SBR was operated with two different detergents. In the first phase LAS liquor was used as a feed to the system for 15 cycles, and in the second phase the mixed WO liquors of different detergent was used. The pH, macro-, and micro-nutrient adjustments were made according to the previous aerobic process (AS280°C) experiments. Due to the high concentration of detergent in the feed, foaming was controlled by adding 1-2 drops of a silicone antifoaming agent in every cycle.

Figs. 6.11 and 6.12 show the organic matter removal from the detergent liquor by the SBR process. Several features of the result are of special interest. In phase I and phase II (Figs. 6.11, 6.12) an average active detergent (AD) removal of 70% COD removal of 80% and Biodegradable COD (BCOD) removal of 95% was observed. Fig. 6.11 shows that the degradation LAS is less than that reported previously by researchers in literature. Fig. 6.12 shows similar active detergent removals from the combination of anionic and cationic detergent liquors.

It appears from the experimental results that the inert COD of the detergent liquor was 15.5% of the total feed COD to the SBR system. A cell growth coefficient for both detergent of 0.4 (kg VTS/kg $COD_{removed}$) was observed for these experiments. This value is double that found for AS280°C, indicating the formation of more sludge during the conversion of soluble COD during detergent biodegradation.

Fig. 6.13 shows the SVI and F/M ratio during the SBR cycles. The SVI was generally below 80 for the first few cycles which implies that the activated sludge in this research settled well. The F/M ratio for LAS liquor and mixed WO liquors was 0.6 and 0.8 respectively which was the reason why pure oxygen was used for the aeration.

Table 6.5 Summary of Operational Conditions Applied for the Laboratory Scale SBR Experiment.

Parameter	Unit	Value
Cycle Duration	hours	8
Volume Exchange Rate	% of total reactor vol.	25-50
Fill Volume	% V total	25
SRT	days	5-10
MLSS	mg/l	2700 LAS, 4995 mixed WO (liquors)
Temperature	°C	22
Influent Conc.		
AD (active detergent)	mg/l	60 LAS, 150 mixed WO (liquors)
COD	mg/l	2000 LAS, 5000 mixed WO (liquors)
Biodegradable COD	mg/l	1690 LAS, 4690 mixed WO (liquors)
SS	mg/l	< 20 (both liquors)
pH		7
Effluent Conc.		
AD	mg/l	18 LAS, 45 mixed WO (liquors)
COD	mg/l	400 LAS, 1000 mixed WO (liquors)
Biodegradable COD	mg/l	100 LAS, 250 mixed WO (liquors)
SS (after 2 hours sedimentation)	mg/l	< 30 (both liquors)
pH		8-8.5 (both liquors)

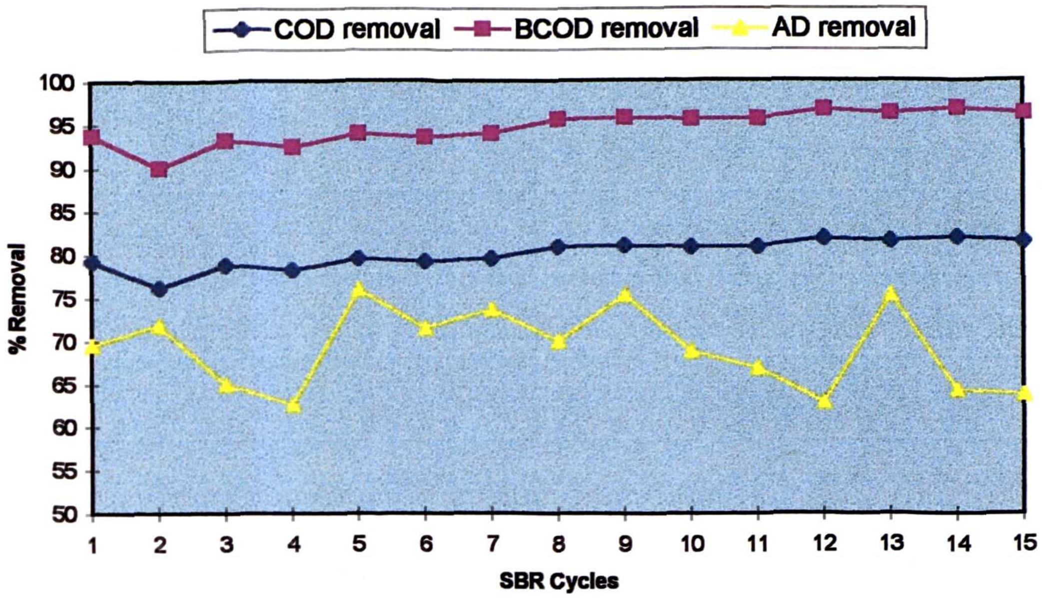


Fig. 6.11 Active-Detergent (AD), COD and BCOD Results for LAS WO Liquor System

Note:
initial COD: 2000 mg/l
inert COD: 308 mg/l
Nitrate initial and final < 1 mg/l

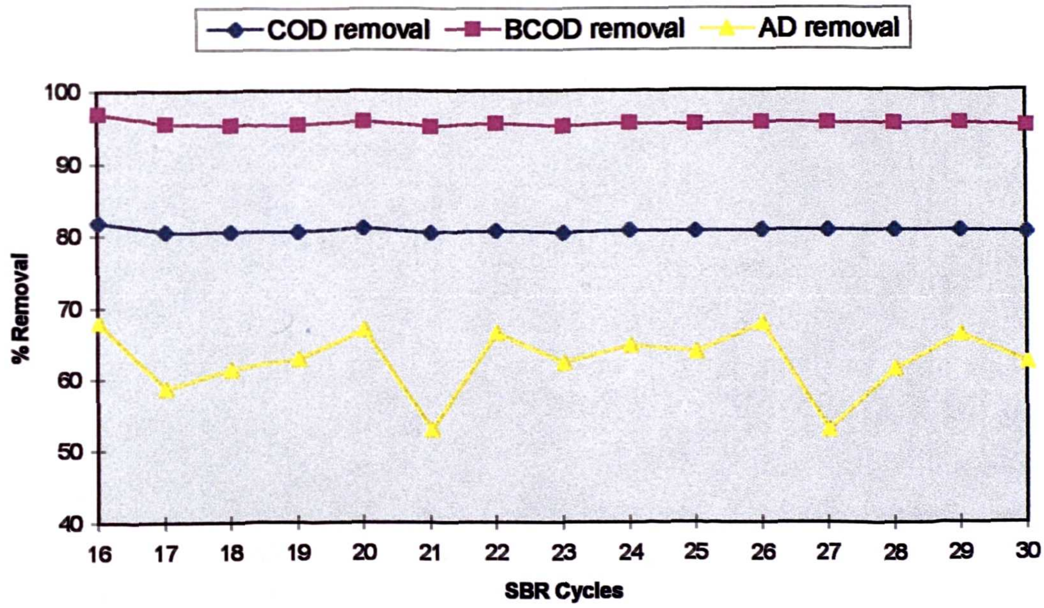


Fig. 6.12 Active Detergent, COD and BCOD results for Mixed WO liquor

Note:
initial COD: 5000 mg/l
inert COD: 780 mg/l
Nitrate initial and final < 1 mg/l

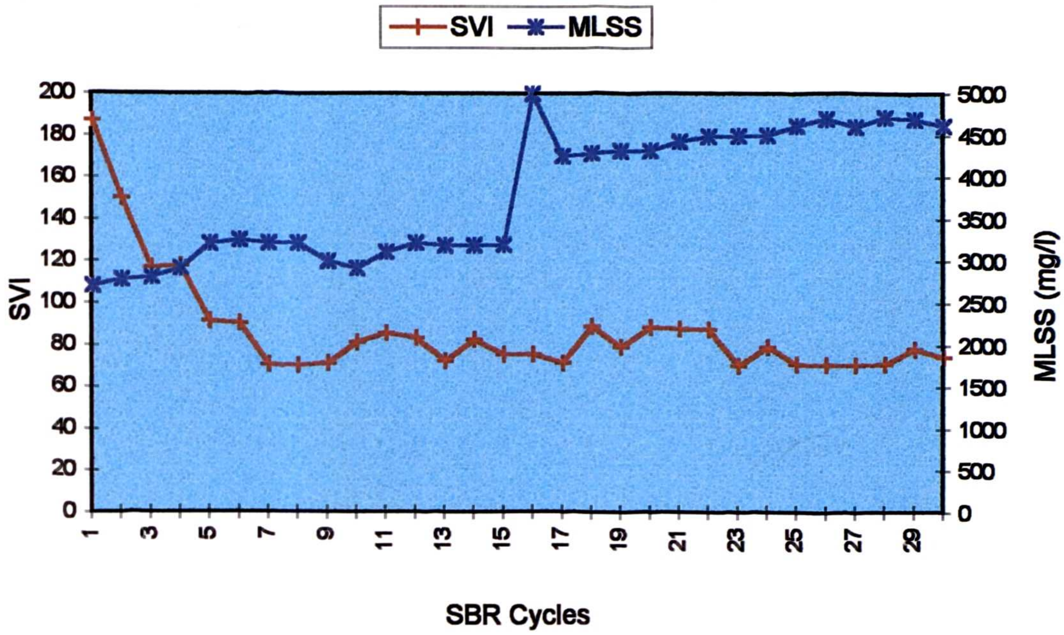


Fig. 6.13 SBR Cycle Characteristics

(II) Discussion

The ability of micro-organisms to degrade detergent molecules depends above all on the type and structure of the molecule itself. For instance, a branched chain molecule is more difficult to degrade than a straight chain one. In general, micro-organisms are capable of metabolising cationic detergents. Anionic surfactants which should normally be present in sewage at levels much higher than those of quaternary ammonium compounds, form stoichiometric complexes with quaternary ammonium compounds, and this reaction by itself may reduce or even eliminate toxicity. As reported in the literature review of this thesis that aerobic biodegradation of detergent is very high due to the presence of enzymes such as mono-oxygenases and dehydrogenases which are believed to be involved in the aerobic degradation of detergent. However, under anaerobic conditions, such enzymes are not able to function due to the absence of oxygen.

The BCOD was determined similar to Section 6.3 of this chapter. The inert COD in the activated sludge liquor treated under similar conditions was 23.5%, indicting that detergent liquors treated under similar conditions are more biodegradable than the activated sludge liquor. Renn et al., (1964) reported that with a feed concentration of 73 mg/l LAS, an activated sludge process removed 95% of it. They also observed that the efficiency of LAS degradation was equal to or slightly greater than the BOD_5 removal.

Fig. 6.11 shows that the degradation of LAS is less than that reported previously in literature. The reason for this might be that due to WO, the liquor may contain some inhibitory compounds which hinder the degradation of detergent molecules as in earlier experiments. Fig. 6.12 shows similar AD removals to Fig. 6.11, although the load to the SBR system in the former case was two and half times greater than the latter. This implies that the inhibitory effect caused by the heat liquor components acted irrespective of the feed COD and active detergent concentration.

The soluble organic matter removal for both detergents was high which can be explained on the basis of the findings of Erickson (1972). He observed a 'k' value of 0.4/day which indicates a very high uptake of oxygen by heat treatment liquor, the details of which have already been given in the previous investigation for AS280°C (Section 6.3). The removal of COD behaviour of SBR indicates that very high uptake of oxygen has taken place in the reactor.

6.6 HIGH RATE AEROBIC TREATMENT OF PARACETAMOL LIQUOR USING PILOT-SCALE JET LOOP REACTOR

6.6.1 Introduction

The JLR was used for the treatment of liquor collected from a local WAO plant treating wastewater from paracetamol production. The laboratory investigation for this part of the work lasted for five weeks. In the first week optimisation and standardisation of the operating parameters of the JLR system (see Chapter 4) were carried out with tap water, as recommended by Bloor (1995). In the second week the JLR was seeded with fresh activated sludge from a local wastewater treatment plant. The activated sludge seed had a MLSS level of 2500 -3000 mg/l and an SVI of 90-150. Spoilt beer was initially used as feed to the JLR system for production of active biomass. In the third week the system was fed with liquor, with a small increase in loading rate for the first three days. In order to maintain a constant dissolved oxygen concentration the hydraulic retention time and the recirculation rate were kept constant.

The start-up time period, suggested by Bloor, (1995) for up to a maximum loading of 50 kg COD/m^3.day was 3-5 days. He also observed that if the initial load was high (20-50 kg COD/m^3.day, i.e. F/M 7-17 kg COD/kg MLVSS.day), then considerable foaming would occur. He also noted less foaming under well acclimatised conditions, and if biomass was lost due to excessive foaming, it would increase the F/M of the system resulting in increased foaming. Bloor (1995) suggested that a low initial load of 5-10 kg COD/m^3.day (F/M 2-3 kg COD/kg MLVSS.day) caused little foaming and good sludge settling. Slowly increasing this load up to 50 kg/m^3.day over 3-5 days resulted in little foam, better effluent quality and better settling.

Due to the presence of the high concentration of inorganic salts in the paracetamol liquor, it was not possible to be treated by either the membrane activated sludge, the SBR or the anaerobic UFAF processes. The JLR was able to treat the liquor irrespective of its high concentration of inorganic compounds.

(I) Results

Three weeks after startup, the JLR was fed only on paracetamol WAO liquor at a loading rate of 10 kg COD/m^3.day. The acclimatisation of the system was completed in three days followed by seven days on paracetamol WAO liquor. In the 5th week, feeding to the system was stopped to determine the inert COD of the liquor. During this period the MLSS of the system had reduced significantly due to endogenous respiration. The inert COD observed after aeration periods of one hour, one day, and one week was almost identical, indicating the high removal of BCOD by the biomass over a very short time period.

It appears from the experimental results that inert COD of the paracetamol WAO liquor was very high compared to the previous liquors studied, with 50% being obtained. The results in Figure 6.14 show that when the feed was only spoilt beer, a removal of 95% COD was obtained but when the concentration of paracetamol WAO liquor was increased at a rate of 25% per day, the COD removals on the subsequent days were 84%, 73.5%, and 62% respectively.

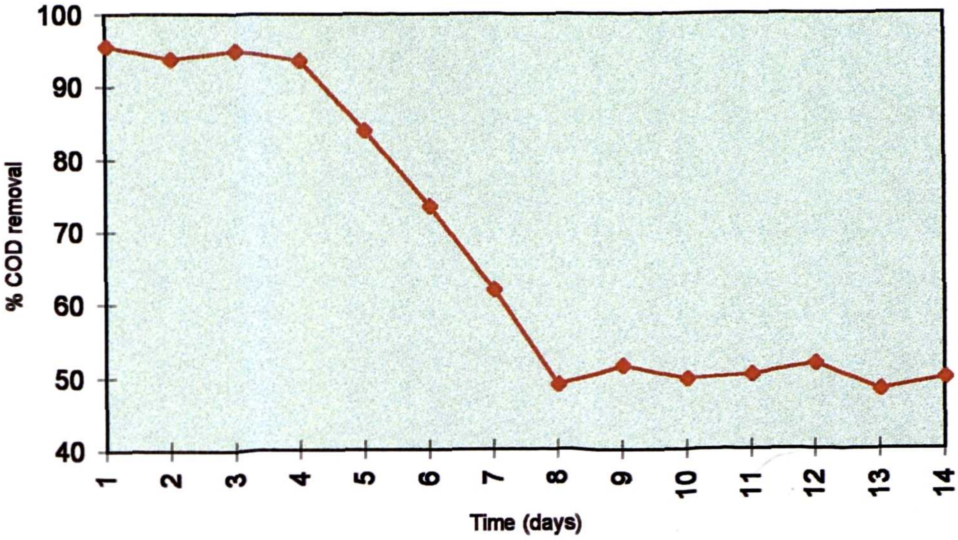


Figure 6.14 COD Removal from Paracetamol WAO Liquor in JLR

Note:

Feed COD: 2300 mg/l

HRT: 5.6 hour

OLR: 10 kg/m^3.day

SO$_4$: 2500 mg/l

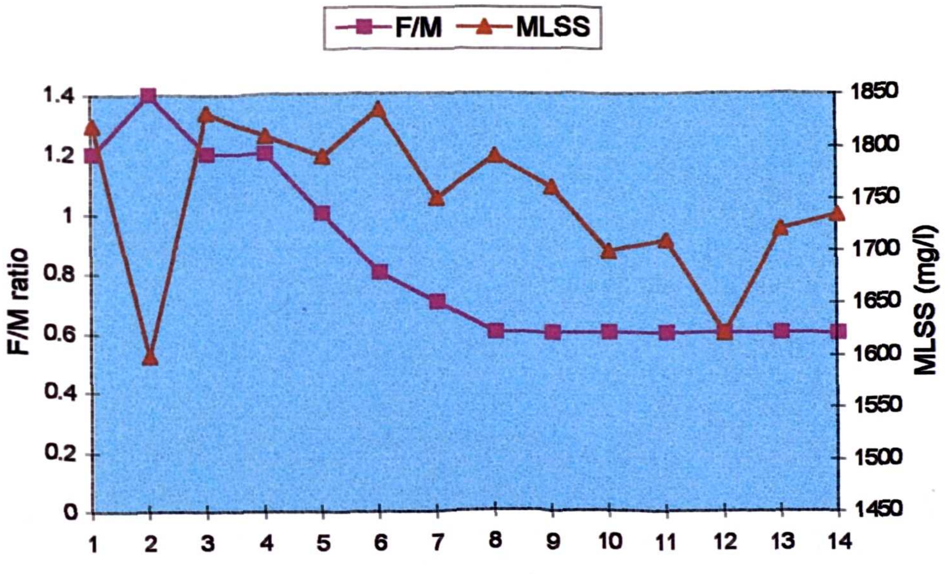


Figure 6.15 JLR MLSS, F/M Results day 1-14

Note:

SVI > 200

Cell growth coefficient: 0.1

The cell growth coefficient of the paracetamol liquor was less than 0.1 (kg VTS/kg $COD_{removed}$). Figure 6.15 shows the F/M and MLSS concentrations in the reactor throughout the JLR operation. If the JLR is to operate at high OLR without increasing the MLSS concentration then a very low sludge age will occur, and also a high F/M ratio.

The sludge volume index (SVI) of the process was above 200, indicating very poor setleabilty of the sludge. In the case of the paracetamol liquor the sulphate content was 2000 mg/l, consequently resulting in the possible presence of sludge bulking bacteria.

Foam formation was not very significant due to the very low OLR value. The colour of the feed was dark brown when applied to the JLR, but after treatment it was a light muddy colour, which imply a significant improvement in the effluent colour.

(II) Discussion

The decrease in COD removal with the increase in paracetamol WAO liquor proportion indicates the presence of inert COD or non-biodegradable COD in the liquor. The exact reason for lower cell yield is not known but it could have been due to the presence of the very high inert COD in the feed liquor or the heat treated liquor and presence of inorganic compounds which could inhibit some bacteria and favour others.

Bloor (1995) observed that an MLVSS above 20 g/l would cause settling problems so it has to be accepted that operation at a high F/M and low sludge age are the characteristics of the JLR and the overall effects of such operation may not be avoidable. There could have been two main causes of sludge bulking of the JLR treated sludge i.e. filamentous and non-filamentous. Filamentous bulking has been attributed to the excessive growth of filamentous bacteria, which hinder the settlability of the flocs. Non-filamentous sludge bulking is thought to be brought about by excessive production of a polysaccharide slime coating [exocellular polymers (ECP)] by floc forming bacteria. This coating reduces the floc density due to both increased water retention and entrapped gas thus hindering settleability of the flocs (Jenkins et al., 1986). Bloor (1995) reported that high shear forces imparted by a jet may strip off ECP which may subsequently be degraded by other bacteria, thus resulting in poor flocculation. During this research no microbiological examination has been carried out so no confirmation of the above statements is possible.

As stated earlier that due to presence of the high concentration of inorganic salts in the liquor, it was not possible to be treated by any other process discussed above in this chapter. The Jet Loop Reactor was able to treat the liquor irrespective of its high inorganic compounds.

6.7 SUMMARY

Table 6.6 gives, at a glance, the difference between and the versatility of, the two processes represented above. The same thermally treated WO effluents were used for both aerobic and anaerobic processes.

It is clear from Table 6.6 that an aerobic process provides better biological treatment for WO liquor than an anaerobic process. An overview of Chapter 6 indicates that aerobic biological processes are more efficient in removal of organic matters from toxic heat liquors than anaerobic process. Due to toxicity, the anaerobic process achieved a 63 % removal during the well-established acclimatised system over a period of 9 months at 12 days HRT. On the other hand the aerobic process showed much better results than those of the anaerobic process although this was operated under much more severe conditions i.e. a high OLR and a lower HRT. For good COD removal by the anaerobic process an HRT of 15 to 20 days should be used for liquors treated at 280 °C. It proved however that, due to toxicity in the anaerobic system, the bacteria utilised the COD very slowly. Other than the high sludge production by aerobic biological process, nearly 60% ammonia removal from the liquor was observed.

Table 6.6 Comparison between Aerobic and Anaerobic Biological Processes

Parameter	Aerobic process	Anaerobic process
COD removal (%)	50 - 80	15 - 63
OLR (kg/m^3.day)	4 - 10	0.25 - 2.5
BCOD removal (%)	86 - 96	<40
Acclimatisation period (days)	3	>100
Gas production	N/A	very low
Temperature (°C)	ambient (22)	22-37
Nutrient	Yes	Yes
a) Macro	Yes	Yes
b) Micro	No	Yes
Sludge production	High	Very low
Sensitivity	Very robust efficient	Lethargic and less efficient

CHAPTER 7

CONCLUSIONS AND RECOMMENDATIONS

As outlined in Chapter 1, this research project was a continuation of a previous study by Luduvice (1992) and, when possible, most of the recommendations were investigated including the use of pure oxygen instead of air in the reactor, the biotreatability of the heat liquor and an evaluation of the chemical characteristics of the liquor. It was not, however, possible to develop a continuous Wet Oxidation process capable of operating at both subcritical and supercritical conditions.

7.1 Wet Oxidation of Sludges and Industrial Wastewaters.

From the investigation the following conclusions may be drawn for Wet Oxidation under subcritical conditions:

i) Comparison between the treatment efficiencies results from the full-scale continuous flow Wet Air Oxidation plant at Sterling Organic's and the laboratory batch-scale Wet Oxidation reactor implied that there could be little justification for installing a continuous flow Wet Oxidation, laboratory-scale reactor because of similarities in results between the two.

ii) The use of pure oxygen in the Wet Oxidation reactor at the stoichiometric oxygen requirement (SOR) is beneficial if a high degree of oxidation is required and would be effective for both domestic wastewater treatment plant sludges and industrial wastewaters.

iii) Hydrolysis of sludges and industrial wastewaters takes place during the heating up process, followed by oxidation after injection of the oxygen.

iv) At high temperatures, and on complete oxidation due to the presence of excess oxygen, no odour production was detected whereas an unpleasant odour was noted when low temperature Wet Oxidation took place.

v) When soluble COD (SCOD) was produced, this was mainly low molecular weight volatile fatty acids and predominantly acetic acid. The level of acetic acid production was found to be temperature dependent, being about 20% of the VFAs at $200^{\circ}C$ compared to 90% at $300^{\circ}C$.

vi) The most significant parameter in Wet Oxidation at the stoichiometric oxygen requirement (SOR) was temperature, followed by retention time and pressure. For a given temperature, the production of SCOD was at a maximum soon after the injection of oxygen, decreasing with time due to the subsequent oxidation of SCOD.

vii) Overall, the settleability of all types of solids investigated was improved by Wet Oxidation and improved with increases in temperature. For a given temperature, the setttleability improved with increases in retention time.

viii) The filterability (i.e. dewaterability) of both primary and activated sludge was significantly improved by Wet Oxidation with both having capillary suction times reduced to less than 50 seconds.

ix) Significant reductions in Total Chemical Oxygen Demand (TCOD) were obtained for all sludges and wastewaters studied, the amount depending upon the nature of the sample and varying from 80% for thickened activated sludge to 100% for some detergent wastewaters.

x) Wet Oxidation was able to greatly reduce the levels of total solids (TS) and volatile total solids (VTS) present in wastewater sludges. For raw, primary sludge TS and VTS could be reduced by over 80% and those for activated sludge by 60% and 90% respectively.

For detergent wastewaters TS and VTS reductions varied from 80% to 99% although for the paracetamol wastewater, an apparent increase in inorganic solids was noted.

xi) In addition to increases in VFAs, ammonia was a major intermediate product, and to a lesser extent formaldehyde. Ammonia concentrations of up to 2.5 g/l were found, with 25 mg/l formaldehyde being measured on one occasion. For activated sludges, at constant temperature, pressure and retention time, the formation of SCOD, acetic acid, ammonia and formaldehyde was a function of the initial VTS although no explanation for the latter two parameters is offered. Based on the oxygen demand of the various organic compounds, little organic matter was present in the effluents other than VFAs and formaldehyde.

xii) A potential application of the residual solids after the Wet Oxidation of primary and activated sludge (treated at 280°C and above) would be its use as an activated carbon source since it was shown to have the capability of removing colour from a complex dye wastewater.

xiii) In the study using catalysts, carried out on the detergent wastewater, it was shown that no significant improvement in effluent quality of detergent liquor resulted which would in turn justify their use in this particular case.

Overall, it may be concluded that since all three operational parameters (temperature, pressure and retention time) may be varied with the consequence of different effluents on sludges and wastewaters, Wet Oxidation is a flexible but predictable treatment process. The decision as to whether oxygen or air should be used would depend upon the strength of the waste, the potential operating costs and the desired degree of treatment.

7.2 Biological Treatment of Liquors Produced by Wet Oxidation.

Both anaerobic and aerobic biological treatment processes were investigated to evaluate the bio-treatability of Wet Oxidation liquors and the following conclusions have been drawn:

7.2.1 Results from the upflow anaerobic filter (UFAF) used for treating the liquor produced from activated sludge treated at 280° C showed that:

i) removal of up to 63% COD could be attained, at 12 days HRT at an organic loading rate of 0.25 kg COD/m^3.day,

ii) removal of ammonia from the liquor and a long biomass acclimatisation period did not reduce the need for long HRTs for the degradation of organic matter in the Wet Oxidation derived liquors,

iii) although there was a high level of acetic acid in the Wet Oxidation liquor there appeared to be inhibition of methanogens throughout the whole of the UFAF operation, possibly due to the presence of toxic compound in the liquor.

7.2.2. An aerobic membrane activated sludge (MAS) process was run to evaluate the potential for aerobic biological processes to treat the same liquor as that used in 7.2.1 above. It was shown that:

i) Chemical Oxygen Demand, Biodegradable Chemical Oxygen Demand, ammonia nitrogen and formaldehyde removal averaged 66%, 86%, 59% and 100% respectively at an organic loading rate of 4-6 kg COD/m^3.day and an HRT of 12 hours.

ii) Ammonia removal was not the result of nitrification since no nitrite or nitrate were produced. It is probable therefore that ammonia was removed by a combination of air stripping and nutrient uptake by the heterotrophic bacteria.

iii) For a 5 day sludge age, the SVI varied from 50 to 80, implying good settleability. An average cell growth coefficient of 0.2 (kg VTS/kg COD removed) was also recorded.

7.2.3. The upflow anaerobic filter (UFAF) was also used to evaluate the anaerobic treatment of liquors produced by Wet Oxidation of detergents. The following can be concluded from this study:

i) Only 51% COD and 25% active detergent (AD) removal could be achieved from the LAS derived liquor and as little as 25% COD and 15% active detergent removal from the "cocktail of detergent" liquors. This was at an OLR of 2.4 kg COD/m^3.day and an HRT of 6 days.

ii) The anaerobic degradation of active detergent is contrary to previous study reports, suggesting that Wet Oxidation has some effect on the nature of the active detergent molecules or active detergent removal from the waste shown was by adsorption onto the biomass rather than biodegradation.

7.2.4. Due to the inefficient anaerobic treatment of Wet Oxidation liquors derived from detergents an attempt was made to use an aerobic, Sequencing Batch Reactor (SBR) system with the following conclusions:

i) Chemical Oxygen Demand, Biodegradable Chemical Oxygen Demand and active detergent removals of 70%, 80%, and 95% respectively could be achieved at an HRT of 8 hours.

ii) A cell growth coefficient of 0.4 kg VTS/kg COD removed was obtained.

iii) Good solids/ liquid separation was shown by an average sludge volume index (SVI) of 80.

7.2.5. For reasons explained in Chapter 5, the Jet Loop Reactor (JLR) was used to treat Wet Oxidation liquor derived from the paracetamol wastewater and at a loading rate of 10 kg COD/m^3.day. The following was concluded:

i) 50% COD was removed from the wastewater (which has a 50% inert COD).

ii) Foaming caused a very high effluent suspended solids concentration, normally greater than 280 mg/l but it is considered that the JLR could be used as a pre-treatment process followed by a chemical or physical process to improve the final effluent.

7.3 Summary

The overall conclusion from this study is that Wet Oxidation has been demonstrated to have considerable potential for the treatment of a wide range of sludges and different wastewaters and that the liquors resulting from the Wet Oxidation process are treatable to a certain extent by aerobic biological processes. However, in all cases, a pilot-scale study Would be necessary to evaluate the most cost-effective system.

7.4 Recommendations For Further Study

Based upon the conclusions of the study, the following ideas may be usefully considered for further investigation:

i) The strength of heat treatment liquor is markedly affected by the process parameters; temperature, pressure, retention and retention time. Evaluation of the liquors liquor produced during WO of detergent manufacture wastewater at various operating parameters with particular emphasis on identifying those toxic materials such as amino acids, heterocyclic nitrogenous compounds, peptides, benzocarbazole etc. which are produced during the process. A wider range of applied physical conditions could be used to judge the optimal conditions for the destruction or formation of specific end products. Improved chromatographic separation of these derivatives should be identified using HPLC and ICP. Toxicity studies should also be carried out to determine their actual ecological effects.

ii) Specific industries which have a potential application for WO should be identified and a two stage, pilot-scale WO and jet loop activated sludge reactor should be used to obtain data for a full scale treatment plant.

iii) An economic evaluation of the Wet Oxidation of high solids sludges should be carried out and a comparison made of this with incineration on identical sludges.

REFERENCES

AKSE H. N., SEDEN M. M. G., TELS M., HAZEWINCKEL J.H.O. (1987) Detoxification and Energy Recovery by Wet Air Oxidation on Waste Streams, Resources and Conservation, 14,351-364.

ALLEN D. C. and IKALAINAN P. E. (1988) Selection and Evaluation of Treatment Technologies for the New Bedford Harbour Super Fund Project, In Superfund 88 Proc. 9th Nat. Conf. Washington DC., 329 - 337.

ALSOP G M and CONWAY R A (1982) Improved Thermal Sludge Conditioning by Treatment with Acids and Bases, Journal Wat. Poll. Control Fed., 54 , 2, 146-152.

ANDERSON G. K. (1993 - 1995) Personal communication

ANON. (1984) Fire On the Water, Water Service, 88, 1059, 172 -173.

ANTONI G. F. (1978) The Operation of the Zimpro Thermal conditioning with Air Sludge Plant at Kwa Dabeka (Clermont) Sewage works, Wat. Poll. control, 77, 75 - 78

APHA (1989) Standards Methods For the Examination of Water, Sewage and Industrial Waste., 17th Edition, Washington D. C.,.

BAILLOD C. R. , LAMPART R. A. and LEDDY D. G. (1979) Wet Oxidation of Toxic Organic Substances, Proc. 34th Purdue Ind. Waste Conf., Ann Arbor Science, Mich., 206 - 213.

BAILLOD C. R., FAITH B. M., and MASI O. (1982) Fate of Specific Pollutants During Wet Oxidation and Ozonation, Envi. Prog. 1, 3, 217 - 227.

BAILLOD C. R., LAMPARTER R. A. BARNA B. A. (1985) Wet Oxidation for Industrial Waste Treatment, Chem. Eng. Prog., 3, 52 - 56.

BARRION J. M. (1989) An Introduction to Waste Management, IWEM Booklet 1.

BASKERVILLE R. C. and GALE R. S. (1968) A Simple Automatic Instrument for Determining the Filterability of Sewage Sludge, Wat. Poll. Control, 67, 2, 233 - 241.

BBC2 OU Programme (1994) Renewable Energy.

BERNARD J. (1977) Heat Conditioning of Sludge - A Technique for Tomorrow, Prog. Wat. Tech., 8, 6, 379 - 387.

BERRIDGE H. B. and BRENDISH K. R. (1967) The Use of Plastic Filter Medium in the Treatment of Sludge Liquors, Wat. Poll. Control, 66, 597.

BEST R. (1980) Want Not, Waste Not! Sensible Sludge Recycling, Wat. Poll. Control, 79, 307 - 321.

BLOOR J. C. (1995) The Application of Jet Loop Reactors fro Industrial Wastewater Treatment, PhD Thesis, Dept. of Civil Eng., University of Newcastle Upon Tyne.

BLOOR J. C., ANDERSON G. K. and WILLEY A. R. (1995) High Rate Aerobic Treatment of Brewary Wastewater Using the Jet Loop Reactor, Wat. Res., 29, 5, 1217 - 1223.

BOON A. G., THOMAS U. K. and ANDERSON L. J. (1995) Department of New Process Technologies and System, Wastewater Treatment Technology Looking to 21lst Century Proceedings of a CIWEM Seminar held in Hong Kong.

BOYLE J. D. and GRUENWALD D. D. (1975) Recycle of Liquor from Heat Treatment of Sludge, Journal Wat. Poll. Control Fed., 47, 2482 -2489 ..

BRETT R. W. J. and GURNHAN F. (1973) Wet Air Oxidation of Glucose with Hydrogen Peroxide and Metal Salts, Journal Applied Chem. Biotech., 23, 239 - 250 ..

BROOKS R. B. (1968) Heat Treatment of Activated Sludge, Water Poll. Control, 67, 6, 592 - 601.

BROOKS R. B. (1970) Heat Treatment of Sludges, Water Poll. Control, 69, 2, 221 - 231.

BROOKS R. B. (1970) Heat Treatment of Sludges, Water Poll. Control, 69, 1, 92 -99.

BROWN V. M. ET AL., (1978) The Accute Lethal Toxicity to Rainbow Trout of an LAS Surfactant and of its Residues and Degradation Products, Tenside Detergents, vol. 15, pp. 57 - 9.

BRUCE A.M., PIKE E. B AND FISHER W. J. (1990) A Review of Treatment Process Options to Meet the EC Sludge Directive, Journal IWEM, 4, 1, 1 - 13.

BUNING W. G. W. (1992) New Techniques of Sludge Management in The Netherlands, European Wat. Poll. Control, 2, 2, 39 - 45.

BUTCHER C. (1994) Supercritical Water Oxidation Destroys Sewage Sludge, Chemical Tech. Europe., 1, 3, 10.

CAIN R. B. (1981) Microbial Degradation of Surfactants and 'Builder' Components, Microbial Degradation of Xenobiotics and Recalcitrant Compounds, 325 - 366.

CALCUTT T. and FROST R. (1987) Sludge Processing - Choices for Tomorrow, Water Poll. Control, 86, 2, 235 - 249.

CALCUTT T. and MOSS J. (1984) Sewage Sludge Treatment and Disposal - the Way Ahead, Water Poll. Control, 83, 162 - 171.

CANNEY P. J. and SCHAEFER P. T. (1983) Wet Oxidation of Toxins; A New Application of Existing Technology, Proc. 15th Mid-Atlantic Industrial Conference.

CANNEY P. J., MORDORSKI C. J., ROLLINS R. M. and BERNDT C. L. (1984) PACT Wastewater Treatment for Toxic Waste cleanup, Proc. 39th Purdue Ind. Waste Conf., Ann Arbor Science, Ann Arbor, Mich., 413 - 430.

CHAREST F. and CHORNET E. (1976) Wet Oxidation of Active Carbon, Can. Journal Chem. Eng., 54, 190 - 196.

CHERMISINOFF, P.N (1987) Hazardous Waste and Sludge Treatment, Poll. Eng., 19, 12, 40.

CHOU C. L. and VERHOFF F. H (1981) Process for Power Generation from Wet Air Oxidation with Application to Coal Gasification Waste Waters, Ind. Eng. chem. Process Des. Dev., 20, 12 - 19.

CHOWDHURY A. K. (1974) Catalytic Wet Oxidation of Strong Waste Waters, PhD Thesis, University of Denver, USA.

CLIFFORD D., CHU. P and LAU A. (1983) Thermal Regeneration of Powdered Activated Carbon (PAC) and PAC Biological Sludge Mixtures, Wat. Res., 17, 9, 1125 - 1138

CRAWFORD G. V., ALKEMA T. YUE M. and THORNE M. (1982) Anaerobic Treatment of Thermal Conditioning Liquors, Journal. Wat Poll. Control Fed., 54, 1458 - 1464

CUTFORTH S. J. (1991) A Feasibility Study on the Treatment of Effluent from Wet Air Oxidation of Sewage Sludge, MSc Thesis, Dept. of Civil Eng., University of Newcastle Upon Tyne.

CUTFORTH S. J. (1995) A Feasibility Study on the Treatment of Effluent from Wet Air Oxidation of Sewage Sludge, Journal of the CIWEM.

DAGUE R. R., BRINDLEY D. R. and LIANG P. S. (1980) Anaerobic Filter Treatment of Recycle From Thermal Sludge Conditioning and Dewatering, 53rd Annual conference of Wat. Poll. Contr. Federation, Las Vegas, Nevada.

DAVIS R. D. (1989) Agricultural Utilisation of Sewage Sludge; A Review, J. IWEM, 3, 351-355.

DAY D. L., HUDGINS R. R. and SILVESTON P. L. (1973) Oxidation of Propionic Acid Solutions, Can. Journal of Chem. Eng., 51, 733 -740

DeBEKKER P. H. A. M. J and SCHWOYER, W. L. K. (1989) Treatment of Sewage Sludge VerTech Treatment Systems Catalogue.

DeBEKKER P. H. A. M. J and van den BERG, J. J. (1989) Wet Oxidation as the Alternative for Sewage Sludge Treatment, in Dirkzwager A. H. and L'Hermite P. (ed.), Sewage Sludge Treatment and Use, Elsivier Applied Science.

DeBEKKER P. H. A. M. J. (1990) Environmental Aspects of Liquid Phase Oxidation of Sewage Sludge, Proceedings of the EC Symposium: Treatment and Use of Sewage Sludge and Liquid Agricultural Wastes., Elsevier Applied Science, 370-380.

DEENY K. J., HEIDMAN J. A. and CONDREN A. J. (1989) An Assessment of Activated Sludge Systems Practising Powdered Activated Carbon Addition With Wet Air Regeneration, Water Sci. Tech., 21, 1707 -1710

DIETRICH M. J., RANDALL F. L. and CANNEY P. J. (1985) Wet Air Oxidation of Hazardous Organics in Wastewater, Env. Prog., 4, 3, 171 -177.

DING J., SNOEYINK V. L., LARSON R. A., RECKTENWALT M. A. and WEDEKING C. A. (1987) Effects of Temperature, Time and Biomass on Wet Air Regeneration of Carbon, Journal Wat. Poll. Control Fed., 59, 139.

DOVER P. (1991) Industrial Waste Minimisation: A Case Study, Institure of Wastes Management, North East Centre Meeting, Gateshead08/March/1991.

ELLIS C. E. and CANNEY P (1987)Wet Air Oxidation as the Solution, Waste Age, 18, 10, 106 -108.

ELLITE D. J. (1993) Personal communication

ERICKSON A. H and KNAPP P. V. (1972) Biological Treatment of Thermally Conditioned Sludge Liquors, In Advances in Water Pollution Research, Pergamon Press New York.

EVERETT J. G. (1971) The Liquor Arising from Heat Treatment of Sewage Sludge, PhD Thesis, Dept. of Mech. Eng., University of Wales.

EVERETT J. G. (1972) Dewatering of Wastewater Sludge by Heat Treatment, Journal Wat. Poll. Control Fed., 44, 92 - 100.

EVERETT J. G. (1974) The Effects if pH on the Thermal Treatment of Sewage Sludges, Wat. Res., 8, 899 - 906.

EVISON L. M (1993) Personal communication.

EYANOER H. F. ET AL., (1985) Effects of Water Hardness and Temperature on the toxicity of Detergents to the Fresh Water Fish, J. Sci. Soc. Thailand, vol. 11, pp. 67 - 77.

FLYNN B. L. (1976) Wet Air Oxidation for Black Liquor Recovery, Chem. Eng. Prog., 72, 5, 66 - 68.

FOUSSARD J. N., DEBELLEFONTAINE H. and BESOMBES-VAILHE J. (1989) Efficient Elimination of Organic Liquid Wastes; Wet Air Oxidation, Journal Env. Eng. ASCE, 115, 2, 367 - 385.

FRANCK E. U. (1973) Properties of Water, in High Temperature High Pressure Electrochemistry in Aqueous, National Association of Corrosion Engineers, 4, 109-116.

FRIEDMAN A. A ET AL., (1987) 64 Characteristics of Residues From Thermally Treated Anaerobic Sludges, Proc. 42nd Industrial Waste Conf. Purdue University, 629 - 647.

FRIEDMAN A. A. and SMITH, J. E. (1987) Methane from Partially Digested Sewage Sludge, NYSERDA Report No 86 - 12, Albany, N.Y.

FRIEDMAN A. A., SMITH J. E., DeSANTIS J., PTAK T. and GANLEY R.C (1988) Characteristics of Residues from Wet Air Oxidation of Anaerobic Sludges, Journal Wat. Poll. Control Fed., 60, 1971 - 1978.

FRISCH M. A. and GLOYNA E. F. (1992) Supercritical Water Oxidation of Acetic Acid Catalysed by CeO_2/MnO_2, Technical Report No. CRWR - 237.

FYFE N. R. (1992) An Investigation into the Effects of the WAO Treatment Process on the Organic and Inorganic Pollutants of Sewage Sludge, MSc Thesis, Dept. of Fossil Fuel (NRG), University of Newcastle Upon Tyne.

GANONG W. F. (1995) Review of Medical Physiology, 17th Ed., Norwalk, Conn: Appletion and Lange; London: Prentice-Hall International.

GARBUTT J. H. (1995) Environmental Law: A Practical Handbook, 2nd Ed. London: Wiley Chancery.

GERMIRLI D., ORHAN D. and ARTAN N. (1991) Assessment of The Initial Inert Soluble COD in Industrial Wastewater, Water Science and Technology, 23, Kyoto, 2, 1077 -1086

GLOYNA E. F. (1989) Supercritical Water Oxidation-Deep Well Technology for Toxic Wastewater and Sludges, Internal Research Document, The University of Texas at Austin, USA.

GRAY N. F. (1989) Biology of Wastewater Treatment, Oxford University Press New York.

GRIFFITH B. S. and GLOYNA E. F. (1994) Destruction of Toxic Organic Materials by Supercritical Water Oxidation, Technical Report No. CRWR - 251.

HALL J. E. (1995) Journal CIWEM, 9, 335 - 343

HANAHAN D. J et al. (1960) Lipid Chemistry, John Wiley and Sons, New York.

HAO O. J., PHULL K. K and DAVIS A. P (1992) Preliminary Results of WAO of TNT Red Water, Procs 24th Mid-Atlantic Industrial Waste Conference West Virginia University Morgantown, 110 - 119.

HAUG R. T. (1977) Sludge Processing to Optimise Digestibility and Energy Production, Journal Wat. Poll. Control Fed., 49, 1713 -1721.

HAUG R. T., STUCKEY D. C., GOSSET J. M. and McCARTY P. L. (1978) Effect of Thermal Pre-Treatment on Digestibility of Organic Sludges, Journal Wat. Poll. Control Fed., 50, 1, 73 -85.

HEINBUCH J. A. and WILHELMI A. R. (1985) Wet Air Oxidation -A Treatment Means for Aqueous Hazardous Waste Streams, Journal Hazardous Materials, 12, 2, 187 - 200.

HELLING R. K. and JEFFERSON W. T. (1988) Oxidation of Simple Compounds and Mixtures in Supercritical Water; Carbon Monoxide, Ammonia and Ethanol, Env. Science Tech., 22, 1319 - 1324.

HEYDA M. B., EDWARDS J. D. and NOLAND R. F. (1980) Chemical and Biological Treatment of Thermal Conditioned Sludge Recycle Liquors, USEPA report 600/2 -80 -020.

HICKEY R. F., VENOERWIELEN J. and SWITZENBAUM M. S. (1989) The Effect of Heavy Metal on Methane Production and Carbon Monoxide Level During Batch Anaerobic Sludge Digestion, Wat. Res., 23, 2, 207 - 218.

HIRST G., MULHALL K. G. and HEMMING M. L. (1971) The Sludge Heat Treatment Plant at Pudsey, Paper Presented to I.W.P.C. Northern Eastern Branch.

HOLBROOK S. A. (1995) Personal communication., Environmental Engineering, Unilever Research Port Sunlight Laboratory, Quarry Road East Bebington Wirral L63 3JW.

HOROBIN W. (1994) Wet Air Oxidation Cracks a Caustic Problem, Water Quality International, 3, 6.

HURWITZ E. and DUNDAS, W. A. (1959) Ultimate Disposal of Sewage Sludge by Wet Oxidation, Proc. 14th Purdue Ind. Conf., Ann Arbor Science, Mich., 211 - 226.

HURWITZ E. and DUNDAS, W. A. (1960) Wet Oxidation of Sewage Sludge, Journal Wat. Poll. Control Fed., 32, 918 - 929.

IKEDA K. R. (1977) Experimental Study on Treatment of Night Soil by the Wet Air Oxidation Process, Wat. Res, 6, 967 - 979.

IMAMURA S., FUKADA I., ISHIDA S. (1988) Wet Oxidation Catalyzed by Ruthenium Supported on Cerium (IV) Oxide, Ind. Engr. Chem. Res., 27, 4, 718.

IMAMURA S., KAWABATA N., NAKAMURA M., YOUSHIDA J. (1986) Wet Oxidation of Poly (ethylene glycol) Cataltzed by Manganese-Cerium Composite Oxide, Ind. Engr. Chem. Prod. Res. Dev., 25, 1, 34.

IRVINE R. L. and KETCHUM JR. L. H. (1989) Sequencing Batch Reactors for Biological Wastewater Treatment, CRC Critical Reviews in Environmental Control, 18, 4 255 - 294.

J. C. and YANG B. S. (1989) Design Considerations for Full-Scale Anaerobic Filters, Journal Wat. Poll. Control Fed., 61, 9, 1576 - 1587.

JENKINS D., RICHARD M. G., DAIGGER G. T (1986) Manual on Caused and Control of Activated Sludge Bulking and Foaming, Water Research Commission, Pretoria, EPA, Cincinnati, USA.

JOGLEKAR H. S., SAMANT S. D. and JOSHI J. B. (1991) Kinetics of Wet Air Oxidation of Phenol and Substituted phenols, Water Research, 25, 2, 135 - 145.

KALMAN J., IZSAKJI Z., KOVACS L., GROPCSIK A and SZEBENYI I. (1989) WAO of Toxic Industrial Effluents, Wat. Sci. Tech., 21, 289 - 295.

KELLEY R. M. (1971) Detergents: in Snell, F. D. and Ettre, L. S. (eds.), Encyclopaedia of Industrial Chemical Analysis, New York, Interscience Publishers, Vol. 11.

Khan Y. (1992) Wet Air Oxidation of Phenol and Landfill Leachate, MSc Thesis, Dept. of Civil Eng., University of Newcastle Upon Tyne.

KLAY H. R (1988) Components for Wet Oxidation Plants, Sulzer Tech. Review, 70, 4, 41 - 43.

KNOPP P. V, UHREN L. J., ROHLICH G. A., and NICHOLS M. S. (1965) Field Study of the Removal of Linear Alkylate Sulfonate Detergent by the Activated Sludge Process, Journal Am. Oil Chem. Soc., 42, 867 - 873.

KOSOWITZ J. J. (1988) Increased Sludge Volume Precedes Program Management Complexities, Eng. News-Rec., 221, 12, 28.

KULANDAI J., HASHIM M. A. and HASSAN R. S. (1984) Treatability Study of a Detergent Wastewater, Symposium on Progress in Microbial Biotechnology, University Sains Malaysia, Penang.

LARSON R. A., JU H. L., SNOEYINK V. L., RECKTENWALT M. A. and DOWD P. A. (1988) Some Intermediates in the Wet Oxidation of Pnenanthrene Adsorbed on Powdered Activated Carbon, Wat. Res., 22, 3, 337 - 342.

LAUGHLIN R. G. W., GALLOT. AND ROBEY H.(1983) Wet Air Oxidation for Hazardous Waste Control, Journal Hazardous Material, 8, 1 - 9.

LeBRUN J. P and TORTORICI L. D (1984) Thermal Treatment of Municipal Sewage Sludges, USEPA report 66/2 - 84 - 104.

LEGLISE J. P. (1981) Heat Conditioning of Sewage Sludge, Wat. Poll. Control, 2, 163 - 171.

LITTLE M. and WILLIAMS P. A. (1978), European Journal of Biochem.

LONGMONT, (1987) Aqueous-Phase Oxidation of Sludge Using the Vertical Reaction Vessel System, USEPA report 600/2-87/022.

LUDUVICE M. (1992) Wet Air Oxidation of Organic Sludges at Low Oxygen Overpressure, PhD Thesis, Dept. of Civil Eng., University of Newcastle Upon Tyne.

LUDZACK F. J. and ETTINGER M. B. (1960) Chemical Structures Resistant to Aerobic Biochemical Stabilisation, Journal Wat. Poll. Contr. Fed., 1173 - 1200.

LUMB C. and BARNES J. P. (1944) The Disposal of Liquor Resulting from the Heat Treatment of Sludge, Journal Inst. Sew. Purif., 77.

McCARTHY J. J. (1982) Technology Assessment of the Vertical Well Chemical Reactor, USEPA report 600/52-82-005.

McELDOWNEY S., ET AL. (1993) Pollution: Ecology and Biotreatment, Harlow, Essex, Eng: Longman Scientific and Technical, 1933.

McGREW J. L. et al., (1986) Wet Oxidation of Municipal Sludge by the Vertical Tube Reactor, USEPA report 600/52-86/043.

METCALF and EDDY, Inc. (1994) Wastewater Engineering: Treatment, Disposal, Reuse, 3rd Edition, McGraw-Hill New York.

MILLER R. A., JONHSON J. D., HELSEL R.W. and PITTS D. M. (1980) Destruction of Toxic Chemicals by Catalysed Wet Oxidation, Proc. 35th, Purdue Ind Waste Conf., Ann Arbor Science, Mich., 425 - 429.

MISHRA V. P. and JOSHI J. B. (1987) Kinetics of Reaction of Cyanide Ion at High Temperature, Indian Journal Tech., 25, 5, 235 - 238.

MYERS D. (1988) Surfactant Science and Technology, New York, VCH Publishers Inc.

NICHOLS M. and KOEPP E. (1961) Synthetic Detergents as a Criterion of Wisconsin Ground Water Pollution, Journal Am. Wat. Wks., 53, 303 - 306.

NOONE G. P. (1994, 1995) Personal Communication.

OLES J. and WILDERER P. A. (1991) Computer Aided Design of Sequencing Batch Reactors Based on the IAWPRC Activated Sludge Model, Wat. Sci. Tech. 23, Kyoto, 1087 - 1095.

OSBURN Q. W. (1982) Analytical Method for a Cationic Fabric Softener in Waters and Wastes, Journal Am. Oil Chem. Soc., 59, 10, 453 - 457.

OSBURN Q. W. (1986) Analytical Methodology for Linear Alkylbenzene Sulphonate (LAS) in Waters and Wastes, Journal Am. Oil Chem. Soc., 63, 2, 257 - 263.

PANDIA S. (1990) The Effects of Detergents in Wastewater on Foaming at Activated Sludge Plants and on Receiving Water Quality, PhD Thesis, Department of Civil Engineering The University of Leeds England.

PINNEKAMP J. (1989) Effects of Thermal Pre-treatment of Sewage Sludge on Anaerobic Digestion, Wat. Sci. Tech., 21, 97 - 108.

PLOOS Van AMSTEL J. J. A and RIETMA K. (1973) Wet Air Oxidation of Sewage Sludge, Chem. Ing. Tech., 45, 20, 1205 - 1211.

PRADT L. A (1972) Developments in Wet Air Oxidation., Chem. Eng. Prog., 68, 12, 72 - 77.

PRUDEN B. B. and LEE H. (1976) Wet Air Oxidation of Soluble Components in Wastewater, Can. Journal Chem., Eng., 54, 319 - 325.

PUCHTA R. (1984) Cationic Surfactants in Laundry Detergent and Laundry after Treatment Aids, Journal Am. Oil Chem. Soc., 61, 2, 367 - 376.

PUNCHIRAMAN C. and HASSAN R. S. (1986) Anaerobic Biodegradation of a Recalcitrant Detergent Wastewater, Effluent and Water Treatment Journal, 26, 85 - 88.

RANDAL T. L. (1981) Wet Oxidation of Toxic and Hazardous Compounds, 13th Mid Atlantic Industrial Waste Conference, 13, 501 - 508.

RANDAL T. L. (1983) Wet Oxidation of PACT Process Carbon Loaded with Toxic Compounds, Proc. 38th Purdue Ind. Conf., Ann Arbor Science, Ann Arbor, Mich., 323 - 338.

RANDAL T. L. and KNOPP P. V. (1980) Detoxification of Specific Organic Substances by Wet Oxidation, Journal Wat. Poll. Control Fed., 52, 2117 - 2130.

RENN C. E., KLINE W. A., and ORGEL G. (1964) Destruction of Linear Alkylate Sulfonates in Biological Waste Treatment by Field Test, Journal of Wat. Poll. Control Fed., 36, 7, 864 - 879.

ROSEN M. J. (1989) Surfactants and Interfacial Phenomena, New York, 2nd Edition, John Wiley and Sons.

SALOTTO B. V. (1981) Pilot-Scale Anaerobic Filter Treatment of Heat Treatment Liquor (EPA-600/2-81-114).

SAWYER C. L. and McCARTY P. L. (1978) Chemistry for Environmental Engineers, 3rd Edition, MacGraw - Hill.

SCHATZBERG P., JACKSON D. F. and KELLY C. M. (1974) Inter-socity Conference on Environmental Systems, Seattle, Wash., ASME Paper No. 74-ENAs-5.

SHAM C. S. Y (1993) Investigation of Oxygen Transfer Performance in High-Rate Compact Reactors, MSc Thesis, Dept. of Civil Eng., University of Newcastle Upon Tyne.

SHANABLEH A. M. and GLOYNA E. F (1992) Subcritical and Supercritical Water Oxidation of Industrial, Excess Activated Sludge, Technical Report No. 211.

SKAATES J. M., BRIGGS B. A., LAMPARTER R. A. and BAILLOD C. R. (1981) Wet Oxidation of Glucose, Can. Journal Chem. Eng., 59, 517 - 521.

SMITH J. M and RAPTIS T. J. (1986) Supercritical Deep Well Wet Oxidation of Liquid Organic Wastes, Paper Presented at the International Symposium on Subsurface Injection of Liquid Wastes.

SOMMERS L. E. and CURTIS E. H. (1976) Effect of WAO on the Chemical Composition of Sewage Sludges, Purdue University Water Resources Research Centre, Tech. Report 78, Purdue University Indiana.

SPEECE R. E. (1994) Personal communication.

SPEECE R. E. and PARKIN G. F. (1983) The Response of Methane Bacteria to Toxicity, Proc. 3rd International Sym. on Anaerobic Digestion, Bost. Mass.

SRINIVASAN G. (1984) Industrial Surfactants - Current and Future Trends, Chem. Age of India, 35, 4, 239 - 248.

STEPANYN I. S., VINOKOUI S. A. and PADARYAN G. M (1972) WAO of Methanol and Formaldehyde, Khim. Prom (Moscow), 48, 430 - 440.

STUCKEY D. C . and McCARTY P. L. (1984) The Effect of Thermal Pre-treatment on the Anaerobic Biodegradability and Toxicity of Waste Activated Sludge, Water Res., 18, 1343 - 1353.

SULLIVAN D. E. (1883) Biodegradation of a Cationic Surfactant in Activated Sludge, Water Res., 17, 9, 1145 - 1151.

SVENSSON P. (1995) Look, No Stack: Supercritical Water Destroys Organic Wastes, Chemical Technology 2, No. 1, January/February.

SWANWICK F. D. and SHURBEN D. G. (1969) Effective Chemical Treatment for Inhibition of Anaerobic Sewage Sludge Digestion due to Anionic Detergents, Water Pollution Control, 68, 190 - 201.

SWISHER R. D. (1963) Biodegradation of ABS in Relation to Chemical Structure, Journal Wat. Poll. Control Fed., 35, 7, 877 - 891.

TAKAMATSU T., HASSHIMJOTO I., and SIOYA S. (1970) Model Identification of WAO Process Thermal Decomposition, Wat. Res., 4, 1, 33 - 59.

TAYLOR B. F., CAMPBELL W. L. and CHINOY I. (1970) Journal Bacteriol.

TAYLOR J. E. and WEYGANDT J. C. (1974) A Kinetic Study of High Pressure Aqueous Oxidation of Organic Compounds Using Elemental Oxygen, Can. Journal Chem., 52, 1925 - 1933.

TELETZKE G. H (1964) Wet Air Oxidation, Chem. Eng. Progress, 60, 1, 33 - 38.

TELETZKE G. H, GITCHEL W. B., DIDDAMS D. G. and HOFFMAN C. A. (1967) Components of Sewage and its Wet Air Oxidation Products, Journal Wat. Poll. Control Fed., 39, 994 - 1005.

TOLBA M. K. (1982) Development Without Destruction: Evolving Environmental Perceptions, Tycooly International, Dublin.

TOLBA M. K. (1992) Saving Our Planet Challenges and Hopes, Chapman and Hall, London.

TORPY M. F. (1988) Anaerobic Digestion, In Standard Handbook of Hazardous Waste Treatment and Disposal, Ed Freeman H. M. McGraw-Hill.

VOGEL A. I. (1958) Elementary Practical Organic Chemistry, Longmans' Green and Co. Ltd.

VOLLSTEDT T. J. (1978) Treatment of Thermally Conditioned Sludge Supernatant with an Anaerobic Packed Bed Reactor, Zimpro, Inc. Technical Bulletin 2303-T, Zimpro Enviro. Control System Rothschild, Wis.

WIGSTON P. (1994) Wet Air Oxidation for Thermally Sludge Conditioning, Proceeding of the One Day Seminar at Manchester.

WILHELMI A. R. and KNOPP P. V. (1979) Wet Air Oxidation - An Alternative to Incineration, Chem. Eng. Prog., 46, 8, 46 - 52.

WU Y. C., HAO D. J., OLMSTEAD D. G. HSIEH K. P. and SCHOLZE R. J. (1987) Wet Air Oxidation of Anaerobically Digested Sludge, Journal Wat. Poll. Control Fed., 59, 39 - 46.

YOUNG J. C and YANG B. S. (1989) Design Considerations for Full-Scale Anaerobic Filters, J. Wat. Poll. Cont. Fed., 61 (9), 1576 - 1587.

YOUNG J. C. (1991) Factors Affecting the Design and Performance of UFAF, Wat. Science and Tech., 24, 8, 133 - 155.

YOUNG J. C. and DAHAB M.F. (1983) Effect of Media Design on the Performance of Fixed-Bed Anaerobic reactors, Wat. Science and Technology, 15, 369 - 383.

ZIMMERMANN F. J. (1958) Sewage Sludge Treatment by Wet Air Oxidation, Proc. 13th, Purdue Ind. Waste Conf., Ann Arbor Science, Mich., 409 - 417

ZIMPRO EVVI. INC. ROTHSCHILD, WIS. (1993) Wet Air Oxidation Cleans Up Black Wastewater, Chemical Engineering, 100, 9, 175 - 176.

APPENDIX-A

Table 1A Analytical Methods and Instrumentation

Parameter	Method	Instrument/Reference
Influent rate (UFAF)	Feed & Recycling pumps setting	Peristaltic Watson Marlow (302S)
Gas : Production Composition (UFAF)	Water displacement Gas chromatography	Graduated bottle Pye Unicam 304 (CH_4, CO_2, Air)
Capillary Suction Time (Wet Oxidation)	CST apparatus	Triton-W.P.R.L Type 92/1
Sulphate (JLR)	Gravimetric method	Standard Methods (1985)
Detergent (WO)	Precipitation and titration	
Solids SS/VSS/TS/VTS (WO, JLR, UFAF, CAS, SBR)	Gravimetric	Standard Methods (1985)
Temperature : WO UFAF	Probe/Indicator automatic Heater controller	PYZ4 Controller/PDS-401 FH15/Grant
TKN	Distillation and titration	Standard Methods (1985)
NH_3-N	Distillation and titration	Standard Methods (1985)
PO_4-P	Ascorbic acid	Standard Methods (1985)
Volatile Fatty Acids	Gas-liquid chromatography	Becker 403 with Pye Unicam autojector and integrator
Formaldehyde	titration	Vogel (1958)
pH	pH meter	Kent EIL 9143
Alkalinity	Titration	Standard Methods (1985)

1.1 A Analytical Detemination of Anionic and Cationic Detergent

Ionic surfactants are sub-diveded into two categories, differentiated by the charge. An anionic surfactant ion is negatively charged and a cationic is positively charged.

Reagents

i) Deionised water, ii) Sodium Lauryl Sulphate, iii) Sodium Lauryl Sulphate Solution (SLS) 0.004 m, iv) Hyamine 1622 Solution 0.004 m, v) Mixed Indicator Stock Solution (Dimidium Bromide/Disulphide Blue), vi) 0.5 m and 2.5 m Sulphuric Acid, vii) Chloroform, viii) Phenolophatalein Indicator, ix) N Sodiun Hydroxide Solution

Apparatus

i) 25 cm^3 Burette Grade "A"
ii) 100 ml Glass Stoppered Conical Flask
iii) Dispenser for both Chloroform and the Mixed Acidicator
iv) Pipettes

Procedure

1) Pipette 25 ml sample into the glass stoppered conical flask.
2) Dispense 25 ml of mixed acid indicator into the flask. A green colour should be observed.
3) Dispense 15 ml of chloroform into the flask.
4) Invert the stoppered sample several times.
5) For anionic surfactant, titrate with the Hyamine solution and for cationic surfactant, titrate with the sodium lauryl sulphonate solution, initially in 1 ml increments. After each addition stopper the bottle,

rapidly invert for 30 seconds and permit the layers to separate. Continue the titration dropwise until the end point is reached, i.e. when the pink colour is completely discharged (Anionic) and when the blue colour is completely discharged from the chloroform layer.

6) Titration Colour Changes:

I. Anionic Surfactant

a. On addition of the mixed acid indicator	- green
b. After addition of chloroform	- pink
c. End-point (AD is complexed)	- grey
d. Overshot (excess Hyamine)	- blue

II. Cationic Surfactant

a. On addition of the mixed acid indicator	- green
b. After addition of chloroform	- blue
c. End-point (CAT is complexed)	- grey
d. Overshot (excess SLS)	- pink

7) Note the volume of titrant at the end point and record it to at least the nearest 0.05 ml.

1.1.1A CALCULATION

The sample results can be calculated from the following expressions.

a) Standardisation

i) For anionic) Molarity of Hyamine 1622 Solution = Molarity SLS × 10 mls/titre

ii) for cationic) Molarity of SLS Solution = Molarity Hyamine × 10 mls/titre

b) For Samples

mg/l AD = titre 1 × (M.wt) × 1000/V

M.wt = molecular weight of the sample

M = molarity of Hyamine 1622 solution for anionic and Molarity of SLS solution for cationic detergent

titre 1 = titre obtained from sample titration with hyamine

Volume of sample used

Table 2A Composition of dye waste

Dye/(Brightener)	Trade name	Supplier
Basic yellow 28 (Methine dye stuff)	Astrazon golden yellow GL	Bayer
Basic yellow 21 (Methine dye stuff)	Astrazon yellow 7GLL	Bayer
C.I. Basic violet 16 (Methine dye stuff)	Astrazon red violet 3RN	Bayer
Basic red 18:1 (Azo dye stuff)	Astrazon red GTLN	Bayer
Basic blue 147 (Methine dye stuff)	Astrazon blue F2RL	Bayer
Basic blue 41 (Azo dye stuff)	Basacyl blue X3GL	BASF
Basic red 46 (Azo dye stuff)	Maxilon red GRL	Ciba-Geigy
Optic brightener	Optic blanc DRS	Bayer
Optic brightener	Hastalux SNRX	--

1.2 A Formulae used in Sections 5.1 - 5.4

$$\%TCOD_d = \frac{(TCOD)_i - (TCOD)_f}{(TCOD)_i} \times 100 \qquad (1.2.1)$$

$$\%AD_d = \frac{(AD)_i - (AD)_f}{(AD)_i} \times 100 \qquad (1.2.2)$$

$$\%SCOD_g = \frac{(SCOD)_f - (SCOD)_i}{(SCOD)_i} \times 100 \qquad (1.2.3)$$

$$\%\,TS_d = \frac{TS_i - TS_f}{TS_i} \times 100 \qquad (1.2.4)$$

$$\%\,VTS_d = \frac{VTS_i - VTS_f}{VTS_i} \times 100 \qquad (1.2.5)$$

Where the subscripts d, i, f denote destruction, initial and final values of variable under consideration.

1.3A Example:

Determine how much oxygen will be inside the WO reactor at the following data.
Pressure in excess of vapour pressure = 20 Bars (290psi or 19.72atm or 2MPa)
Volume of the WAO reactor = 3.78 litre
Volume of sample= 2 litre
Temperature = 300°C
Solution: Using gas law Pv = nRT
Putting the value in the above equation
19.72*(3.78-2) = n * 0.082 (300+273)
n = 0.7473
Mass of oxygen = n * 32
=24 grams of oxygen will be inside the reactor.

1.4 A MICRO NUTRIENTS

1.4.1 A: Trace metal solution A

$MgSO_4 7H_2O$ 5.0 (g/l)

1.4.2 A: Trace metal solution B

Chemical	Concentration
$FeCl_3$	5.0 (g/l)
$CaCl_2$	5.0 (g/l)
KCl	5.0 (g/l)
$CoCl_2$	1.0 (g/l)
$NiCl_2$	1.0 (g/l)

Trace metal solutions were added in according to 1 ml/8000 mg/l feed COD.

APPENDIX-B

Results of Chapter 5 Section 5.1 - 5.5

Raw Primary Sludge Data

Table B1: Raw Primary Sludge at 200°C

RUN	1A	1B	1C	2A	2B	2C
% TSi	2.2	2.2	2.2	2.2	2.2	2.2
%VTSi	78	78	78	78	78	78
%TS dest	20	23.2	25	26.2	38.2	31.7
%VTS dest	35	30.3	35.5	59.1	62.8	63.9
%TCODdest	20	21.3	41.2	31.5	35.2	30.7
%SCOD gen	157.2	149.2	153.8	132	130.5	141
VFA	7383	6220	5290	4820	2210	5210
%acetic acid	36	25	31	25.8	32.1	33.2
RT(min)	30	30	30	30	30	30
Pressure (MPa)	2	2	2	4	4	4
Settled Volume (ml/l)	114	128	230	122	160	114
Colour oH	1800	1820	1890	1690	1710	1550
CST (sec)	41.5	40.2	42.1	41.2	38.7	37.5
Temp. C	200	200	200	200	200	200
SOR	1	1	1	2	2	2
pH	5.2	5.3	5.4	4.9	4.2	4.7

Table B2: Raw Primary Sludge at 280°C

RUN	1A	1B	1C	2A	2B	2C	3A	3B	4A	4B
% TSi	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2
%VTSi	78	78	78	78	78	78	78	78	78	78
%TS dest	68	62.9	65.7	63.1	64.1	62.9	65	67.2	_	_
%VTS dest	75.1	70.2	73.7	71.3	74.2	68.5	74.3	70.1	_	_
%TCODdest	60.3	60	62.1	57.2	67.2	62.3	53	59	90.75	90.75
%TSCOD gen	152.4	127	141	147	151.2	103.6	140	101.1	45.6	29.2
VFA	4290	3911	4112	4211	5001	3002	4290	4310	3750	4210
%acetic acid	62	61.9	62.2	63.1	65	60.2	62.3	57.92	93.8	91.2
RT(min)	30	30	30	30	30	30	10	10	60	60
Pressure (MPa)	2	2	2	4	4	4	4	2	2	2
Settled Volume (ml/l)	110	115.5	145	85	98	98	97	110	80	116
Colour ^{o}H	400	455	425	400	390	460	400	410	_	_
CST (sec)	23.9	21.3	22.7	23.2	21	22.1	23.7	22.9	23	24
SOR	1	1	1	2	2	2	1	1	1	1
pH	6.2	5.8	6.1	5.2	6.1	5.3	6.1	4.6	5.6	5.3

Table B3: Raw Primary Sludge at 300°C

RUN	1	2	3	4	5	6	7	8	9	10	11
% TSi	3.92	3.92	3.92	3.92	3.92	3.92	3.92	3.92	3.92	2.5	2.5
%VTSi	76.7	76.7	76.7	76.7	76.7	76.7	76.7	76.7	76.7	76	73
%TS dest	94.3	73	73.11	77.3	59.1	85.1	69.13	73	68.5	81	78
%VTS dest	84.5	86	85.5	87.5	94.3	83.2	84.5	83.8	81.2	86	84
%TCODdest	62	60	50.5	80.5	65	68	48	66	67.5	80	78
%SCOD gen	-9.1	-44.5	22	28.3	22.1	25	36.36	32.5	31.2	22	18
VFA	4600	4560	5200	4500	5087.5	3558.1	4551.1	4560	4290	2800	2420
%aceticacid	81	91	93	93.3	95	92.6	92.75	93	91.2	87	
RT(min)	30	30	30	30	30	30	60	60	60	60	60
Settled Volume (ml/l)	95	85	87	96	84	85	81	79	82.5	80	82
Colour °H	100	40	120	80	100	40	40	40	40	40	50
CST (sec)	16	25	23	16.3	16.6	16.2	20.3	18.3	17.3	15	17
SOR	1	1	1	1	1	1	1	1	1	1	1
pH	8	6.7	6.9	5.5	4.9	5.5	6.4	6.3	5.8	6.2	6.8

Activated Sludge Data

Table B4: Efficiency Tests at 280 °C

RUN	1A	1B	1C	2A	2B	2C	3A	3B	3C
% TSi	2.65	2.65	2.65	2.65	2.65	2.65	2.65	2.65	2.65
%VTSi	2.1	2.1	2.1	2.1	2.1	2.1	2.1	2.1	2.1
TCODi mg/l	22250	22250	22250	22250	22250	22250	22250	22250	22250
TCODf mg/l	12400	11950	12005	5500	5601	4910	12311	11993	12395
%TCOD dest	44.3	46.2	46	75.3	74.82	78	44.6	46	44.3
SCOD gen mg/l	4810	6110	4991	4760	4801	4696	6010	5990	6253
%SCOD gen	97.29	97.87	97.39	97.26	97.29	97.23	97.83	97.82	97.92
VFA	7600	7000	6895	8000	8710	7920	7410	7812	7502
%aceticacid	73.8	85.8	76.2	74.2	80.1	82.3	71	76.2	78.5
RT(min)	60	60	60	60	60	60	60	60	60
Pressure (MPa)	1	1	1	2	2	2	4.5	4.5	4.5
SOR	0.5	0.5	0.5	1	1	1	0.5	0.5	0.5

Table B5: Activated Sludge at 200 °C

RUN	1A	1B	2A	2B	3A	3B
% TSi	0.6	0.6	0.6	0.6	0.6	0.6
%VTSi	83	83	83	83	83	83
%TS dest	14.5	10.6	17.2	20.2	18.6	19.2
%VTS dest	26	32.5	39	38.6	33	29
%TCODdest	15.2	19.1	30.1	21.6	22.5	26.2
%TSCOD gen	910	807	417	407	869	792

Table B5 Cont.

RUN	1A	1B	2A	2B	3A	3B
VFA	160	212	241	271	259	301
%aceticacid	28.5	10.6	19.5	20.1	15	18.5
RT(min)	10	10	30	30	30	30
Settled Volume (ml/l)	120	140	160	110	115	119
Colour oH	495	520	620	490	580	495
CST (sec)	44.2	40.3	54	26	38	24.5
SOR	1	1	1	1	2	2

Table B6: Activated Sludge at 260 °C

RUN	1A	1B	2A	2B
% TSi	0.6	0.6	0.6	0.6
%VTSi	83	83	83	83
%TS dest	25.6	26.1	35.7	30.1
%VTS dest	38	47	45	48.6
%TCODdest	52.6	49.9	53.1	56.7
%TSCOD gen	530	488	254	292
VFA	770	873	373	385
%aceticacid	61.3	55.2	70.2	68.8
RT(min)	10	10	30	30
Pressure (MPa)	0.5	0.5	0.5	0.5
Settled Volume (ml/l)	98	102	106	88
Colour oH	690	510	695	555
CST (sec)	16	15	12	13
SOR	1	1	1	1

Table B7: Activated Sludge at 280 °C

RUN	1A	1B	2A	2B
% TSi	2.65	2.65	2.65	2.65
%VTSi	2.1	2.1	2.1	2.1
%TS dest	29.2	38	38.6	36.1
%VTS dest	70	64	84	87
%TCODdest	45.9	58.75	68.5	64.8
%TSCOD gen	98	1.9.2	97.3	89.9
VFA	2500	2300	2200	2100
%aceticacid	58	63	61	71
RT(min)	10	10	30	30
Settled Volume (ml/l)	105.5	108.6	110	98
Colour oH	455	490	495	405
CST (sec)	8	11	9	7.2
SOR	1	1	1	1

Table B8 Activated Sludge at 300 °C

RUN	1A	1B	2A	2B
% TSi	0.6	0.6	0.6	0.6
%VTSi	83	83	83	83
%TS dest	40.5	51	48.2	56.2
%VTS dest	84	81.1	83.6	88.7
%TCODdest	71.6	69.9	70.9	78.5
%SCOD gen	181	195	102.5	135
VFA	2200	1860	2100	1750
%aceticacid	89	91.1	90	96
RT(min)	10	10	30	30
Settled Volume (ml/l)	84	89	84	80
Colour oH	335	370	640	355
CST (sec)	6.6	5.9	6	6.2
SOR	1	1	1	1

Regression Model Data (Section 5.4.2 i))

Table B9 Temperatre 200 °C, Oxygen Over-Pressure 4MPa

VTS	SCOD	NH3-N	CH_3COOH	HCHO	Log(VTS)	Log(SCOD)	Log(NH_3-N)	Log (CH_3COOH)
1206	892	101.2	152	10.8	3.081347	2.950365	2.005181	2.181844
2412	1620	173.6	332	6	3.382377	3.209515	2.23955	2.521138
4825	2690	280	675	3.6	3.683497	3.429752	2.447158	2.829304
9650	5140	627.2	1487	2	3.984527	3.710963	2.797406	3.172311
19300	8400	1176	2299	1.2	4.285557	3.924279	3.070407	3.361539
38600	16980	2320	3972	0.6	4.586587	4.229938	3.365488	3.599009

Table B10 Temperatre 200 °C, Oxygen Over-Pressure 2.5 MPa

VTS	SCOD	NH3	CH_3COOH	HCHO	LogVTS	LogSCOD	LogNH3-N	LogCH3COOH
1206	901	81	152	0.6	7.095064	6.803505	4.394449	5.023881
2412	1700	156.8	349	1.35	7.788212	7.438384	5.054971	5.855072
4825	2580	236	454	2.12	8.481566	7.855545	5.463832	6.118097
9650	5520	385	642	4.4	9.174713	8.616133	5.953243	6.464588
19300	9480	512	820	7.7	9.86786	9.15694	6.238325	6.709304
38600	19201	643	1113	17.1	10.56101	9.862718	6.466145	7.014814

Table B11 Temperatre 260 °C, Oxygen Over-Pressure 2.5MPa

VTS	SCOD	NH_3-N	CH_3COOH	CH_3COOH	Log(VTS)	Log(SCOD)	Log(NH_3-N)	Log(CH_3COOH)
1855	360	84	131.5	131.5	7.52564	5.886104	4.430817	4.879007
3710	1240	196.5	635	635	8.218787	7.122867	5.280662	6.453625
6970	2000	280	993	993	8.849371	7.600902	5.63479	6.900731
7425	2440	324.8	1459	1459	8.912608	7.799753	5.78321	7.285507
14856	3900	403.2	1210	1210	9.606159	8.268732	5.999433	7.098376
26300	11120	875.2	2100	2100	10.17732	9.316501	6.774452	7.649693

Table B12 Temperatre 280 °C, Oxygen Over-Pressure 2.5 MPa

VTS	SCOD	NH_3-N	HCHO	CH_3COOH	Log(VTS)	Log(SCOD)	Log(NH_3-N)	Log(CH_3COOH)
1855	500	112	0.09	195.3	7.52564	6.214608	4.718499	5.274537
3710	840	162.5	0.324	642.6	8.218787	6.733402	5.090678	6.465522
6970	1580	176.5	0.28	710	8.849371	7.36518	5.173321	6.565265
7425	1880	241	0.622	852	8.912608	7.539027	5.484797	6.747587
14856	3200	661	1.371	1320	9.606159	8.070906	6.493754	7.185387
26300	9440	1120	5	2660	10.17732	9.152711	7.021084	7.886081

Table B13 Temperatre 300 °C, Oxygen Over-Pressure 2.5 MPa

VTS	SCOD	NH_3-N	HCHO	CH_3COOH	Log(VTS)	Log(SCOD)	Log(NH_3-N)	Log(CH_3COOH)
1855	470	84	0.21	345	7.52564	6.152733	4.430817	5.843544
3710	690	150.2	0.36	696	8.218787	6.536692	5.011968	6.54535
6970	912	165.9587	0.48	1304	8.849371	6.81564	5.111739	7.173192
7425	1760	221.2	0.71	1021	8.912608	7.473069	5.399067	6.928538
14856	2340	314	1.6	1438	9.606159	7.757906	5.749393	7.271009
26300	9200	1232	6.6	3010	10.17732	9.126959	7.116394	8.009695

Ref:LQ 38, Anionic ; Molecular Weight 362

Table B14 WO of LAS Detergent

[all the experiments in Table B14- B19 were repeated 2-3 times, the value given are an average of the tests except pH]

Parameter	5% LAS	2.5% LAS	2% LAS (60 min)	2% LAS (30 min)	2% LAS (15 min)	2% LAS(160C)	2%LAS (200C, 15min)	2%LAS (200C, 30min)	2%LAS (200C, 60min))	2%LAS (240C,60m in)	2% LAS (240C, 30min)
TCOD$_i$ (mg/l)	107200	53600	42880	42880	42880	42880	42880	42880	42880	42880	42880
TCOD$_f$ (mg/l)	17800	7200	6400	8900	11480	28400	32600	27400	21700	16900	17600
%TCOD(Dest or GEN)	83.4	86.57	85.07	79.25	73.23	33.77	24	36.1	49.4	61.32	59.73
AD initial(mg/l)	52000	26000	20800	20800	20800	20800	20800	20800	20800	20800	20800
AD final(mg/l)	173.7	41.7	26.6	23.2	133	6000	3475	1535	116	139	60
%AD removal	99.65	99.83	99.87	99.88	99.36	71.15	83.3	92.62	99.44	99.33	99.71
VFA (mg/l)	29000	8850	2200	4800	11220	13880	6700	3300	19600	22300	19900
%aceticacid/ pro-val	89/4	76/10	100/-	100/-	94/1.7	51/29	23/70	75/pv	60/23	82/9.5	68/18
Temp °C	280	280	280	280	280	160	200	200	200	240	240
R. Time (min)	60	60	60	30	15	60	15	30	60	60	30
pH after WO	2.4	2.7	2.1	2.3	2.3	3	4	2.9	2.6	2.4	2.4
NH_3-N (mg/l)	00	58	3	00	00	56	00	00	00	00	00

Ref.: 95/028, Zeolite HDL Anionic; Molecular Weight 468.75 (Calculated)

Table B15 **WO of HDL Detergent**

Parameter	1/2% HDL	1/2% HDL	1/2% HDL	4.5% HDL	4.5% HDL	4.5% HDL	6% HDL	12% HDL	30% HDL
TCODi (mg/l)	17700	17700	17700	159000	159000	159000	212000	424000	1060000
TCODf (mg/l)	17500	9500	5000	106800	75200	47600	106000	266200	654000
%TCOD(Dest or GEN)	1.13	46.32	71.75	32.83	52.7	70.06	50	37.22	38.3
AD initial(mg/l)	5000	5000	5000	45000	45000	45000	60000	120000	300000
AD final(mg/l)	2343	280.5	45	9000	8100	937.5	27750	132000	358000
%AD removal	53.14	94.38	99.1	80	82	97.9	53.75	00	00
VFA (mg/l)	1100	2100	2020	9360	1700	—	33000		00
%aceticacid/pro-val	100/-	90/3	100/-	89/3	40/60v	—	—		00
Pressure (MPa)	3.5	6	8	3.5	6	8	3.5	8	8
Temp °C	200	200	280	200	200	280	200	280	280
R. Time (min)	60	60	60	60	60	60	60	120	60
pH after WO	5.9	5.2	6.1	6	6.6	6	7.1	9	?
Ammonia (mg/l)	00	00	00	00	5	—	56	136	300

Table B16 Catalytic WAO of Zeolite (HDL)

Parameter	Catalyst	COD_i (mg/l)	COD_f (mg/l)	%COD removal	AD_i (mg/l)	AD_f mg/l)	%AD removal	pH final
1/2% HDL	$CuSO_4$ (500mg/l)	17700	7900	55.36	5000	1640	67.2	5.7
1/2% HDL	MnO_2 (500mg/l)	17700	18600	0	5000	4880	2.4	8
1/2% HDL	$MnSO_4$ (500mg/l)	17700	18560	0	5000	4875	2.5	8.8
4.5 %HDL	$CuSO_4$ (500mg/l)	159000	101200	36.35	45000	31875	29.16	10.5

Ref:LQ 40 and Comfort fabric conditioner, Cationic; Molecular weight= 678

Table B17 WO of HEQ and Comfort Detergent

Parameter	5% HEQ	2% HEQ	1.63% Comfort	1.63% Comfort	10.84% (Comfort, original product)
TCODi (mg/l)	135600	54240	367000	367000	2440000
TCODf (mg/l)	30000	8450	19100	5500	54600
%TCOD(Dest or GEN)	77.87	84.43	94.8	98.5	97.76
AD initial(mg/l)	50000	20000	16300	16300	108400
AD final(mg/l)	00	8.136	43.4	10.85	1084
%AD removal	100	99.96	99.73	99.93	99
VFA (mg/l)	4200	1650	9.1	55	3600
%aceticacid/pro-val	97.7/2	100/-	76.5	90.2	11.2/87 Valaric
Temp °C	280	280	200	280	280
R. Time (min)	60	60	60	60	30
pH after WO	1.6	1.7	3	3.9	2.5
Ammonia (mg/l)	340	00	196	400.5	980

Table B18 **WO of Persil Dish Washing Liquid (Molecular weight 362)**

Parameter	4.5% Persil	4.5% Persil	15% (Persil	30% Persil
TCODi (mg/l)	125550	125550	418500	837000
TCODf (mg/l)	4400	9900	218000	112600/79000
%TCOD(Dest or GEN)	96.5	92.2	48	25.7+/90.6- (Net Dest=40.5%)
AD initial(mg/l)	45000	45000	150000	300000
AD final(mg/l)	27.1	27.1	362++(SLS was used)	00/295++
%AD removal	99.9	99.9	100	100
VFA (mg/l)	3.43	5.75	00	00
%aceticacid/pro-val	100/-	94.8	00	00
Temp °C	280	200	280	280
R. Time (min)	60	60	60	60
pH after WO	1.95	2.1	1.2	1.3/4
NH_3-N (mg/l)	334	166	1540	560/2800

Table B19 **WO of LES (Molecular weight: 446.5)**

Parameter	5% LES	2%LES	2% LES
TCODi (mg/l)	88000	35200	35200
TCODf (mg/l)	12100	4800	4550
%TCOD(Dest or GEN)	86.25	86.36	87.07
AD initial(mg/l)	50000	20000	20000
AD final(mg/l)	21.437	14.5	2.14
%AD removal	99.96	99.92	99.989
VFA (mg/l)	4200	1880	1650
%aceticacid/pro-val	88/3	41/57	100/-
Temp °C	280	200	280
R. Time (min)	60	60	60
pH after WO	1.3	2.2	1.7
NH_3-N (mg/l)	2.8	00	00

APPENDIX-C

Results of Chapter 6

Table C1 **Aerobic Biological Treatment of AS280 °C**

Days	COD_{Feed} (mg/l)	COD_{Eff} (mg/l)	$BCOD_{Feed}$ (mg/l)	$BCOD_{Eff}$ (mg/l)	%COD removal	%BCOD removal	F/M	MLSS (mg/l	NH_3-N feed (mg/l)	NH_3-N Effluent (mg/l)	%NH_3-N removal
1	3000	809.5	2294	338.5	73.0167	85.2441	1.2	1800	610	280	54.0984
2	3000	814	2294	343	72.8667	85.048	1.15	1900	610	275	54.918
3	3000	805.8	2294	334.8	73.14	85.4054	1.09	2005	610	281	53.9344
4	3000	822.3	2294	351.3	72.59	84.6861	1.08	2001	610	269	55.9016
5	3000	835.4	2294	364.4	72.1533	84.1151	1.14	1896	610	267.5	56.1475
8	3000	752	2294	281	74.9333	87.7507	1.24	1798	610	265	56.5574
10	3000	763	2294	292	74.5667	87.2711	1.23	1810	610	259.3	57.4918
12	2000	692	1529	221	65.4	85.5461	0.57	1820	360	167	53.6111
14	2000	675	1529	204	66.25	86.6579	0.62	1880	360	180	50
16	2000	691	1529	220	65.45	85.6115	0.621	1895	360	156	56.6667
17	2000	632	1529	161	68.4	89.4702	0.66	1801	360	163.5	54.5833
18	2000	654	1529	183	67.3	88.0314	0.61	1830	360	155	56.9444
19	2000	642	1529	171	67.9	88.8162	0.61	1835	360	145.6	59.5556
20	2000	632	1529	161	68.4	89.4702	0.6	1871	360	147.6	59
21	2000	648	1529	177	67.6	88.4238	0.62	1869	360	142.8	60.3333
25	2000	678	1529	207	66.1	86.4617	0.63	1832	360	158	56.1111
28	2000	691	1529	220	65.45	85.6115	0.64	1840	360	154.2	57.1667
30	2000	631	1529	160	68.45	89.5356	0.63	1880	360	153.6	57.3333
31	2000	633	1529	162	68.35	89.4048	0.64	1855	360	159.7	55.6389
32	2000	647	1529	176	67.65	88.4892	0.63	1890	360	152.4	57.6667
34	2000	652	1529	181	67.4	88.1622	0.65	1892	360	150	58.3333
35	2000	638	1529	167	68.1	89.0778	0.65	1872	360	151.9	57.8056
40	2000	658	1529	187	67.1	87.7698	0.65	1861	360	152.3	57.6944
41	2000	620	1529	149	69	90.2551	0.65	1885	360	145.2	59.6667
42	769	610	298	139		53.3557	0.72	1811			
45	769	470	298	-1		100.336	0.2	1520			
48	769	471	298	0		100	0.26	1210			
51	471	471	0				0	1101			

Table C2 Anaerobic Biological Treatment (UFAF) of AS280 °C

Date	days	COD$_{Feed}$ (mg/l)	COD$_{effluent}$ (mg/l)	VFA$_{Feed}$ (mg/l)	VFA$_{effluent}$ (mg/l)	%COD removal	%VFA removal	HRT (Hrs)
Period I								
15/2/1994	1	3159	690	1900	690	78.15764	63.68421	24
16-Feb	2	3000	710	1920	710	76.33333	63.02083	24
17-Feb	3	3000	712	1938	712	76.26667	63.26109	24
18-Feb	4	2500	620	1885	620	75.2	67.10875	24
19-Feb	5	4140	1100	1912	1100	73.42995	42.46862	24
20-Feb	6	4140	2900	2700	2900	29.95169	-7.40741	24
21-Feb	7	4000	2012	2610	2010	49.7	22.98851	24
22-Feb	8	4000	1810	2100	1810	54.75	13.80952	24
23-Feb	9	4000	1990	2160	1990	50.25	7.87037	24
28-Feb	14	4000	2710	2300	2710	32.25	-17.8261	24
1-Mar	15	3990	2750	2310	2750	31.07769	-19.0476	24
2-Mar	16	3995	2410	2210	2410	39.67459	-9.04977	24
3-Mar	17	3992	2230	2160	2230	44.13828	-3.24074	24
4-Mar	18	3985	2310	2138	2310	42.03262	-8.0449	24
5-Mar	19	3900	2410	2011	2410	38.20513	-19.8409	24
6-Mar	20	3995	2416	2081	2416	39.52441	-16.098	24
7-Mar	21	3995	2410	2175	2413	39.67459	-10.9425	24
8-Mar	22	3895	2520	2182	2385	35.30167	-9.30339	24
11-Mar	25	3882	2485	2022	2365	35.9866	-16.9634	24
12-Mar	26	3880	2523	2071	2520	34.97423	-21.6803	24
15-Mar	28	3870	2400	1966	2485	37.9845	-26.3988	24
16-Mar	29	3850	2150	1985	2523	44.15584	-27.1033	24
17-Mar	30	3840	2201	1992	2400	42.68229	-20.4819	24
18-Mar	31	3835	2566	2610	2150	33.08996	17.62452	24
19-Mar	32	3840	2601	2001	2201	32.26563	-9.995	24
23-Mar	35	3990	2505	2650	256	37.21805	90.33962	24
25-Mar	37	3992	2595	2565	2603	34.99499	-1.48148	24
26-Mar	38	3990	3432	2046	2501	13.98496	-22.2385	24
28-Mar	40	3498	3478	1995	2595	0.571755	-30.0752	24
30-Mar	42	3495	3397	1980	2500	2.804006	-26.2626	24
5-Apr	48	3505	3402	2010	2433	2.938659	-21.0448	24
8-Apr	51	3499	3422	1950	2354	2.200629	-20.7179	24
12-Apr	55	3501	3306	1240	1893	5.569837	-52.6613	24
15-Apr	58	3482	3343	1620	1850	3.991959	-14.1975	24
17-Apr	60	3492	3331	1520	1434	4.610538	5.657895	24
21-Apr	64	3482	3341	1890	2010	4.049397	-6.34921	24
25-Apr	68	3481	3389	1668	1840	2.642919	-10.3118	24
27-Apr	70	3485	3299	1523	1453	5.337159	4.596192	24
Period II								
27-Apr	70	3485	3299	1523	1453	5.337159	4.596192	24
30-Apr	73	3479	3360	1622	1380	3.420523	14.91985	72
2-May	75	3489	3372	1496	1390	3.353396	7.085561	72
5-May	78	3500	3373	1566	1501	3.628571	4.150702	72

Table C2 Cont.

10-May	83	3500	3385	1534	1426	3.285714	7.040417	72
15-May	88	3500	3320	1678	1590	5.142857	5.244338	72
20-May	93	3510	3270	1642	1598	6.837607	2.679659	72
25-May	98	3501	3317	1532	1460	5.255641	4.699739	72
30-May	103	3495	3329	1580	1280	4.749642	18.98734	72
4-Jun	108	3485	3349	1690	1390	3.902439	17.75148	72
8-Jun	112	3490	3355	1520	1455	3.868195	4.276316	72
12-Jun	116	3495	3852	1478	1820	-10.2146	-23.1394	72
15-Jun	119	3492	3933	1520	1687	-12.6289	-10.9868	72
17-Jun	121	3489	3269	1420	1431	6.305532	-0.77465	72
21-Jun	125	3499	3322	1520	1320	5.058588	13.15789	72
26-Jun	130	3486	3322	1476	1220	4.704532	17.34417	72
26-Jun	132	3491	3372	1490	1260	3.408765	15.43624	72
29-Jun	133	3472	3269	1570	1350	5.846774	14.01274	72
30-Jun	134	3482	3268	1520	1800	6.145893	-18.4211	72
5-Jul	139	3492	3269	1460	1380	6.386025	5.479452	72
8-Jul	142	3482	3280	1230	1240	5.801264	-0.81301	72
12-Jul	146	3491	3291	1240	1100	5.729017	11.29032	72
15-Jul	149	3510	3295	1500	1360	6.125356	9.333333	72
17-Jul	151	3500	3299	1460	1380	5.742857	5.479452	72
21-Jul	155	3501	3260	1360	1280	6.883748	5.882353	72
25-Jul	159	3502	3268	1580	1380	6.681896	12.65823	72
29-Jul	163	3500	3397	1580	1420	2.942857	10.12658	72
Period III								
30-Jul	164	3500	2960	850	1230	15.42857	-44.7059	72
1-Aug	166	3000	2930	360	372	2.333333	-3.33333	72
2-Aug	167	3000	2980	840	376	0.666667	55.2381	72
3-Aug	168	2980	2950	490	560	1.006711	-14.2857	72
6-Aug	171	2991	2956	821	950	1.170177	-15.7125	72
7-Aug	172	3001	2959	921	586	1.399533	36.37351	72
8-Aug	173	3005	3200	890	1012	-6.48918	-13.7079	72
10-Aug	175	3115	2500	830	995	19.74318	-19.8795	72
12-Aug	177	3000	1495	685	827	50.16667	-20.7299	72
14-Aug	179	3015	1895	764	945	37.1476	-23.6911	72
16-Aug	181	3020	2600	850	621	13.90728	26.94118	72
18-Aug	183	3035	2710	512	832	10.7084	-62.5	72
20-Aug	185	3010	2650	923	821	11.96013	11.05092	72
23-Aug	188	3011	2201	721	942	26.90136	-30.6519	72
24-Aug	189	3002	2301	845	912	23.3511	-7.92899	72
26-Aug	191	3015	2512	625	852	16.68325	-36.32	72
28-Aug	193	3021	1590	456	852	47.36842	-86.8421	72
30-Aug	195	3000	1401	753	951	53.3	-26.2948	72
31-Aug	196	3095	2500	941	821	19.22456	12.75239	72
1-Sep	197	3250	2212	548	875	31.93846	-59.6715	72
2-Sep	198	3245	2201	851	864	32.17257	-1.52761	72
3-Sep	199	3210	2110	831	875	34.26791	-5.29483	72
4-Sep	200	3222	1590	920	960	50.65177	-4.34783	72

Table C2 Cont.

5-Sep	201	3210	3325	354	754	-3.58255	-112.994	72
6-Sep	202	3000	3300	452	654	-10	-44.6903	72
7-Sep	203	3000	2153	354	752	28.23333	-112.429	72
8-Sep	204	3001	1150	854	753	61.67944	11.8267	72
12-Sep	208	3000	1180	752	458	60.66667	39.09574	72
14-Sep	210	3000	1201	854	452	59.96667	47.0726	72
16-Sep	212	3020	1225	725	485	59.43709	33.10345	72
18-Sep	214	3100	1680	360	451	45.80645	-25.2778	72
20-Sep	216	3000	1230	450	360	59	20	72
22-Sep	218	3000	1894	478	321	36.86667	32.84519	72
23-Sep	219	3000	2006	485	420	33.13333	13.40206	72
25-Sep	221	3000	2572	850	456	14.26667	46.35294	72
27-Sep	223	3000	1365	456	652	54.5	-42.9825	72
30-Sep	226	3000	2162	752	456	27.93333	39.3617	72
1-Oct	227	3002	1114	452	520	62.89141	-15.0442	72
5-Oct	231	3020	1129	352	382	62.61589	-8.52273	72
7-Oct	233	3000	1858	475	352	38.06667	25.89474	72
9-Oct	235	3115	2001	345	450	35.76244	-30.4348	72
12-Oct	238	3015	1956	750	350	35.12438	53.33333	72
15-Oct	241	3012	2070	852	350	31.2749	58.92019	72
16-Oct	242	3010	2125	752	412	29.40199	45.21277	72
17-Oct	243	3001	2052	652	446	31.62279	31.59509	72
18-Oct	244	3001	2224	425	455	25.89137	-7.05882	72
19-Oct	245	2995	2795	520	480	6.677796	7.692308	72
Period IV								
21-Oct	247	2991	2110	850	920	29.45503	-8.23529	288
2-Nov	259	3000	1390	451	620	53.66667	-37.4723	288
4-Nov	261	3000	1477	541	750	50.76667	-38.6322	288
6-Nov	263	3000	993	380	271	66.9	28.68421	288
8-Nov	256	3000	900	399	201	70	49.62406	288
10-Nov	269	3000	901	450	180	69.96667	60	288
11-Nov	270	3000	912	560	210	69.6	62.5	288
14-Nov	273	3000	895	580	214	70.16667	63.10345	288
15-Nov	274	3000	1101	540	210	63.3	61.11111	288
21-Nov	280	3000	850	459	201	71.66667	56.20915	288
24-Nov	283	3000	845	480	205	71.83333	57.29167	288
28-Nov	287	3000	912	460	214	69.6	53.47826	288
3-Dec	292	3000	978	430	221	67.4	48.60465	288
10-Dec	299	3000	854	448	210	71.53333	53.125	288
15-Dec	304	3000	852	520	234	71.6	55	288
20-Dec	309	3000	871	475	258	70.96667	45.68421	288
26-Dec	315	3000	843	421	189	71.9	55.10689	288
31/12/94	320	3000	945	436	178	68.5	59.17431	288
Period V								
5-Jan	325	3000	1750	378	191	41.66667	49.4709	144
10-Jan	330	3000	1730	450	245	42.33333	45.55556	144
15-Jan	335	3000	1880	380	278	37.33333	26.84211	144

Table C2 Cont.

20-Jan	340	3000	1872	780	348	37.6	55.38462	144
25-Jan	345	3000	2522	651	360	15.93333	44.70046	144
30-Jan	350	3000	2532	480	360	15.6	25	144
5-Feb	356	3000	2501	820	730	16.63333	10.97561	144
10-Feb	361	3000	2372	852	621	20.93333	27.11268	144
15-Feb	366	3000	2370	450	320	21	28.88889	144
20-Feb	371	3000	2371	460	368	20.96667	20	144
25-Feb	376	3000	1931	520	387	35.63333	25.57692	144
1-Mar	380	3000	1982	469	560	33.93333	-19.403	144
6-Mar	385	3000	1743	740	582	41.9	21.35135	144
10-Mar	389	3000	2220	452	582	26	-28.7611	144
15-Mar	394	3000	2343	475	360	21.9	24.21053	144
20-Mar	399	3000	2310	547	421	23	23.03473	144
25-Mar	404	3000	2309	460	389	23.03333	15.43478	144
30-Mar	409	3000	2307	481	321	23.1	33.26403	144
5-Apr	415	3000	2308	338	389	23.06667	-15.0888	144
10-Apr	420	3000	1771	478	352	40.96667	26.35983	144
15/4/1995	425	3000	1781	360	332	40.63333	7.777778	144
20	430	3000	1792	850	281	40.26667	66.94118	144
25	435	3000	1832	360	372	38.93333	-3.33333	144
30	440	3000	1981	478	345	33.96667	27.82427	144
5	445	3000	1935	746	582	35.5	21.98391	144
10/5/95	450	3000	1545	438	336	48.5	23.28767	144
ALKALINITY = 870 mg/l TO 1722 mg/l								

Table C3 **Aerobic Treatment of Detergent Liquor**

Cycle	COD_{Feed}	COD effluentt	$\text{BCOD}_{\text{Feed}}$ (mg/l)	$\text{BCOD}_{\text{effluent}}$ (mg/l)	MLSS mg/l	SVI	F/M	AD_{Feed} (mg/l)	% AD removal	%COD removal	%BCOD removal
1	2000	414	1690	106	2700	187	0.59	60	69.5	79.3	93.72
2	2000	478	1690	170	2775	150.2	0.54	60	71.8	76.1	89.94
3	2000	425	1690	117	2812	117.1	0.56	60	64.9	78.75	93.07
4	2000	438	1690	130	2912	117.6	0.53	60	62.5	78.1	92.30
5	2000	412	1690	104	3201	91.4	0.5	60	75.8	79.4	93.84
6	2000	419	1690	111	3250	90.5	0.48	60	71.3	79.05	93.43
7	2000	412	1690	104	3210	70.7	0.5	60	73.5	79.4	93.84
8	2000	384	1690	76	3212	70.3	0.51	60	69.8	80.8	95.50
9	2000	382	1690	74	2992	71.3	0.55	60	75.2	80.9	95.6213
10	2000	384	1690	76	2910	81.2	0.56	60	68.75	80.8	95.506
11	2000	384	1690	76	3100	85.5	0.53	60	66.75	80.8	95.50
12	2000	365	1690	57	3210	83.4	0.51	60	62.8	81.75	96.62
13	2000	372	1690	64	3182	72.2	0.52	60	75.2	81.4	96.21
14	2000	362	1690	54	3181	82.3	0.52	60	64.2	81.9	96.80
15	2000	372	1690	64	3190	75.1	0.52	60	63.7	81.4	96.21
16	5000	910	4220	130	4995	75.2	1.4	150	67.8	81.8	96.91
17	5000	969	4220	189	4250	71.3	1.3	150	58.76	80.62	95.52
18	5000	981	4220	201	4280	89	1.2	150	61.2	80.38	95.23
19	5000	977	4220	197	4310	79	1.2	150	62.8	80.46	95.33
20	5000	959	4220	179	4312	88.3	1.2	150	66.8	80.82	95.75
21	5000	991	4220	211	4420	87.6	1.2	150	52.8	80.18	95
22	5000	969	4220	189	4480	87.4	1.2	150	66.3	80.62	95.52
23	5000	987	4220	207	4490	70	1.2	150	62.1	80.26	95.09
24	5000	971	4220	191	4498	79	1.2	150	64.5	80.58	95.47
25	5000	977	4220	197	4612	71	1.1	150	63.7	80.46	95.33
26	5000	969	4220	189	4691	70.7	1.1	150	67.6	80.62	95.52
27	5000	972	4220	192	4595	70.3	1	150	52.8	80.56	95.450
28	5000	973	4220	193	4712	71	1.1	150	61.3	80.54	95.42
29	5000	970	4220	190	4691	78	1.1	150	66.1	80.6	95.49
30	5000	986	4220	206	4610	74.25	1.1	150	62.1	80.28	95.118

Table C4 Anaerobic Treatment of Detergent Liquor

Date	DAYS	SCOD $_{Feed}$ (mg/l)	SCOD $_{effluent}$ (mg/l)	SCOD removal	OLR kg COD/m^3.day	HRT in hours	Detergent type	AD $_{feed}$	AD $_{Eff.}$	% AD removal
1/6/95	1	15200	7700	49.34211	2.53	144	LAS	200	100	50
2-Jun	2	15200	6980	54.07895	2.53	144	LAS	200	150	25
3-Jun	3	15200	7200	52.63158	2.53	144	LAS	200	160	20
4-Jun	4	15200	7380	51.44737	2.53	144	LAS	200	170	15
6-Jun	6	15200	8050	47.03947	2.53	144	LAS	200	168	16
11-Jun	11	15200	7680	49.47368	2.53	144	LAS	200	180	10
16-Jun	16	15200	7990	47.43421	2.53	144	LAS	200	179	10.5
21-Jun	21	15200	7882	48.14474	2.53	144	LAS	200	190	5
27-Jun	27	15200	7952	47.68421	2.53	144	LAS	200	192	4
2-Jul	32	15200	7200	52.63158	2.53	144	LAS	200	190	5
7-Jul	37	15200	7150	52.96053	2.53	144	LAS	200	180	10
17-Jul	47	15200	7315	51.875	2.53	144	LAS	200	173	13.5
20-Jul	50	15200	7378	51.46053	2.53	144	LAS	200	179	10.5
26-Jul	56	13920	6680	52.01149	2.32	144	Coctail	200	165	17.5
22-Jul	62	13920	11220	19.39655	2.32	144	Coctail	200	169	15.5
28-Jul	68	13920	11800	15.22989	2.32	144	Coctail	200	170	15
3-Aug	74	13920	10500	24.56897	2.32	144	Coctail	200	165	17.5
9-Aug	80	13920	8230	40.87644	2.32	144	Coctail	200	164	18
15-Aug	86	13920	11280	18.96552	2.32	144	Coctail	200	175	12.5
21-Aug	92	13920	11500	17.38506	2.32	144	Coctail	200	178	11
27-Aug	98	13920	11750	15.58908	2.32	144	Coctail	200	168	16
2-Sep	104	13920	10950	21.33621	2.32	144	Coctail	200	159	20.5
8-Sep	110	13920	9890	28.95115	2.32	144	Coctail	200	160	20

COCTAIL= 2%LAS, 0.5%HDL, 1.63%COMFORT, 4,5% PERSIL, 1-5%LES, 2% HEQ

Table C5 **Aerobic Treatment of Paracetamol Liquor (JLR)**

[n = 3]

Time (days)	% COD removal	MLSS	F/M	$SS_{Effluent}$ (mg/l)
1	95.6	1820	1.2	290
2	93.8	1600	1.4	299
3	95	1832	1.2	325
4	93.6	1810	1.2	320
5	84	1790	1	425
6	73.5	1835	0.8	425
7	62	1750	0.7	385
8	48.9	1790	0.6	367
9	51.6	1760	0.6	411
10	49.6	1698	0.6	398
11	50.3	1710	0.6	467
12	51.7	1620	0.6	348
13	48.2	1720	0.6	490
14	49.8	1735	0.6	323