EVALUATION OF DIFFERENT METHODS TO PRODUCE FREE RADICALS FOR THE OXIDATION OF ORGANIC MOLECULES IN INDUSTRIAL EFFLUENTS AND POTABLE WATER WITH REFERENCE TO CAV-OX®

WRC Report

submitted to the

Water Research Commission

by

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WRC Report No 388/1/99
ISBN No 1 86845 484 3

EXECUTIVE SUMMARY

EVALUATION OF DIFFERENT METHODS TO PRODUCE FREE RADICALS FOR THE OXIDATION OF ORGANIC MOLECULES IN INDUSTRIAL EFFLUENTS AND POTABLE WATER
WITH SPECIAL REFERENCE TO CAV-OX®

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July 1995

Supplementary to Final Report to the Water Research Commission on Project No. 388 :
Evaluation of Different Methods to produce Free Radicals for the Oxidation of Organic Molecules in Industrial Effluents and Potable Water (with special reference to CAV-OX®)

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1 BACKGROUND TO THE PROJECT

Environmental legislation and the increasing pollution of water supplies have necessitated the evaluation of existing technologies and the development of new technologies for the removal of organic pollutants from industrial effluents and potable water, and for the disinfection of potable water by the inactivation of bacteria and pathogens.

Recently, advanced oxidation processes have developed as potentially powerful methods for the treatment of organic pollutants in water and the disinfection of potable water. These processes involve the generation of highly reactive free radical intermediates such as the hydroxyl radical. The advantage of these oxidation processes is that organic pollutants can be completely mineralised to carbon dioxide, water and a small amount of acids, while the degradation process usually operates at or near ambient temperature and pressure. In some cases, complete mineralisation may not be achieved due to excessive reaction times, nevertheless, advanced oxidation processes are potentially beneficial as pretreatment steps that complement other treatment processes. For example, advanced oxidation processes can be used to enhance the biodegradation of highly toxic pollutants.

The rates of advanced oxidation processes are greatly enhanced compared to those of oxidation with conventional oxidants because of the high reactivity of the radical species, primarily hydroxyl radicals. The reaction rates of hydroxyl radicals are typically 10^6 to 10^9 times faster than the corresponding reaction rates of strong oxidants such as ozone (Yue, 1992). In order for advanced oxidation processes to be used for water treatment purposes, hydroxyl radicals must be generated in excess. One way in which to achieve this is the irradiation of hydrogen peroxide with ultraviolet (UV) light which induces the decomposition of hydrogen peroxide to form two hydroxyl radicals. Advanced oxidation technologies include processes involving hydrogen peroxide, ozone, ultrasound and UV radiation, or combinations of these.

The rates of chemical reactions can be increased by concentration, pressure, catalysts, ultraviolet light and **cavitation**. Cavitation is defined as the formation, expansion and implosion of bubbles in a liquid (Perry, 1973; Suslick, 1988; Young, 1989; Riesz, et al., 1990). Bubbles are formed due to the reduction of local pressure in a liquid to the vapour pressure of the liquid at a specific temperature. Theoretical calculations indicate that a minimum pressure (known as the cavitation threshold) of 1 013 MPa is required to form bubbles (Shutilov, 1988). However, experimental observations indicate that the cavitation threshold varies from 101 to 2 532 kPa, although a cavitation threshold of 20 260 kPa has also been reported (Chetty, 1994). The cavities collapse when the local pressure is greater than the vapour pressure of the liquid. Collapse of these bubbles leads to the release of considerable energy which is claimed to generate sufficient localised temperatures and pressures to form hydroxyl and hydrogen radicals from the thermal dissociation of water molecules (Chang, et al., 1981). It has been predicted that localised temperatures between 2 273 K and 5 000 K and pressures ranging from 101 MPa to 101 300 MPa occur upon collapse of the bubbles (Noltingk and Neppiras, 1950 in Hughes and Nyborg, 1962; Petersen and Zaleiko, 1981; Suslick, 1988; Mason, 1990a). Cavitation can be produced in a liquid by four different methods :

- *Hydrodynamic cavitation* is produced as a result of pressure variations in a flowing liquid due to the geometry of the system.
- *Acoustic cavitation* is produced by sound waves in a liquid which cause pressure variations.
- *Optic cavitation* is produced by photons of high intensity light (i.e. laser) that rupture a liquid.
- *Particle cavitation* is a result of any type of elementary particles, e.g. protons, rupturing a liquid.

The formation of free radicals due to the dissociation of water molecules into hydroxyl and hydrogen radicals has been reported under the conditions of acoustic cavitation (Makino, et al., 1982) and hydrodynamic cavitation has claimed to result in the production of hydroxyl radicals (Petersen and Zaleiko, 1981).

Watergroup (USA) has developed an advanced oxidation technology (CAV-OX® process) that employs UV radiation, hydrogen peroxide and hydrodynamic cavitation to degrade organic compounds present in water at mg/ℓ concentrations to nondetectable levels by photolysis and oxidation (EPA, 1993). Ideally, the end products of the process are water, carbon dioxide, halides and, in some cases, organic acids. The major components of a CAV-OX® system are the cavitation chamber, UV reactor and control panel. In addition to the production of hydroxyl radicals by the UV photolysis of hydrogen peroxide in the UV reactor, it is claimed that hydrodynamic cavitation, induced in a venturi nozzle in the cavitation chamber, generates hydroxyl and hydrogen radicals which recombine to form hydrogen peroxide and hydrogen gas (EPA, 1993). The CAV-OX® system has been used to treat groundwater contaminated with volatile organic compounds such as trichloroethylene, benzene, toluene and xylene (EPA, 1993). A similar oxidative process combining hydrogen peroxide, hydrodynamic cavitation and ultraviolet radiation has resulted in up to 98 % decreases in the organic concentrations of various wastes, e.g. beverage-making effluent, tannery waste, activated sludge and raw sewerage (Lipowicz, 1981; Petersen and Zaleiko, 1981).

Preliminary evaluation of a CAV-OX® system in 1990 by the Pollution Research Group on the behalf of Diarec Diamonds indicated that hydrodynamic cavitation enhanced the effect of hydrogen peroxide and UV radiation on the decolourisation of dye effluent thus supporting the claims that hydrodynamic cavitation generates hydroxyl radicals (Neytzell-de Wilde and Chetty, 1990). It was also proposed that hydrodynamic cavitation alone may have the potential to inactivate pathogenic bacteria since UV radiation and hydrogen peroxide, the other constituents of the CAV-OX® system, are known to successfully inactivate bacteria. Hydrodynamic cavitation could therefore provide a less capital intensive technique to the present use of chlorine as a disinfectant for raw water treatment since cavitation venturi nozzles could be installed in water systems to exploit the existing pressure/velocity head, e.g. for rural water supply.

2 PROJECT AIMS

This project was initiated to evaluate different methods for the production of free radicals for the oxidation of organic molecules in industrial effluents and potable water. The aims of this project were to :

☐ Investigate the oxidation rate and daughter products of various advanced oxidation processes, or combinations thereof, on a sequence of model organic compounds.

☐ Investigate the disinfection properties of various advanced oxidation processes on model microbiological indicators.

☐ Investigate the effectiveness of these processes on a selected number of process streams such as coloured textile effluent and toxic organic chemical steams.

Due to the possible application of hydrodynamic cavitation as a method for the production of free radicals without further chemical addition, the emphasis of this research project was to investigate hydrodynamic cavitation and evaluate its ability to produce free radicals for the treatment of potable water and industrial effluents, with particular reference to the CAV-OX® system. Ultrasonic cavitation was also investigated during this research project; as a comparative technique to hydrodynamic cavitation since the cavitation effects of sonic waves have been well documented , as well as a treatment method for industrial pollutants.

3 PROJECT OBJECTIVES

The aims of the project were to be achieved by investigation of the following research areas:

☐ The microbiological assessment of hydrodynamic cavitation for the treatment of raw water.

☐ The evaluation of hydrodynamic cavitation in the CAV-OX® system.

☐ The effect of ultrasonic cavitation on organic pollutants in industrial effluents.

☐ The computational fluid dynamics of hydrodynamic cavitation in a venturi.

The potential for the use of hydrodynamic cavitation as a raw water treatment process was assessed by determining the effect of hydrodynamic cavitation on the inactivation of viable bacteria in raw water. The original intention was to use a model, single bacteria species, e.g. *Escherichia coli*, as an indicator of the effectiveness of hydrodynamic cavitation for bacterial inactivation. However, as naturally-occuring bacteria are believed to be more resilient to treatment than laboratory-cultured species, raw water containing a variety of bacteria, was initially used as the indicator since it provided a realistic representation of the bactericidal efficiency of hydrodynamic cavitation. Once the efficiency of a process has been established, the microbiological quality of the water can be evaluated by using selected species of bacteria as indicators.

The CAV-OX® system supplied to the Pollution Research Group by Diarec Diamonds was investigated primarily to determine the concentration of hydrogen peroxide produced by hydrodynamic cavitation in the cavitation chamber. Prior to this, the efficiency of hydrodynamic cavitation produced by the venturi nozzle of the cavitation chamber was determined. Factors affecting the rate of peroxide formation during cavitation were also investigated.

The effect of ultrasonic cavitation on organic pollutants in industrial effluents was investigated as part of an allied Sasol research project in which the viability of ultrasound to degrade hydantoin compounds to more biodegradable products was considered. Hydantoin compounds are formed during the coal gasification process by combination of cyanide, ammonia, carbon dioxide and a ketone, and accumulate in the effluent stream from the coal gasification plant at Sasol. Ultrasound was used as a degradation technique instead of hydrodynamic cavitation since it is widely reported that ultrasound produces cavitation from which hydroxyl radicals are formed. It was postulated that the hydroxyl radicals formed during sonication would oxidise the hydantoin compounds and the degradation products could then be identified and assessed for their biodegradability.

Computational fluid dynamics was investigated as a method to determine the experimental conditions which could lead to cavitation in a venturi. The STAR-CD program was used to determine numerical results for experimental flow conditions in a venturi. Good agreement of the experimentally determined and numerically simulated results for the same flow conditions was used to validate the numerical results.

4 SUMMARY OF RESULTS

In this report, the results from the four areas of research that compiled this project are organised and discussed in terms of the theoretical, physical, chemical and biological effects of cavitation as each of the research topics could encompass more than one of these aspects.

4.1 Theoretical Effects of Cavitation

This section discusses the results obtained from the investigation of the flow conditions that initiate hydrodynamic cavitation using computational fluid dynamics. The STAR-CD program was used to numerically simulate the flow conditions in a venturi (the dimensions of which were reported in literature) and these numerical results were validated by comparison with the published experimental results. It was concluded from this investigation that the numerical method using the STAR-CD program is capable of simulating flow conditions up to cavitation, i.e. to indicate the potential of cavitation in a fluid. In addition, using computational fluid dynamics, it is possible to estimate the local velocities at any point within a venturi thus enabling the determination of local cavitation conditions (as defined by a cavitation number) at any point in a fluid.

4.2 Physical Effects of Cavitation

The characteristics and events of ultrasonic cavitation produced in an ultrasonic cleaning bath and hydrodynamic cavitation produced in two sets of equipment, i.e. the cavitation chamber of the CAV-OX® system (Figure 1) and specially constructed hydrodynamic cavitation rig (Figure 2), were investigated.

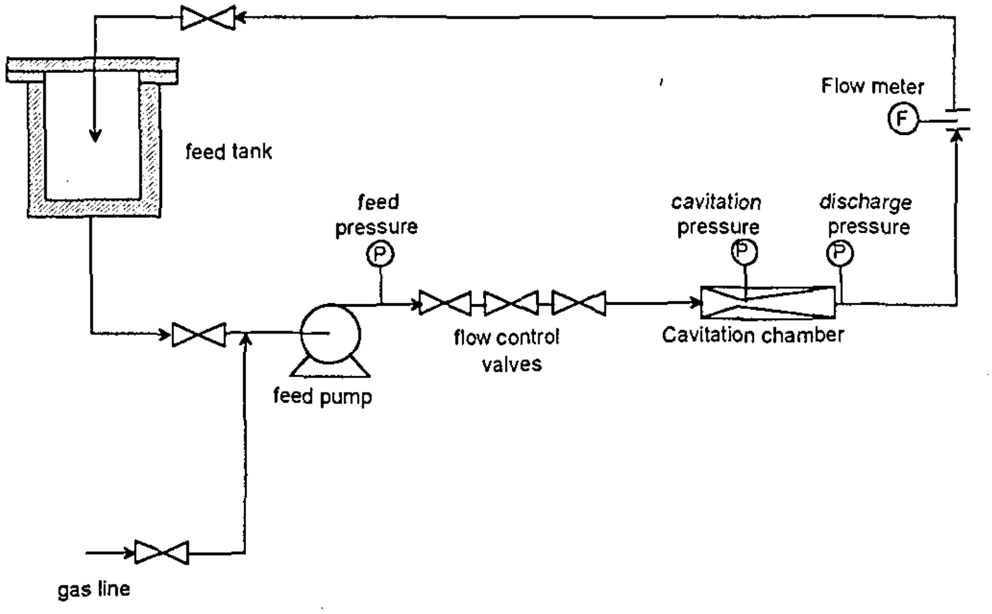

FIGURE 1 : Modified CAV-OX® system used for experiments

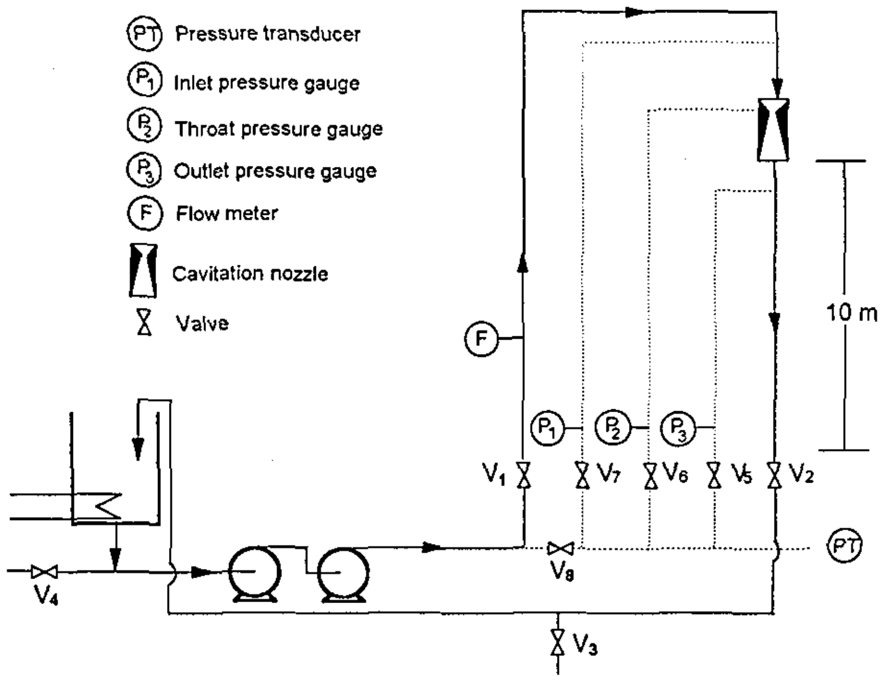

FIGURE 2 : Process instrumentation diagram of the hydrodynamic cavitation rig

Prior to experimentation, the CAV-OX® system was modified by disconnecting the cavitation chamber from the ultraviolet reactors and connecting the system so that water could be recirculated through the cavitation chamber that contained the nozzle. The hydrodynamic cavitation rig was constructed to maximise the intensity of cavitation and thus facilitated a large range of operating conditions. This rig was designed to enable the recirculation of feed water (raw water) through a venturi nozzle which was a perspex replica of the nozzle used in the CAV-OX® unit. The nozzle was installed about 10 metres above the free liquid surface in the feed tank thereby creating a low pressure on the discharge side of the nozzle which favours cavitation.

The physical characteristics of the hydrodynamic cavitation produced in the CAV-OX® chamber and the hydrodynamic cavitation rig were investigated in terms of appearance of bubbles (a phenomenon of cavitation), nozzle flow characteristics, cavitation number (this indicates the intensity of cavitation; the lower the cavitation number, the greater the intensity of cavitation produced) and sound emission. The presence of bubbles, which formed in the throat and collapsed in the divergent section of the chamber, indicated that hydrodynamic cavitation occurred in both systems. The mass of bubbles increased with increasing flow rate, increasing throat pressure and decreasing discharge pressure. From this it was concluded that the degree (intensity) of hydrodynamic cavitation increases with increasing flow rate and as the pressure drop across the nozzle is increased (this was also observed in the investigation of computational fluid dynamics of hydrodynamic cavitation). This was confirmed by the results for the cavitation numbers for the CAV-OX® chamber and hydrodynamic cavitation rig.

The cavitation number is a dimensionless parameter which describes the susceptibility of a fluid to cavitate. It is the ratio of static pressure ($P - P_v$) to dynamic pressure ($\frac{1}{2} \rho u^2$) where P is the local fluid static pressure; P_v is the saturated vapour pressure at the fluid temperature; ρ is the fluid density; and u is the local fluid velocity (Young, 1989). The lower the cavitation number, the more intense the cavitation. Throat cavitation numbers in the CAV-OX® chamber ranged from 0,006 to 0,563 and hydrodynamic cavitation, as indicated by the presence of bubbles, was only observed in the CAV-OX® chamber when the throat cavitation number was less than the threshold cavitation number (which was predicted from extrapolation of literature results to be 0,250 for the CAV-OX® chamber). Cavitation numbers in the hydrodynamic cavitation rig ranged from 0,025 to 0,482; the greatest flow rate and pressure drop across the nozzle resulted in the lowest cavitation number thus confirming that these flow conditions produced the greatest degree of cavitation. Since the collapse of bubbles emit sound, the sound pressure levels determined in the CAV-OX® chamber and hydrodynamic cavitation rig increased with increasing flow rate and pressure drop across the nozzle. The sound pressure levels emitted by the hydrodynamic cavitation rig reached at maximum of 82 dB at 4 000 Hz for the most intense condition of cavitation.

The ultrasonic cavitation produced in a ultrasonic cleaning bath was also characterised in terms of its physical effects. It was proposed that stable ultrasonic cavitation occurs with an intensity of 9,6 kW/m^2 in the ultrasonic cleaning bath. However, this intensity is reduced in the reaction vessel.

4.3 Chemical Effects of Cavitation

The chemical characteristics of hydrodynamic cavitation were determined by evaluating the concentration of hydrogen peroxide produced in the CAV-OX® chamber and hydrodynamic cavitation rig. No detectable amount of hydrogen peroxide was produced by the hydrodynamic cavitation of water in the CAV-OX®

chamber, even in the presence of oxygen (which enhances hydrogen peroxide production). Similarly, no detectable amount of hydrogen peroxide was produced by the hydrodynamic cavitation (using the most intense cavitation conditions) of water in the hydrodynamic cavitation rig. The minimum detection limit of hydrogen peroxide for these experiments was 0,034 mg/ℓ using the spectrophotometric analytical method of Baga, et al. (1988).

The concentration of hydrogen peroxide produced by the ultrasonic cavitation of water in the ultrasonic cleaning bath was determined to be approximately 0,06 mg/ℓ. This result supports the reports that hydroxyl radicals (which combine to form hydrogen peroxide) are formed during ultrasonic cavitation. Saturation of water with oxygen prior to ultrasonic cavitation (sparged for 15 min prior to sonication) significantly enhanced the concentration of hydrogen peroxide (3,5 mg/ℓ) formed. It was concluded that continuous sparging with oxygen was necessary in order to maintain the enhancement of the radical reactions in the presence of oxygen.

The degradation of 1-methylhydantoin by ultrasonic cavitation was investigated and it was demonstrated that partial degradation (approximately 25 to 30 %) occurs, possibly due to oxidation by the radical species (especially hydroxyl radicals) that are formed during ultrasonic cavitation. Degradation of 1-methylhydantoin is enhanced by the addition of 1 332 mg/ℓ hydrogen peroxide (approximately 62 % degradation), and further degradation (approximately 68 %) occurs with the addition of hydrogen peroxide and oxygen saturation prior to sonication.

Investigation into the identification of the sonochemical and photochemical[1] degradation products of 1-methylhydantoin in the presence of hydrogen peroxide indicated that similar products were formed. One of the products formed in the photochemical and sonochemical degradation of 1-methylhydantoin in the presence of hydrogen peroxide was tentatively identified as 1-methylparabanic acid. Oxamide was a suspected product in the sonochemical degradation of 1-methylhydantoin in the presence of hydrogen peroxide and oxygen.

4.4 Biological Effects of Cavitation

As there was no detectable decrease in the colony forming units of raw water bacteria as enumerated by the heterotrophic plate count technique, it was concluded that hydrodynamic cavitation does not inactivate raw water bacteria. However, it was observed from scanning electron micrographs that hydrodynamic cavitation of raw water caused increased dispersal of bacterial aggregates which caused a increase in the turbidity measurements. Consequently, the combination of hydrodynamic cavitation and ultraviolet irradiation was assessed to determine if the dispersal of bacterial aggregates by hydrodynamic cavitation prior to ultraviolet irradiation would enhance bacterial inactivation by ultraviolet light. No significant enhancement in bacterial inactivation was observed when compared with only ultraviolet irradiation. Significant inactivation of raw

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[1] Hydrogen peroxide and UV radiation were used to enable the degradation of more concentrated solutions of 1-methylhydantoin in shorter time periods to produce sufficient quantities of products for separation, collection and identification.

water bacteria (1,6 to 2 log reduction units) occurred upon ultrasonic cavitation of the water in the ultrasonic cleaning bath.

5 REALISATION OF OBJECTIVES

From the results obtained during the project, it would appear that the objectives of the project have been achieved. The potential use of hydrodynamic cavitation for the treatment of raw water without the addition of chemicals has been disproved since hydrodynamic cavitation is not an effective method the inactivation of bacteria in raw water. Similarly, the application of hydrodynamic cavitation as a single advanced oxidation process is not recommended as the concentration of hydrogen peroxide produced by the hydrodynamic cavitation of water (less than 0,034 mg/ℓ) would be ineffective for the oxidation of organic pollutants in industrial effluents and potable water. These results also invalidate the manufacturer's claims about role of hydrodynamic cavitation in the production of hydroxyl and hydrogen radicals in the CAV-OX® system. From the results obtained during this research project, it was concluded that the function of hydrodynamic cavitation produced in the cavitation chamber of the CAV-OX® system is to disperse the effluent to be treated prior to its oxidation with hydrogen peroxide and ultraviolet light. The results obtained for the degradation of 1-methylhydantoin (an organic pollutant in Sasol effluent) by ultrasonic cavitation in the ultrasonic cleaning bath indicate the potential of sonochemistry as an advanced oxidation process for the treatment of industrial effluents. The sonochemical formation of hydroxyl radicals by ultrasonic cavitation can be enhanced for industrial treatment purposes by the addition of hydrogen peroxide and oxygen. The flow conditions, i.e. fluid velocities and pressure drops, which initiate hydrodynamic cavitation in a fluid can be simulated using computational fluid dynamics. However, whilst it has been demonstrated that computational fluid dynamics is a useful tool to indicate the potential of a fluid to undergo cavitation, the numerical simulation of hydrodynamic cavitation which involves two-phase flow using computational fluid dynamics has not been achieved in this project because the flow system is too complex.

6 RECOMMENDATIONS

- ☐ No further investigation into the CAV-OX® process.
- ☐ Further investigation into ultrasonic cavitation on a laboratory and pilot-plant scale for the treatment of industrial effluents.
- ☐ Investigation of the combination of ultrasonic cavitation and ultraviolet treatment using industrial effluents.
- ☐ Investigation of effect of dispersion using hydrodynamic cavitation prior to disinfection with chlorine or ozone on the dose of these disinfectants.
- ☐ No further work on the computational fluid dynamics of hydrodynamic cavitation since detailed flow conditions that occur during cavitation cannot be modelled at present.

7 TECHNOLOGY TRANSFER

☐ The use of computational fluid dynamics in this project by the University of Potchefstroom for Christian Higher Education to describe hydrodynamic cavitation in a venturi has resulted in further application of this method in the Water Research Commission Project No. 648 : *The Application of Computational Fluid Dynamics to Improve the Design and Operation of Water and Wastewater Treatment Works.*

☐ Technical assistance and information has been given to Sasol, Eskom, CG Smith and the University of Durban-Westville on aspects of advanced oxidation technology, in particular sonochemistry.

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Acknowledgements

The work in this report was undertaken for the Water Research Commission sponsored project entitled *Evaluation of Different Methods to produce Free Radicals for the Oxidation of Organic Molecules in Industrial Effluents and Potable Water (with special reference to CAV-OX®)*. The funding of this project by the Water Research Commission is gratefully acknowledged.

The guidance and assistance of the following people involved in the Steering Committee are appreciated :

Dr OO Hart	Water Research Commission (Chairman)
Mr Z Ngcakani	Water Research Commission (Chairman)
Mr PW Weideman	Water Research Commission (Secretary)
Mr P Smit	Water Research Commission (Secretary)
Mr G Offringa	Water Research Commission
Mr JA McWilliam	Diarec Diamonds
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Dr P Stegman	SASTECH, Secunda
Prof FG Neytzell-de Wilde	University of Natal, Durban
Mr RJJ Egenes	University of Natal, Durban
Dr M Starzak	University of Natal, Durban

The research team for the project consisted of the following people :

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Ms B Duvel	University of Natal, Durban
Mr DJ Meyer	Potchefstroom University for Christian Higher Education
Mr GW Schwikkard	University of Natal, Durban

The contributions of various people and organisations to this work are gratefully appreciated. Thanks is extended to:

Mr RG Tracey	Diarec Diamonds
Mr J McWilliam	Diarec Diamonds
Mr I Bailey and Ms J Abbot	Umgeni Water, Pietemaritzburg
Dr P Stegman	SASTECH, Secunda

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ANNEXURE C :	Candace J Botha and Chris A Buckley, *A Study of Hydrodynamic Cavitation as a Method of Water Disinfection*, **Journal of Water Supply Research and Technology** - Aqua, 1995, Vol. 13, No. 2, in print

Abbreviations

AOP	Advanced oxidation process
CFU	Colony forming unit
DMP	2,9-Dimethyl-1,10-phenanthroline
EPA	Environmental Protection Agency, United States of America
GAC	Granulated activated carbon
HPLC	High performance liquid chromatography
1MH	1-Methylhydantoin
RO	Reverse osmosis
UV	Ultraviolet
WRC	Water Research Commission, South Africa

Glossary

Agar	A polysaccharide obtained from *Gelidium* (red alga) and other seaweeds; used as a solidifying agent in culture media.
Bactericidal	Capable of killing bacteria.
Carcinogenic	A cancer-producing substance.
Colony	A macroscopically visible growth of microorganisms on a solid culture medium.
Culture	Any growth, population, or cultivation of microorganisms.
Disinfection	Destruction (or removal) of organisms capable of causing infection.
Disinfectant	An agent that destroys the vegetative cells of infectious microorganisms.
Escherichia coli	Faecal coliforms which test indole-positive at 44,5 °C. Indication of faecal contamination.
Faecal coliforms	Coliform bacteria that produce gas from lactose in a specially-buffered broth incubated at 44,5 °C. Indicator of faecal pollution.
Fluorescence	The immediate emission of visible light from a substance which has absorbed radiation of a shorter wavelength from another source.
***Heterotrophic* Plate Count (HPC)**	An enumeration technique which selects for aerobic heterotrophic microorganisms. Also referred to as Standard Plate Count.
Hydantoin	Five-membered ring compound containing two nitrogen atoms and two carbonyl groups.
Inactivation	Loss of the ability to reproduce (cf death).
Oxidation	A chemical reaction in which a substance loses electrons, or hydrogen atoms, or gains an oxygen atom.
Radical	An atom or group of atoms that posses an unpaired electron.
Raw water	Water in an untreated state.
Spore	A type of resting cell characterised by its resistance to unfavourable environmental conditions.

Chapter 1

Introduction

Environmental legislation and the increasing pollution of water supplies have necessitated the evaluation of existing technologies and the development of new technologies for the removal of organic pollutants from industrial effluents and potable water, and for the disinfection of potable water by the inactivation of bacteria and pathogens.

Traditionally, organic contaminants in industrial effluents and potable water have been removed by separation processes such as adsorption by granulated activated carbon (GAC), air stripping, flocculation and filtration. However, these methods merely transfer the pollutants from one phase to another resulting in problems in the disposal of the waste. Chemical disinfectants, such as chlorine, chlorine dioxide and ozone, are currently used in the production of potable water but there is increasing concern over the formation of potentially hazardous by-products of these processes, e.g. trihalomethanes are toxic residuals formed in the chlorination of potable water and are believed to be carcinogenic.

Recently, advanced oxidation processes (AOP's) have developed as potentially powerful methods for the treatment of organic pollutants in water and the disinfection of potable water. These processes involve the generation of highly reactive free radical intermediates such as the hydroxyl radical. The advantage of AOP's is that organic pollutants can be completely mineralised to carbon dioxide, water and a small amount of acids, while the degradation process usually operates at or near ambient temperature and pressure. In some cases, complete mineralisation may not be achieved due to excessive reaction times, nevertheless, AOP's are potentially beneficial as pretreatment steps that complement other treatment processes. For example, advanced oxidation processes can be used to enhance the biodegradation of highly toxic pollutants.

The rates of advanced oxidation processes are greatly enhanced compared to those of oxidation with conventional oxidants because of the high reactivity of the radical species, primarily hydroxyl radicals ($^{\cdot}OH$). The reaction rates of hydroxyl radicals are typically 10^6 to 10^9 times faster than the corresponding reaction rates of strong oxidants such as ozone, as can be seen from Table 1.1 (Yue, 1992). The rate constants assume second order kinetics.

TABLE 1.1 : Second order reaction rates of ozone and hydroxyl radicals with various categories of organic compounds (Yue, 1992)

Categories of organic compounds	Rate constant (mol/ℓs)	
	O_3	$^{\cdot}OH$
Olefins	1 to 450 x 10^3	10^9 to 10^{11}
S-containing organics	10 to 1,6 x 10^3	10^9 to 10^{10}
Phenols	10^3	10^9
N-containing organics	10 to 10^2	10^8 to 10^{10}
Aromatics	1 to 10^2	$10^8$to 10^{10}
Acetylenes	50,00	10^8 to 10^9
Aldehydes	10,00	10^9
Ketones	1,00	10^9 to 10^{10}
Alcohols	10^{-2} to 1	10^8 to 10^9
Alkanes	10^{-2}	10^6 to 10^9
Carboxylic acids	10^{-3} to 10^{-2}	10^7 to 10^9

The hydroxyl radicals must be generated in excess for AOP's to be efficient for water purification purposes. One way in which to achieve this is the irradiation of hydrogen peroxide (H_2O_2) with ultraviolet (UV) light which induces the decomposition of hydrogen peroxide to form two hydroxyl radicals. Advanced oxidation technologies include processes involving hydrogen peroxide, ozone, ultrasound and UV radiation, or combinations of these. The broad objective of this project was to evaluate different methods for the production of free radicals for the oxidation of organic compounds in industrial effluents and potable waters. This was to be achieved by :

☐ The investigation of the oxidation rate and daughter products of various advanced oxidation processes, or combinations thereof, on a sequence of model organic compounds.

☐ The investigation of the disinfection properties of various advanced oxidation processes on model microbiological indicators.

☐ The investigation of the effectiveness of these processes on a selected number of process streams such as coloured textile effluent and toxic organic chemical steams.

Watergroup (USA) has developed an advanced oxidation technology (CAV-OX® process) that employs UV radiation, hydrogen peroxide and hydrodynamic cavitation to degrade organic compounds present in water at mg/ℓ concentrations to nondetectable levels by photolysis and oxidation (EPA, 1993). Ideally, the end products of the process are water, carbon dioxide, halides and, in some cases, organic acids. The CAV-OX® system has been used to treat groundwater contaminated with volatile organic compounds such as trichloroethylene, benzene, toluene and xylene (EPA, 1993). A similar oxidative process combining hydrogen peroxide, hydrodynamic cavitation and ultraviolet radiation has resulted in up to 98 % decreases in the organic concentrations of various wastes, e.g. beverage-making effluent, tannery waste, activated sludge and raw sewerage (Lipowicz, 1981; Petersen and Zaleiko, 1981). The major components of a CAV-OX® system are the cavitation chamber, UV reactor and control panel. Figure 1.1 shows the configuration of the CAV-OX® system.

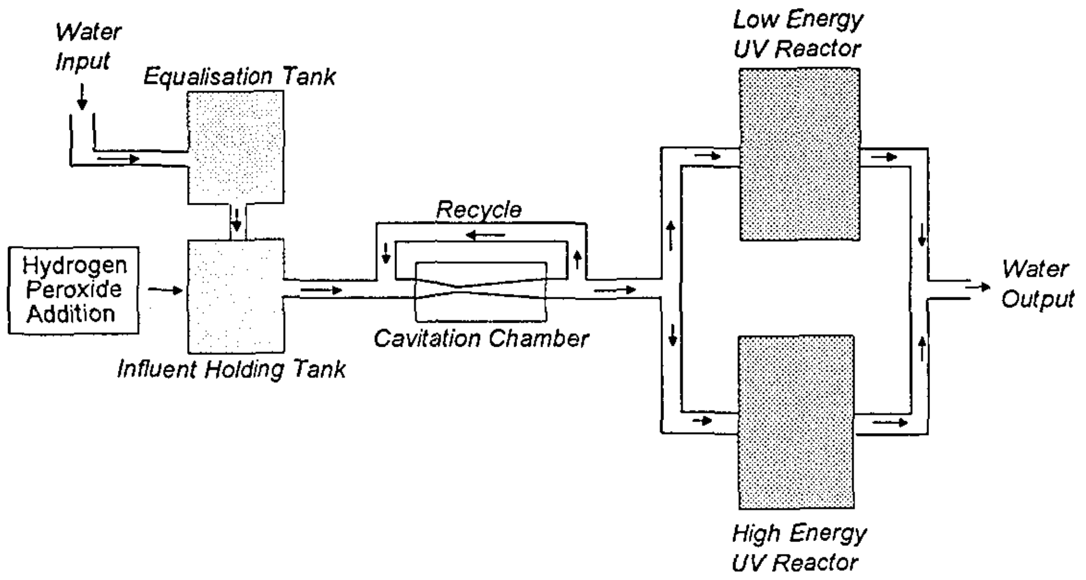

FIGURE 1.1 : Schematic diagram of the CAV-OX® system (EPA, 1993)

In addition to the production of hydroxyl radicals by the UV photolysis of hydrogen peroxide in the UV reactor, it is claimed that hydrodynamic cavitation, induced in a venturi nozzle in the cavitation chamber, generates hydroxyl radicals and hydrogen atoms which recombine to form hydrogen peroxide and hydrogen gas (EPA, 1993). Hydrodynamic cavitation is the reduction of pressure in a liquid stream by increasing the velocity of the liquid by constricting the fluid flow, e.g. in a valve, orifice, etc., and subsequent collapse of the resulting bubbles.

Preliminary evaluation of a CAV-OX® system in 1990 by the Pollution Research Group on the behalf of Diarec Diamonds indicated that hydrodynamic cavitation enhanced the effect of hydrogen peroxide and UV radiation on the decolourisation of dye effluent thus supporting the claims that hydrodynamic cavitation generates hydroxyl radicals (Neytzell-de Wilde and Chetty, 1990). It was also proposed that hydrodynamic cavitation alone may have the potential to inactivate pathogenic bacteria since UV radiation and hydrogen peroxide, the other constituents of the CAV-OX® system, are known to successfully inactivate bacteria.

Hydrodynamic cavitation could therefore provide a less capital intensive technique to the present use of chlorine as a disinfectant for raw water treatment since cavitation venturi nozzles could be installed in water systems to exploit the existing pressure/velocity head. It could therefore find application in the production of potable water in rural areas. Therefore, the emphasis of this research project was the investigation of hydrodynamic cavitation for the production of free radicals for the treatment of potable water and industrial effluents with particular reference to the CAV-OX® system. Ultrasonic cavitation was also investigated during this research project, mainly as a comparative technique since the cavitation effects of sonic waves has been well documented. Consequently, this project investigated the following areas:

☐ The microbiological assessment of hydrodynamic cavitation for the treatment of raw water.

☐ The evaluation of hydrodynamic cavitation in the CAV-OX® system.

☐ The effect of ultrasonic cavitation on organic pollutants in industrial effluents.

☐ The computational fluid dynamics of hydrodynamic cavitation in a venturi..

The potential for the use of hydrodynamic cavitation as a raw water treatment process was assessed by determining the effect of hydrodynamic cavitation on the inactivation of viable bacteria in raw water. The original intention was to use a model, single bacteria species, e.g. *Escherichia coli*, as an indicator of the effectiveness of hydrodynamic cavitation for bacterial inactivation. However, as naturally-occuring bacteria are believed to be more resilient to treatment than laboratory-cultured species, raw water containing a variety of bacteria, was initially used as the indicator since it provided a realistic representation of the bactericidal efficiency of hydrodynamic cavitation. Once the efficiency of a process has been established, the microbiological quality of the water can be evaluated by using selected species of bacteria as indicators.

The CAV-OX® system supplied to the Pollution Research Group by Diarec Diamonds was investigated primarily to determine the concentration of hydrogen peroxide produced by hydrodynamic cavitation in the cavitation chamber. Prior to this, the efficiency of hydrodynamic cavitation produced by the venturi nozzle of the cavitation chamber was determined. Factors affecting the rate of peroxide formation during cavitation were also investigated.

The effect of ultrasonic cavitation on organic pollutants in industrial effluents was investigated as part of an allied Sasol research project in which the viability of ultrasound to degrade hydantoin compounds to more biodegradable products was considered. Hydantoin compounds are formed during the coal gasification process by combination of cyanide, ammonia, carbon dioxide and a ketone, and accumulate in the effluent stream from the coal gasification plant at Sasol. Ultrasound was used as a degradation technique instead of hydrodynamic cavitation since it is widely reported that ultrasound produces cavitation from which hydroxyl radicals are formed. It was postulated that the hydroxyl radicals formed during sonication would oxidise the hydantoin compounds and the degradation products could then be identified and assessed for their biodegradability.

The investigation of computational fluid dynamics as a method to determine the experimental conditions which could lead to cavitation in a venturi was undertaken by the Department of Mechanical Engineering at Potchefstroom University for Christian Higher Education. The STAR-CD program was used to determine numerical results for experimental flow conditions in a venturi. Good agreement of the experimentally determined and numerically simulated results for the same flow conditions was used to validate the numerical results.

This report combines the results from these different investigations by highlighting the aspects of the work achieved, the results obtained and the conclusions reached. This report is divided into three parts.

Chapter 2 consists of *a discussion of cavitation and summary of its characteristics as reported in literature.* Also included are the experimental setups of the equipment used in the project.

Chapter 3 summarises the experiments performed and discusses the results obtained from the projects. This chapter is organised in terms of the theoretical, physical, chemical and biological effects caused by cavitation. The section on theoretical aspects considers the work undertaken on the computational fluid dynamics of cavitation. The physical characteristics observed in the CAV-OX® system, hydrodynamic cavitation rig and ultrasonic cleaning bath are described in the section on the physical effects of cavitation. Similarly, the chemical effects produced in the CAV-OX® system, hydrodynamic cavitation rig and ultrasonic cleaning bath are reported in their own section. The section on the biological effects of cavitation contains the work undertaken to evaluate the microbiological effectiveness of hydrodynamic cavitation produced in the hydrodynamic cavitation rig.

The conclusions from this project are presented in **Chapter 4** and recommendations for future work are discussed in **Chapter 5** of the report. **Chapter 6** details the list of publications and technology transfer actions taken during this project. The data resulting from the project is available in the **Annexures** to this report.

Chapter 2

Cavitation

Cavitation is defined as the formation, expansion and implosion of bubbles in a liquid (Perry, 1973; Suslick, 1988; Young, 1989; Riesz, et al., 1990). Bubbles are formed due to the reduction of local pressure in a liquid to the vapour pressure of the liquid at a specific temperature. Theoretical calculations indicate that a minimum pressure (known as the cavitation threshold) of 1 013 MPa is required to form bubbles (Shutilov, 1988). However, experimental observations indicate that the cavitation threshold varies from 101 to 2 532 kPa, although a cavitation threshold of 20 260 kPa has also been reported (Chetty, 1994). The bubbles, which contain gas, vapour or a mixture of both, expand as a result of the reduction in pressure at constant temperature (cavitation) or by an increase in temperature (boiling). The vapour bubbles formed by cavitation consist mainly of gases which have come out of solution. The formation of these cavities is also dependent on the presence of nuclei which can either be submicroscopic gas bubbles or solid particles.

The cavities collapse when the local pressure is greater than the vapour pressure of the liquid. Collapse of these bubbles leads to the release of considerable energy which is claimed to generate sufficient localised temperatures and pressures to form hydroxyl radicals and hydrogen atoms from the thermal dissociation of water molecules (Chang, et al., 1981). Localised temperatures of up to 2 273 K and pressures up to 20 260 MPa have been reported (Petersen and Zaleiko, 1981). However, instantaneous localised temperatures have been predicted to be 5 000 K with pressures ranging from 101 MPa (Suslick, 1988;. Mason, 1990a) to 101 300 MPa (Noltingk and Neppiras, 1950 in Hughes and Nyborg, 1962) upon collapse of the bubbles. Noise, vibration and extensive pitting of boundary materials is caused in the regions of bubble collapse (Perry, 1973).

Cavitation can be produced in a liquid by four different methods :

- **Hydrodynamic cavitation** is produced as a result of pressure variations in a flowing liquid due to the geometry of the system.
- **Acoustic cavitation** is produced by sound waves in a liquid which cause pressure variations.
- **Optic cavitation** is produced by photons of high intensity light (i.e. laser) that rupture a liquid.
- **Particle cavitation** is a result of any type of elementary particles, e.g. protons, rupturing a liquid.

The formation of free radicals due to the dissociation of water molecules into hydroxyl radicals and hydrogen atoms has been reported under the conditions of acoustic cavitation (Makino, et al., 1982) and hydrodynamic cavitation has been claimed to result in the production of hydroxyl radicals (Petersen and Zaleiko, 1981). Free radicals are defined as an atom or group of atoms that possess an unpaired electron (Morrison and Boyd, 1987).

Hydrodynamic cavitation was investigated for its potential to produce hydroxyl radicals and its ability to inactivate bacteria in raw water since this is the form of cavitation utilised in the CAV-OX® system. Since there is much information available in literature on ultrasonic cavitation, this was used as a comparative technique for the inactivation of raw water bacteria. Ultrasonic cavitation was selected as the process for the degradation of hydantoin compounds in industrial effluent.

2.1 ULTRASONIC CAVITATION

In a stationary liquid, the ambient pressure can be varied by the transmission of sound waves through the medium. **Ultrasonic cavitation** occurs if the pressure amplitude of the applied sound is greater than a certain minimum pressure called the cavitation threshold (Webster, 1963). Two types of cavitation result : ***transient cavitation*** and ***stable cavitation***. Transient cavitation involves a relatively violent activity in which spots of high temperatures and pressures occur in very short bursts at localised points in the sonicated medium. These implosions may be accompanied by localised shock waves and/or the generation of free radicals. Stable cavitation is a much less violent phenomenon associated with vibrating gaseous cavities. Due to oscillations of the bubbles, the adjacent liquid flows. This effect can be increased by the collapse of cavities which results in shock waves that enhance the flow of liquid. This is termed as microstreaming.

Inactivation of bacteria by ultrasound has been proposed to result from the microstreaming effect of ultrasonic cavitation (Scherba, et al., 1991). However, ultrasonic cavitation also gives rise to various effects such as mechanical forces due to surface resonances of the bacterial cell wall, pressure gradients resulting from the collapse of cavities near the cell wall or the radial resonances of bubbles, velocity effects of the direct sound beam and free radical formation (Neppiras and Hughes, 1964). In addition, shearing stresses can result from shock waves (Thacker, 1973). Although doubt exists as to the exact cause of bacterial inactivation by ultrasonic cavitation, it seems unlikely that free radical attack of the bacterial cell wall is responsible since cell rupture and free radical formation occur independently of one another (Hughes and Rogers, 1959 in Neppiras and Hughes, 1964). A possible explanation for this is that the peroxide radicals that are formed during cavitation are scavenged by the suspending medium (Thacker, 1973). It is, however, suggested that bacterial cell rupture occurs as a result of the mechanical stresses that occur during ultrasonic cavitation (Hughes and Nyborg, 1962; Thacker, 1973).

The high temperatures and pressures resulting from the collapse of the bubbles produce hydroxyl and hydrogen radicals[1] from the dissociation of water molecules according to the following reaction (Weissler, 1959; Webster, 1963; Todd, 1970; Makino, et al., 1982; Bremner, 1986; Riesz, et al., 1990) :

$$H_2O \rightarrow {}^{\bullet}H + {}^{\bullet}OH \qquad (2.1)$$

One of the observations that supports the formation of free radicals from water by ultrasound is the weak emission of light during cavitation (sonoluminescence). This probably occurs due to the recombination of hydroxyl and hydrogen radicals in water according to the following reaction (Jarman and Taylor, 1970; Young, 1989).

$${}^{\bullet}OH + {}^{\bullet}H \rightarrow H_2O + h\nu \qquad (2.2)$$

Hydroxyl and hydrogen radicals formed in ultrasonic cavitation can be initiators of chemical reactions. The primary reactions that occur in pure water are recombination of the radicals, i.e.

$${}^{\bullet}H + {}^{\bullet}OH \rightarrow H_2O, \qquad (2.3)$$

$${}^{\bullet}OH + {}^{\bullet}OH \rightarrow H_2O_2 \qquad (2.4)$$

and

$${}^{\bullet}H + {}^{\bullet}H \rightarrow H_2. \qquad (2.5)$$

The presence of hydrogen peroxide in sonicated water has been reported by various researchers (Schmitt, et al., 1929; Weissler, 1959; Suslick, 1988). Hydrogen peroxide is formed by the recombination of the radical species (Reaction 2.4) resulting from the dissociation of water (Reaction 2.1). The presence of hydrogen peroxide in cavitated water provides indirect evidence for the formation of free radical species by cavitation.

The hydrogen peroxide yield upon sonolysis of water increases in the order O_2 > Air > Ar > N_2 when these gases are present in solution. In the presence of oxygen gas, the yield of hydrogen peroxide is increased by the following reactions (Weissler, 1959; Mead, et al., 1976)

$${}^{\bullet}H + O_2 \rightarrow HO_2^{\bullet} \qquad (2.6)$$

and

---

[1] A hydrogen radical and a hydrogen atom are identical electronic species, i.e. both have a single unpaired electron, therefore hydrogen radicals are often referred to in literature as hydrogen atoms. In this report, the hydrogen species resulting from the homolysis of a water molecule will be referred to as a hydrogen radical.

$$HO_2^\bullet + HO_2^\bullet \rightarrow H_2O_2 + O_2 . \qquad (2.7)$$

The addition of hydrogen gas to oxygenated water can further enhance the yield of hydrogen peroxide by increasing the yield of hydrogen radicals from the dissociation of hydrogen gas. These hydrogen radicals subsequently react with the oxygen present (Reaction 2.6) thus increasing the yield of hydrogen peroxide as a result of Reaction 2.7. However, enhancement of the hydrogen peroxide yield only occurs for a maximum concentration of hydrogen of 20 %. Above this concentration, the yield of hydrogen peroxide decreases due to the reaction of hydroxyl radicals with hydrogen gas according to Reaction 2.8 :

$$^\bullet OH + H_2 \rightarrow H_2O + {}^\bullet H \qquad (2.8)$$

Various other radical reactions occur which lead can lead to complex chemical reactions (Mead, et al., 1976; Weissler, 1979). Schwikkard (1994) discusses these reactions in detail. The hydroxyl radicals generated in ultrasonic cavitation can react with organic compounds present in solution resulting in the oxidation of these compounds.

Laboratory-scale sonochemical experiments can either be performed using an ultrasonic bath or probe. Ultrasonic reactors are available for large-scale industrial uses of sonochemistry. Generally, the use of different equipment makes comparison of published results for sonochemical experiments in literature difficult since factors such as the frequency and power output of the bath, size of the bath, the type of the reaction vessel and its position in the bath (Mason, 1991). Consequently, each ultrasonic bath and probe will give an unique result. Indirect comparison of the intensity of cavitation induced by sonic waves can be made by the quantitation of the hydrogen peroxide produced by the recombination of hydroxyl radicals formed during ultrasonic cavitation. This was carried out during the investigation of hydantoin degradation by ultrasonic cavitation (Schwikkard, 1994).

A KERRY Pulsatron cleaning bath was used for the experiments involving ultrasonic cavitation. This bath has a capacity of 8 ℓ and operates at a frequency of 38 kHz (220/240 V; 50/60 Hz phase). A temperature control system was installed by Schwikkard (1992). Figure 2.1 illustrates the setup of the ultrasonic bath used in the experiments.

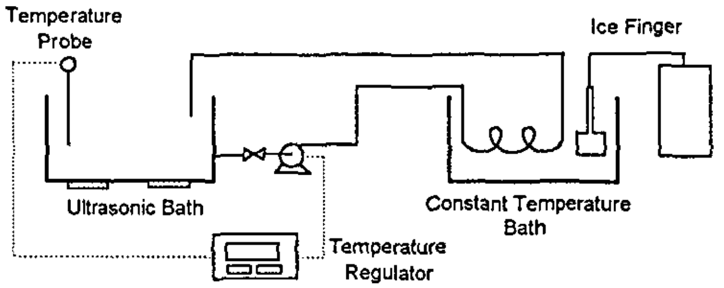

FIGURE 2.1 : Schematic diagram of the ultrasonic bath and temperature control system (Schwikkard, 1992)

2.2 HYDRODYNAMIC CAVITATION

Hydrodynamic cavitation occurs when the pressure of a fluid liquid stream can be decreased by increasing the velocity of the liquid. This causes a decrease in the local pressure to less than the vapour pressure of the liquid resulting in the formation of vapour-filled cavities in the liquid (Young, 1989).

There are three cases of flow cavitation :

- **Travelling cavitation** occurs when bubbles form within a liquid which, as they travel with the liquid, expand and subsequently collapse.
- **Fixed cavitation** occurs when a bubble forms that is attached to an immersed body, or to the surface of the flow channel, and remains fixed in position in an unsteady state.
- **Vortex cavitation** occurs in the cores of vortices that form in regions of high shear.

Travelling cavitation occurs in the cavitation nozzle of the CAV-OX® system. It is possible that free radical formation can be produced by hydrodynamic cavitation in a nozzle due to the high temperatures generated on collapse of the bubbles. This appears to be confirmed by reports that luminescence has been observed in venturi nozzles (Jarman and Taylor, 1964, 1965; Peterson and Anderson, 1967). The formation of hydroxyl radicals in the CAV-OX® system as a result of hydrodynamic cavitation was therefore investigated (Chetty, 1994). Prior to experimentation, the CAV-OX® system was modified by disconnecting the cavitation chamber from the ultraviolet reactors and the system connected so that water could be recirculated through the cavitation chamber that contained the nozzle. A transparent tube was connected after the outlet to the cavitation chamber to observe if cavitation persisted in the liquid after the cavitation chamber. A gas inlet was added to the system before the feed pump to the cavitation chamber so as to facilitate mixing of the two phases. Valves were added between the feed pump and the cavitation chamber to control the flow rate. Figure 2.2 illustrates the modified CAV-OX® system.

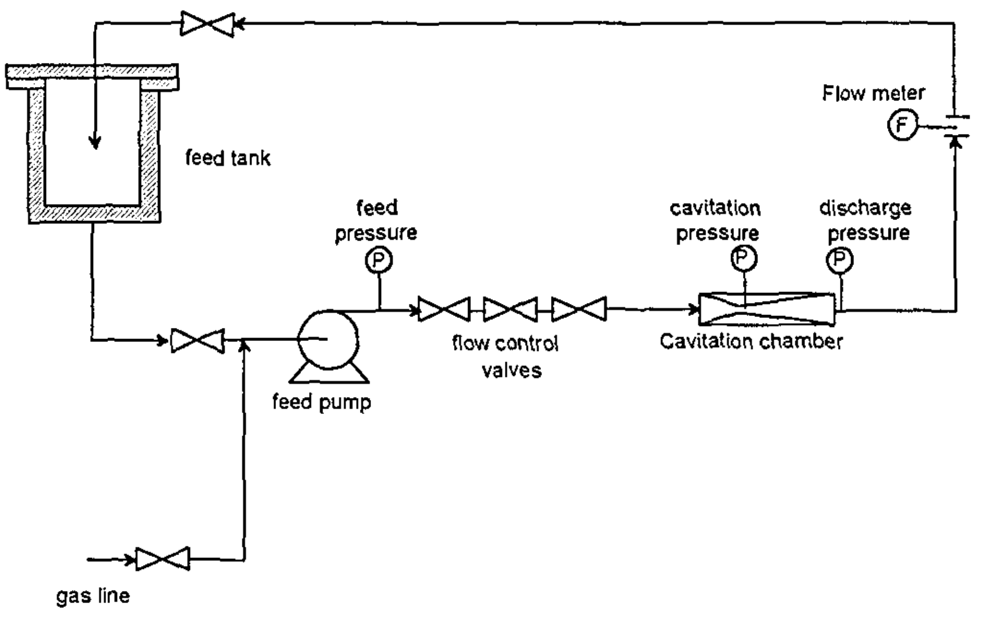

FIGURE 2.2 : Modified CAV-OX® system used for experiments (Chetty, 1994)

Since hydrodynamic cavitation is known to produce mechanical stresses, such as shock waves and pressure gradients, which are similar to the effects produced by ultrasound, *the destruction of bacteria by hydrodynamic* cavitation is a possibility. The effect of hydrodynamic cavitation on bacteria was assessed by the construction of a cavitation rig which maximised the intensity of cavitation and thus facilitated a large range of operating conditions. This rig was designed to enable the recirculation of feed water (raw water) through a venturi nozzle which was a perspex replica of the nozzle used in the CAV-OX® unit. The nozzle was installed about 10 metres above the free liquid surface in the feed tank thereby creating a low pressure on the discharge side of the nozzle which favours cavitation. A schematic diagram of the hydrodynamic cavitation rig is shown in Figure 2.3.

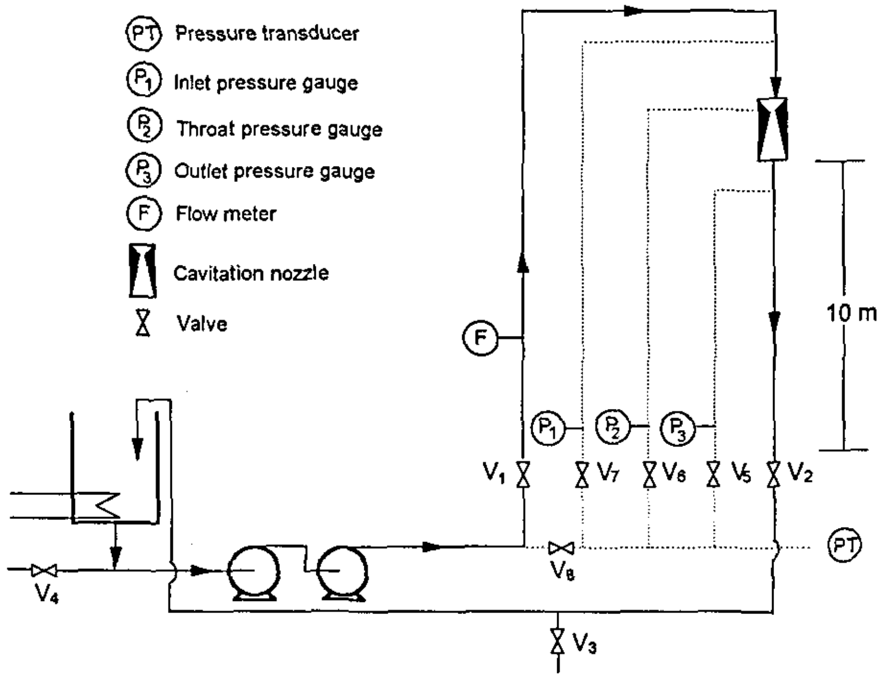

FIGURE 2.3 : Process instrumentation diagram of the hydrodynamic cavitation rig *(Botha, 1993)*

Both pieces of equipment, i.e. the CAV-OX® system and the hydrodynamic cavitation rig, were evaluated for their ability to produce cavitation by characterising the nozzle hydraulics in terms of flow rate, sonic pressure levels, energy input and cavitation number. The results are summarised in **Chapter 3** of this report.

A venturi was used in the numerical simulation of the flow conditions leading to hydrodynamic cavitation using computational fluid dynamics (Meyer, 1993a). The dimensions of the venturi used in this investigation were identical to those of the venturi used in the experimental investigation of the damage caused by cavitating flow in a venturi on metal inserts to ascertain the cavitation damage that occurs on bladed profiles such as propeller blades (Hamit, et al.,1965). The venturi which consists of a nozzle, throat and diffuser, is illustrated in Figure 2.4.

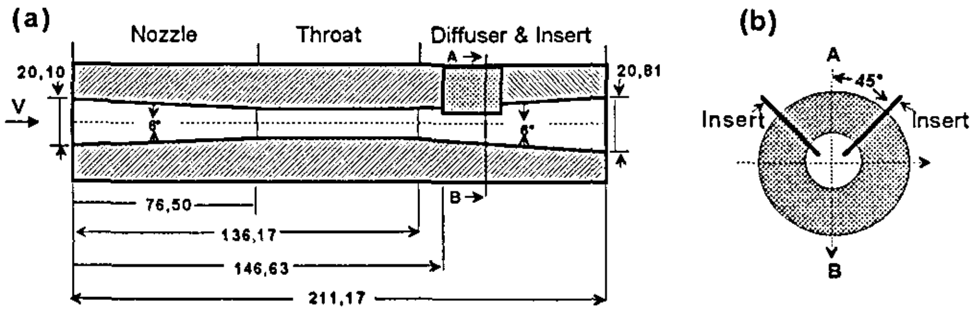

FIGURE 2.4 : Geometry and dimensions of the venturi used in the simulation of hydrodynamic cavitation from a transverse view (a) and a cross-sectional view (b). Unless specified, all the measurements are in mm (from Meyer, 1993a)

The nozzle is the convergent section of the venturi, i.e. the area of the venturi through which the flow decreases, and has a length of 76,0 mm and an included angle of 6 °. The throat section of the venturi has a constant radius of 6,477 mm and is 59,67 mm in length. The convergent section of the venturi is the diffuser which has a length of 64,54 mm and an included angle of 6 °. The total length of the venturi is 211,17 mm. Two bladed-profile inserts were placed in the diffuser of the venturi, 143,46 mm from the inlet of the throat (Figure 3.3(a)). As illustrated in Figure 3.3(b), these inserts were placed at right angles to each other.

Chapter 3 summarises the results obtained from the investigations of ultrasonic and hydrodynamic cavitation using the equipment reported in this chapter.

Chapter 3

Effects of Cavitation

This chapter consolidates the results obtained from the four areas of research that comprised this project, namely,

- ☐ The computational fluid dynamics of hydrodynamic cavitation in a venturi.
- ☐ The microbiological assessment of hydrodynamic cavitation for the treatment of raw water.
- ☐ The evaluation of hydrodynamic cavitation in the cavitation chamber of the CAV-OX® system.
- ☐ The effect of ultrasonic cavitation on organic pollutants in industrial effluents.

The results from the various areas are organised and discussed in terms of the theoretical, physical, chemical and biological effects of cavitation since each of the above research topics could encompass more than one of these aspects.

3.1 THEORETICAL EFFECTS OF CAVITATION

This section reviews the results obtained using computational fluid dynamics (CFD) to investigate the flow conditions that initiate hydrodynamic cavitation. In order to verify the numerical simulation, the results from the computer simulation of the flow in a venturi were compared with the experimental results available in the literature (Hamit, 1963; Hamit, et al., 1965; Ivany, et al., 1966).

3.1.1 Numerical Method

The flow through a venturi under cavitating conditions was simulated using an academic version of the STAR-CD program run on a convex parallel-processing minicomputer. This program can successfully simulate three-dimensional flow with heat transfer in complex geometries (STAR-CD manual, 1993).

3.1.1.1 Assumptions

- As mentioned in the previous chapter, hydrodynamic cavitation involves the formation of vapour-filled cavities (bubbles) in a fluid, i.e. two-phase flow occurs during hydrodynamic cavitation. However, since the STAR-CD program used in this study could not simulate two-phase flow, it was assumed that the bubbles are a minor component of the flow when evaluated from the whole perspective and therefore only the fluid phase (single-phase flow) was simulated.
- The flow was assumed to be incompressible due to the fact that the gaseous phase, which causes extreme pressures in a cavitating fluid, was not simulated.

- The flow through the venturi nozzle was assumed to be steady due to the absence of the gaseous phase (bubbles).
- To enable comparison of the numerical results with the experimental results (Hamit, 1963; Hamit, et al., 1965; Ivany, et al., 1966), turbulent flow through a venturi was simulated.
- As the gaseous component of cavitation was not considered in the simulation and heat is only generated upon gaseous bubble collapse (Mason, 1990a; Suslick, 1989 in Mason, 1991), the flow was assumed to be isothermal.

3.1.1.2 Modifications of the Numerical Method

The above assumptions enable the simplification of the Navier-Stokes equations which describe flow conditions such that the numerical method is less involved (Anderson, et al., 1984; STAR-CD manual, 1993). However, the Navier-Stokes equations cannot numerically simulate the macroscopic effects of turbulent flow since the time and distance increments used in the numerical simulation have to be extremely small. Consequently, the simulation is time-consuming as a number of equations are required to be solved for every grid point, in addition, only a small part of the flow can be simulated in this way. This problem can be overcome by solving the effect of turbulence, and not the details of turbulent flow, with the k-ε turbulence model (Anderson, et al., 1984).

As pressure is not a primary variable in the equations that describe flow, the SIMPLE-algorithm, which calculates a pressure field from the continuity equation and then solves for the velocities in the momentum equations (Patankar, 1980), was used in the STAR-CD program. The conjugant-gradient method is used to solve the algebraic equations (STAR-CD manual, 1993).

3.1.2 Verification of the Numerical Method

Evaluation of the STAR-CD program for the simulation of various flow problems and benchmarks[1] has resulted in good correlation with experimental results. However, in order to use this program to numerically simulate the flow conditions required for the development of cavitation in a venturi, it was necessary to determine the inlet flow conditions for a venturi. Therefore, fully-developed, turbulent flow through a pipe was simulated using the STAR-CD program and the numerical results verified by comparison with the published experimental results in Martinuzzi & Pollard (1989) and Pollard & Martinuzzi (1989). The turbulent flow in this simulation had a Reynolds number of 380 000 in order to conform with the experimental flow conditions.

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[1] A benchmark is a standardised experiment carried out to evaluate numerical results to verify a numerical method, simulation or algorithm. The conditions of the experiment are very controlled (all the necessary boundary conditions are known) hence the results should be extremely accurate (Meyer, 1993b).

A fully turbulent flow profile in a pipe is only established after 50 to 80 pipe diameters. Thus, to model turbulent flow in a pipe with a radius of 6,477 mm, simulation of more than 640 mm of pipe before the venturi is required. The simulation of this pipe section could be avoided by specifying a velocity profile at the inlet to the venturi which would numerically simplify the simulation by reducing its size. The Blasius $\frac{1}{7}$ Law (Daugherty, et al., 1989) was used to specify the velocity profile at the inlet of a hydraulic smooth pipe :

$$\frac{u}{u_{\max}} = \frac{(R - R)^{\frac{1}{7}}}{R} \tag{3.1}$$

where :

u = the axial velocity for a pipe of radius, r

u_{max} = the maximum velocity in the pipe

R = the radius of the pipe wall

The grid used in the pipe had 50 x 17 x 9 (7 650) points in the axial, radial and angular directions respectively. The first point was chosen close enough to the wall to enable the use of the wall-functions to simulate the effect of the rigid wall on the flow as described by Launder and Spalding (1973) and the STAR-CD manual (1993). Prior to simulation with the STAR-CD program, the velocity was normalised by using the mean velocity in the pipe (u_{mean}) and the radial position mormalised with the pipe radius (R) of 6,477 mm. The normalised, numerically simulated velocity profile for fully-developed turbulent flow in a pipe (Reynolds number of 380 000) was compared with the *experimental results of Nikuradse (Martinuzzi & Pollard, 1989; Pollard &* Martinuzzi, 1989) and the numerically simulated results using Launder's method (Launder and Spalding, 1973). The results are illustrated in Figure 3.1.

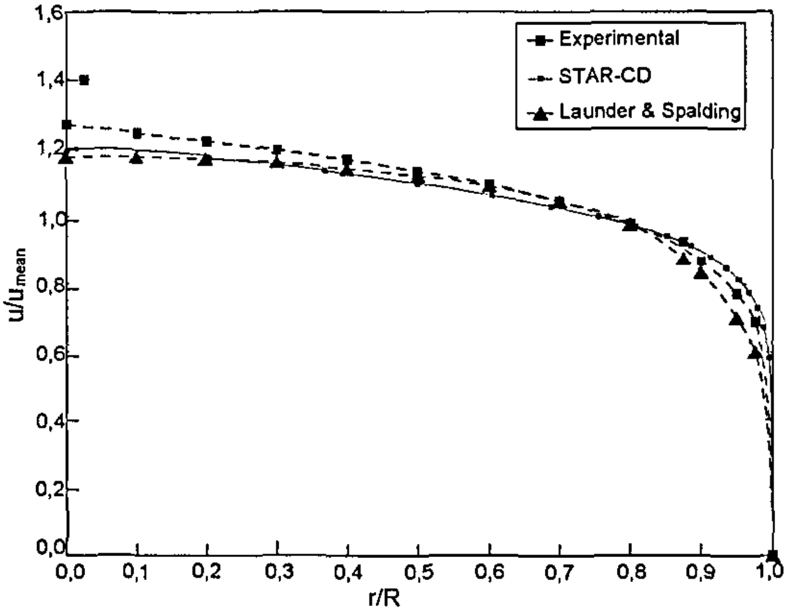

FIGURE 3.1 : Comparison of normalised, numerically simulated velocity profile from STAR-CD *and the numerical reults* obtained *using* Launder's method (Launder and Spalding, 1973) with the experimentally determined velocity profile (Nikaradse in Martinuzzi & Pollard, 1989; Pollard & Martinuzzi, 1989) for fully developed, turbulent flow in a pipe at a Reynolds number of 380 000

From Figure 3.1, it can be seen that, near the symmetry axis (r/R < 0,3), there is a better fit of the numerically-simulated results from STAR-CD with the experimental results than those from Launder's method. However, between r/R = 0,3 and r/R = 0,8, Launder's results compare better with the experimental results , but near the wall of the pipe (r/R > 0,8), the STAR-CD results agree more with the experimental results. This region is important since prediction of the correct velocities and pressures near the wall of a pipe is essential for the simulation of cavitation near a rigid wall where cavitation erosion could occur. The deviations between the simulated and experimental results are probably due to the unknown wall roughness used in the experiments and the simulations (a hydraulically smooth pipe was used in the STAR-CD program). It was therefore concluded that the numerically-simulated results from the STAR-CD program satisfactorily predict the experimental conditions for turbulent flow in a pipe.

The axial pressure drop profile in the pipe was also determined using the STAR-CD program and the results are illustrated in Figure 3.2.

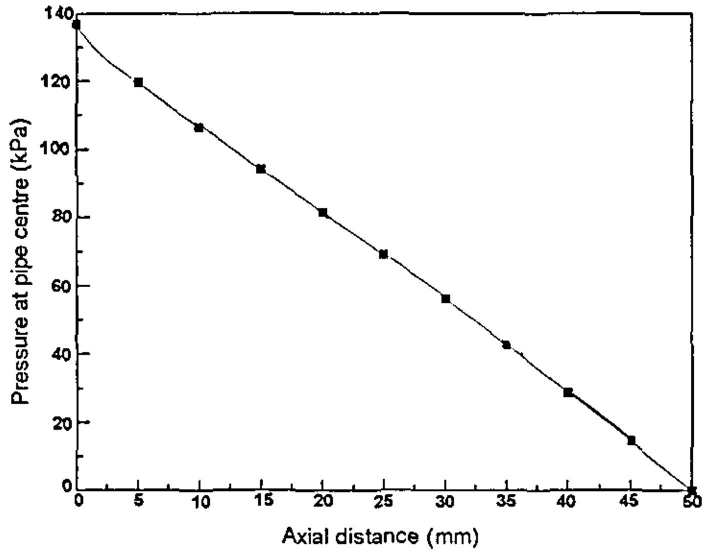

FIGURE 3.2 : Numerically-simulated axial pressure drop profile for turbulent flow conditions having a Reynolds number of 380 000 in a hydraulically smooth pipe with a radius of 6,477 mm using the STAR-CD program

Initially, the pressure drop is non-linear as the inlet velocity used in the simulation was estimated by Equation 3.1. From Figure 3.2, the simulated pressure drop across the pipe was determined to be 2,666 kPa/m. A pressure drop of 2,895 kPa/m was calculated from the Moody chart (Daugherty, et al., 1989). Since the wall roughness is unknown, the correlation between the simulated and experimental results is satisfactory.

3.1.3 Cavitation in a Venturi

The simulation of cavitation in a venturi (refer to Figure 2.4) was performed for flow having a Reynolds number of 302 000 and under standard cavitation conditions. Standard cavitation refers to the condition in which termination of cavitation occurs approximately 155 mm from the inlet of the venturi. The numerical results were then compared with experimental results which were obtained for standard cavitation conditions in a venturi (Hamit,1963; Hamit, et al., 1965).

For incompressible flow conditions in the numerical simulation, the pressure field is calculated relative to an arbitary zero pressure at the outlet of the venturi, i.e. only the pressure drop is important as this causes the flow. However, for standard cavitation conditions, the absolute static pressure is required and can be determined from the experimental results for a specific point in the venturi. In the numerical simulation, this point was chosen at the beginning of the divergent part of venturi, 136,17 mm from the inlet and the static pressure at this point can be calculated from the cavitation number. The cavitation number, σ_C, is defined as :

$$\sigma_c = \frac{P - P_v}{\frac{1}{2}\rho u_m^2} \qquad (3.2)$$

where :

P = local static pressure (kPa)

P_v = saturated vapour pressure at the fluid temperature (kPa)

ρ = fluid density (kg/m^3)

u_m = mean throat velcity (m/s).

Hammit, et al. (1965) experimentally determined a cavitation number, σ, of 0,01 for standard cavitation of water (density of 998 kg/m^3) in a venturi containing bladed inserts at a Reynolds number of 302 000, i.e. for a mean throat velocity of 23,36 m/s. A calculated static pressure of 2,45 kPa therefore exists in the fluid at the point 136,17 mm from the inlet of the venturi for a vapour pressure of 2,339 kPa and the experimental cavitation conditions of Hamit, et al. (1965). The pressure used in the numerical simulation of cavitation at this point was adjusted so that it would equal the experimental static pressure at this point in the venturi.

Figure 3.3 compares the experimental results of Hamit, et al. (1965) with the numerically simulated results obtained for the cavitation numbers at the different axial points where pressure was measured in the venturi. Point **d** on the graph is the reference point, 136,17 mm from the inlet of the venturi, where the static pressure of 2,45 kPa exists.

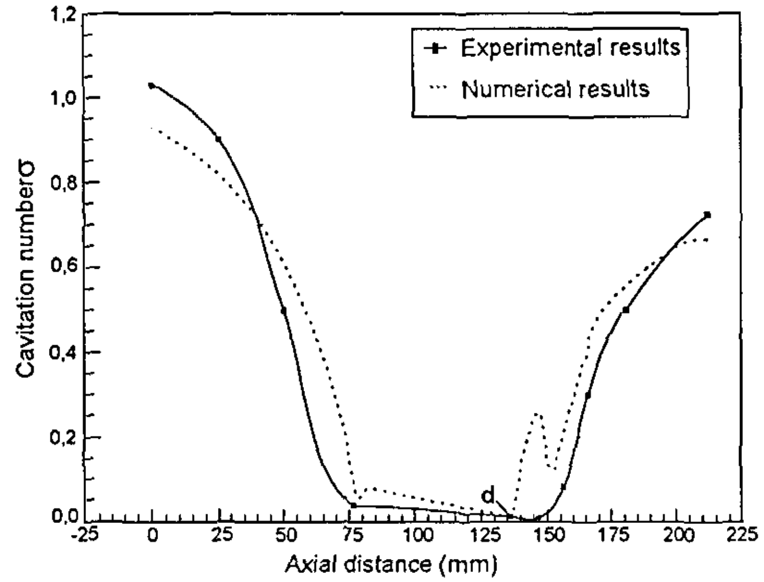

FIGURE 3.3 : Comparison of cavitation in a venturi for numerically simulated results and experimentally determined results (Hamit, et al., 1965) under the same flow conditions (Reynolds number of 302 000)

The numerically simulated cavitation number profile was calculated using a series of axial program points on the wall of the venturi and shows reasonable agreement with the experimental values. The numerically calculated cavitation number is lower than the experimental results at the inlet of the venturi due to the lower pressure loss resulting from the simplified inlet geometry used in the program. In addition, the pressure defined at the inlet in the simulation and experiments is different which would also affect the results. The unspecified wall roughness and local effects caused at the pressure taps from which the pressure measurements were made in the experiment could also result in discrepancies in the experimental and numerical results. The slight 'bump' in the numerical cavitation number profile that occurs on the graph after point d is caused by the presence of the bladed inserts and is observed due to the ability of computational fluid dynamics to determine the cavitation number at every point in the venturi throat.

The numerical results indicate that the increase in velocity and drop in the static pressure in the nozzle decreases the cavitation number. The cavitation number decreases in the throat of the venturi due to a pressure drop caused by frictional losses. However, in the diffuser, there is recovery of static pressure therefore the velocity decreases which causes an increase in cavitation number.

3.1.4 Cavitation Number

The cavitation number indicates the intensity of cavitation at various points in a fluid : in principle, the lower the cavitation number, the greater the intensity of cavitation. The cavitation number as defined in

Equation 3.2 is an average cavitation number for a fluid at a certain point in a pipe of specific geometry as it only takes into account the average throat velocity in the fluid. However, since CFD solves for the entire flow field, local velocities can be determined for specific points in a venturi (Meyer, 1993a). Hence, a local cavitation number (Equation 3.3) was defined to calculate the cavitation intensity at specific points in the flow field.

$$\sigma_l = \frac{P - P_v}{\frac{1}{2}\left(\frac{U_m + U_l}{2}\right)^2} \tag{3.3}$$

The subscript *l* denotes the local value available from the numerical results.

The average of the mean throat velocity and the local velocity was used in the calculation of the local cavitation number in order to obtain a characteristic velocity for a specific point and geometry. However, this local cavitation number has to be verified by comparison of the numerically simulated results with experimentally determined results.

3.2 PHYSICAL EFFECTS OF CAVITATION

Various characteristics of cavitation, both hydrodynamic and ultrasonic, were investigated in the project and this section reviews these results.

3.2.1 Hydrodynamic Cavitation

The occurrence of hydrodynamic cavitation in two sets of equipment was investigated. These were the CAV-OX® system that was donated by Diarec Diamonds and modified as described in the previous section, and the hydrodynamic cavitation rig which was constructed in the Department of Chemical Engineering at the University of Natal, Durban. Both the systems were illustrated in Figures 2.2 and 2.3.

3.2.1.1 Operating Conditions of the CAV-OX® System

The operating conditions of the CAV-OX® chamber listed in Table 3.1 were used to determine the cavitation characteristics of the CAV-OX® system. The flow rate was varied with the three gate valves connected in series upstream of the cavitation nozzle and measured using a magnetic induction flowmeter. The discharge pressure was varied using the valve in the exit line.

TABLE 3.1 : Gauge pressures and flow rates measured in the cavitation chamber of the CAV-OX® system during operation

Flow rate (ℓ/min)	Discharge pressure (kPa)	Feed pressure (kPa)	Throat pressure (kPa)
25	0	620,2	- 12,0
25	70	620,2	- 94,0
35	10	613,3	- 94,5
35	70	613,3	- 94,5
48	18	599,5	- 95,0
48	70	599,5	- 95,0

The data in Table 3.1 was used to calculate theoretical velocities and pressures for the venturi nozzle in the cavitation chamber of the CAV-OX® system (Chetty, 1994). Figure 3.4 illustrates the theoretical velocity and pressure distributions for the CAV-OX® venturi.

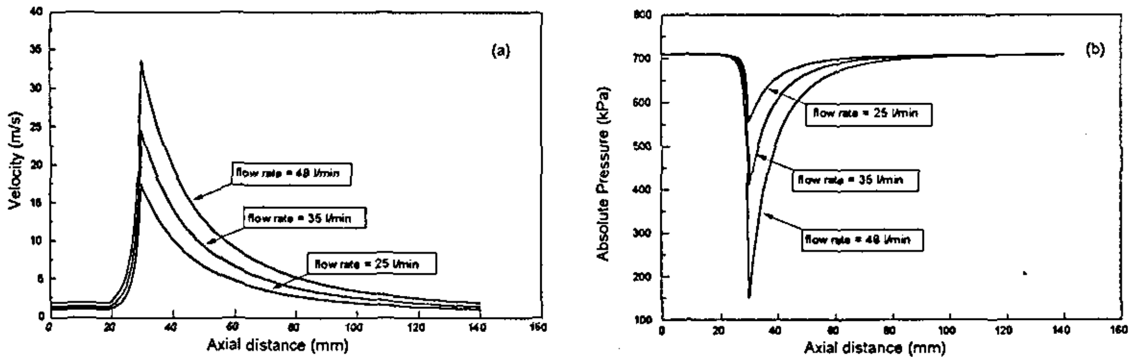

FIGURE 3.4 : Theoretical velocity and pressure distributions in the CAV-OX® chamber (graphs (a) and (b) respectively)

The formation of cavities in a hydrodynamic system occur in regions of high velocities and low pressures. Figure 3.4 indicates that the maximum velocity and minimum pressure region for the CAV-OX® chamber is at the venturi throat.

From Figure 3.4(b), it would appear that the pressure in the CAV-OX® chamber is greater than the ambient pressure of 101 kPa therefore no tensile pressures are created in the liquid (in order for cavitation to occur, the local pressure has to be reduced to the vapour pressure of the liquid). Consequently, the theoretical pressures indicate that cavitation does not occur in the CAV-OX® chamber. However, according to Table 3.1, the experimental throat pressures measured in the CAV-OX® chamber indicate that cavitation does occur in the CAV-OX® unit.

3.2.1.2 Operating Conditions of the Hydrodynamic Cavitation Rig

The various characteristics of the hydrodynamic cavitation rig that were experimentally investigated included the hydraulic characteristics of the nozzle, energy dissipation and the intensity of cavitation generated in the cavitation rig. The hydraulic characteristics of the nozzle in the cavitation rig were determined by investigating the relationship between the inlet and outlet pressures difference and flow rate. Figure 3.5 shows the graphical relationship between this pressure difference and flow rate. In this figure, each line represents different inlet pressure conditions (as absolute pressures).

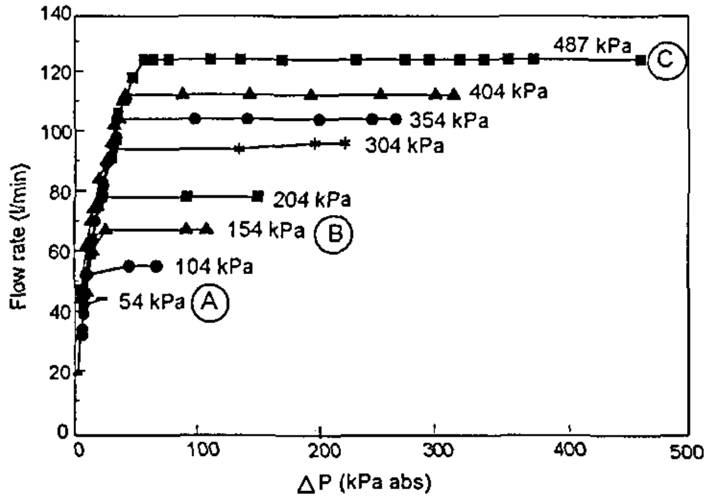

FIGURE 3.5 : Experimental hydraulic characteristics of the nozzle in the hydrodynamic cavitation rig for different absolute inlet pressures. ΔP is equal to the difference in the inlet and outlet pressures of the nozzle. Points A, B and C on the graph represent operating conditions of low, medium and high intensities of cavitation

Cavitation occurs at constant flow rate which is illustrated in Figure 3.5 by the horizontal portion of the lines. It can also be seen from Figure 3.5 that the intensity of cavitation decreases, and eventually ceases to occur, as the pressure drop across the nozzle is reduced. At this point, the flow rate decreases. In these situations, the throat pressure is increased to above the vapour pressure of the liquid thus preventing bubble formation.

Three operating conditions in the hydrodynamic cavitation rig, which are detailed in Table 3.2, were selected for further study. These conditions are represented by points A, B and C on the graph is Figure 3.5 and correspond to low, medium and high intensities of cavitation respectively.

TABLE 3.2 : Operating conditions in the hydrodynamic cavitation rig selected for study where $\Delta P_{nozzle} = P_{inlet} - P_{outlet}$ (as absolute pressures)

Condition	Flow rate (ℓ/min)	P_{inlet} (kPa)	P_{outlet} (kPa)	ΔP_{nozzle} (kPa)
A	44	54	32	22
B	78	204	52	152
C	124	487	15	472

The hydraulic characteristic data for the hydrodynamic cavitation rig were used to investigate the energy dissipated by the nozzle at various conditions of cavitation (Botha, 1993). The condition of highest cavitation intensity (Point C) showed the greatest dissipation of energy because of the large pressure drop across the nozzle.

3.2.1.3 Cavitation Numbers

Hydrodynamic cavitation can be defined by a dimensionless parameter known as the cavitation number, σ_C (this was defined in Equation 3.2) which expresses the state of a fluid near to, or, cavitating (Lehman and Young, 1964). As the static pressure (P) approaches the vapour pressure of the liquid (P_v), the system becomes more susceptible to cavitation. The pressure of the system can also be decreased by increasing the liquid velocity (u_m). Hence, the lower the cavitation number for a particular condition, the greater the intensity of cavitation.

(a) CAV-OX® system

The data from Table 3.1 was used to determine the velocities and pressures at the throat of the venturi in the CAV-OX® chamber. These were then used to determine the cavitation numbers at the venturi throat of the CAV-OX® chamber (see Table 3.3).

TABLE 3.3 : Cavitation numbers and flow parameters for the venturi throat of the CAV-OX® chamber

Flow rate (ℓ/min)	Discharge pressure (kPa)	Upstream fluid velocity (m/s)	Throat fluid velocity (m/s)	Absolute throat pressure (Pa)	Throat cavitation number
25	0	0,82	17,5	7 325	0,027
25	70	0,82	17,5	89 325	0,563
35	10	1,15	24,4	6 825	0,012
35	70	1,15	24,4	6 825	0,012
48	18	1,58	33,5	6 325	0,006
48	70	1,58	33,5	6 325	0,006

It can be observed that the cavitation numbers generally decrease with increasing flow rates. The critical throat or threshold cavitation number is defined as the maximum cavitation number at which cavitation occurs. For the venturi in the CAV-OX® chamber which has an internal diameter of 24 mm, the critical throat cavitation number is predicted to be 0,250 by extrapolation of literature data (Young, 1989 in Chetty, 1994). This indicates that hydrodynamic cavitation will be produced in the CAV-OX® chamber for all the operating conditions reported in Table 3.3, except the flow rate of 25 ℓ/min and discharge pressure of 70 kPa. This was confirmed by the photographic studies undertaken, the results of which will be discussed in the following section.

(b) Hydrodynamic Cavitation Rig

Cavitation numbers determined for the selected operating conditions in the hydrodynamic cavitation rig, specified in Table 3.2, are tabulated in Table 3.4. It can be seen that the most intense cavitation conditions in the hydrodynamic cavitation rig (C) has the lowest cavitation number.

TABLE 3.4 : Cavitation numbers for the operating conditions selected for study in the hydrodynamic cavitation rig

Conditions	Cavitation number
A	0,482
B	0,258
C	0,025

Direct comparison of the cavitation numbers for in the CAV-OX® chamber and the cavitation rig cannot be made since the cavitation numbers for both systems were determined under different operating conditions.

3.2.1.4 Photographic Studies

The occurence of hydrodynamic cavitation was observed in both the hydrodynamic cavitation rig and the CAV-OX® chamber by photographing the water passing through the venturi nozzles. Cavitation was observed in the photographs as a mass of bubbles, the volume of which varied depending on the flow rate and discharge pressure. Figures 3.6 and 3.7 present some of the results obtained which illustrate that cavitation occurs in the CAV-OX® chamber and the hydrodyanmic cavitation rig respectively. Bubbles are produced at the throat of the nozzles except for the operating condition in the CAV-OX® chamber for a flow rate of 25 M/min and discharge pressure of 70 kPa (Figure 3.6(a)) which confirms the results obtained for the cavitation numbers for the CAV-OX® venturi (Table 3.3). It was concluded from the photographs that hydrodynamic cavitation does occur in both the hydrodynamic cavitation rig and the cavitation chamber of the CAV-OX® system when the ambient pressure equals, or is greater than, the fluid vapour pressure.

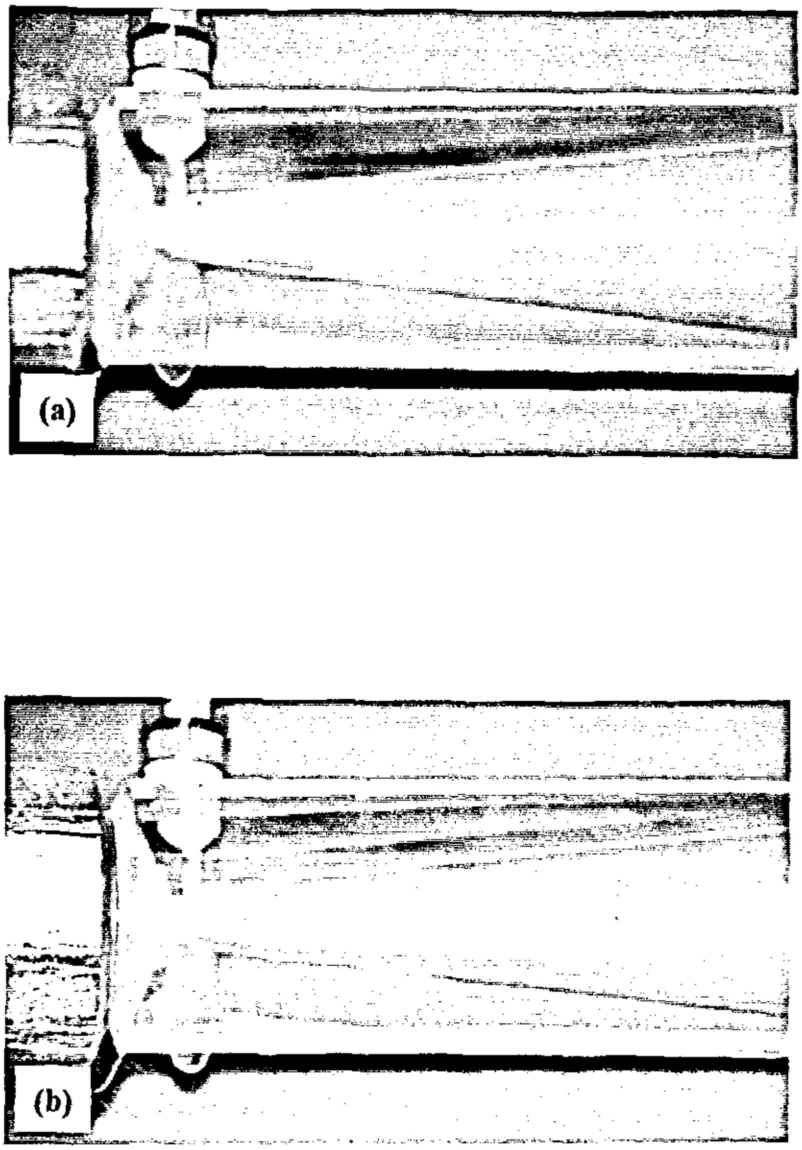

FIGURE 3.6(i) : Photographs of hydrodynamic cavitation produced in the CAV-OX® chamber for a flow rate of 25 ℓ/min and discharge pressures of (a) 0 kPa (a) and (b) 70 kPa

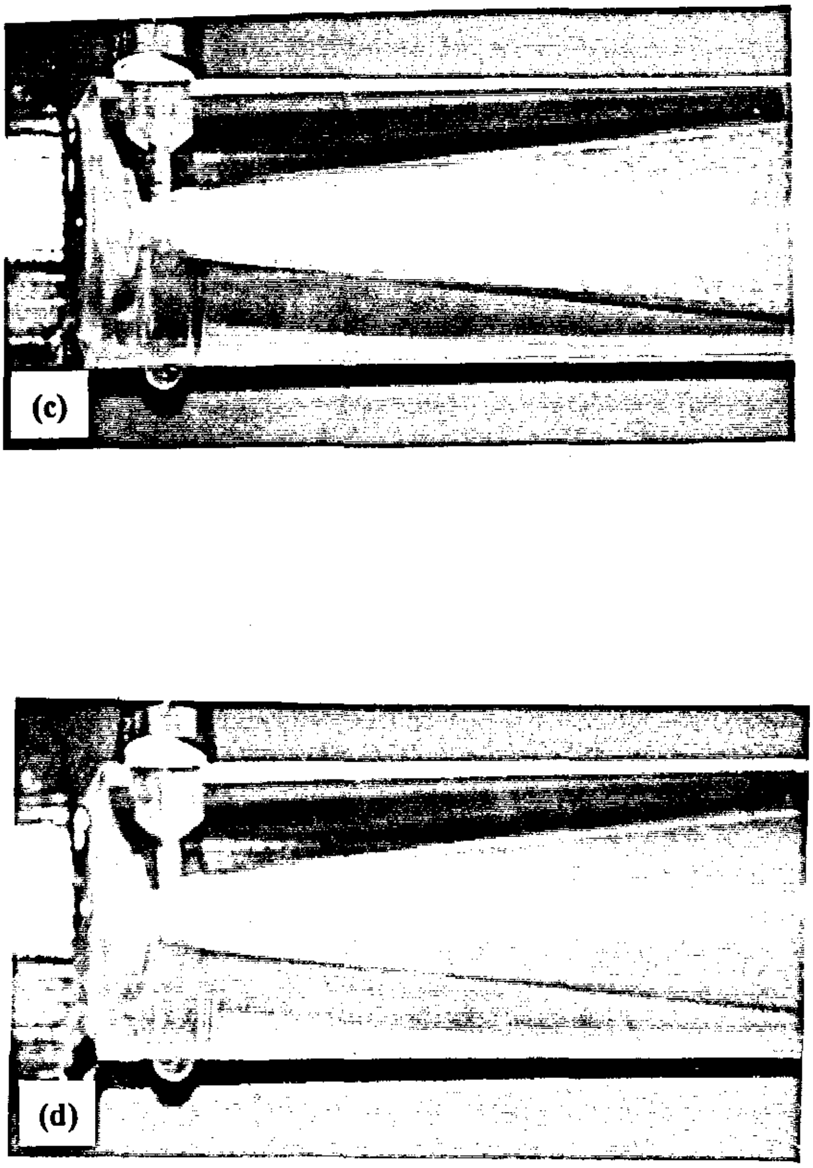

FIGURE 3.6(ii) : Photographs of hydrodynamic cavitation produced in the CAV-OX® chamber for a flow rate of 48 ℓ/min and discharge pressures of (c) 18 kPa and (d) 70 kPa

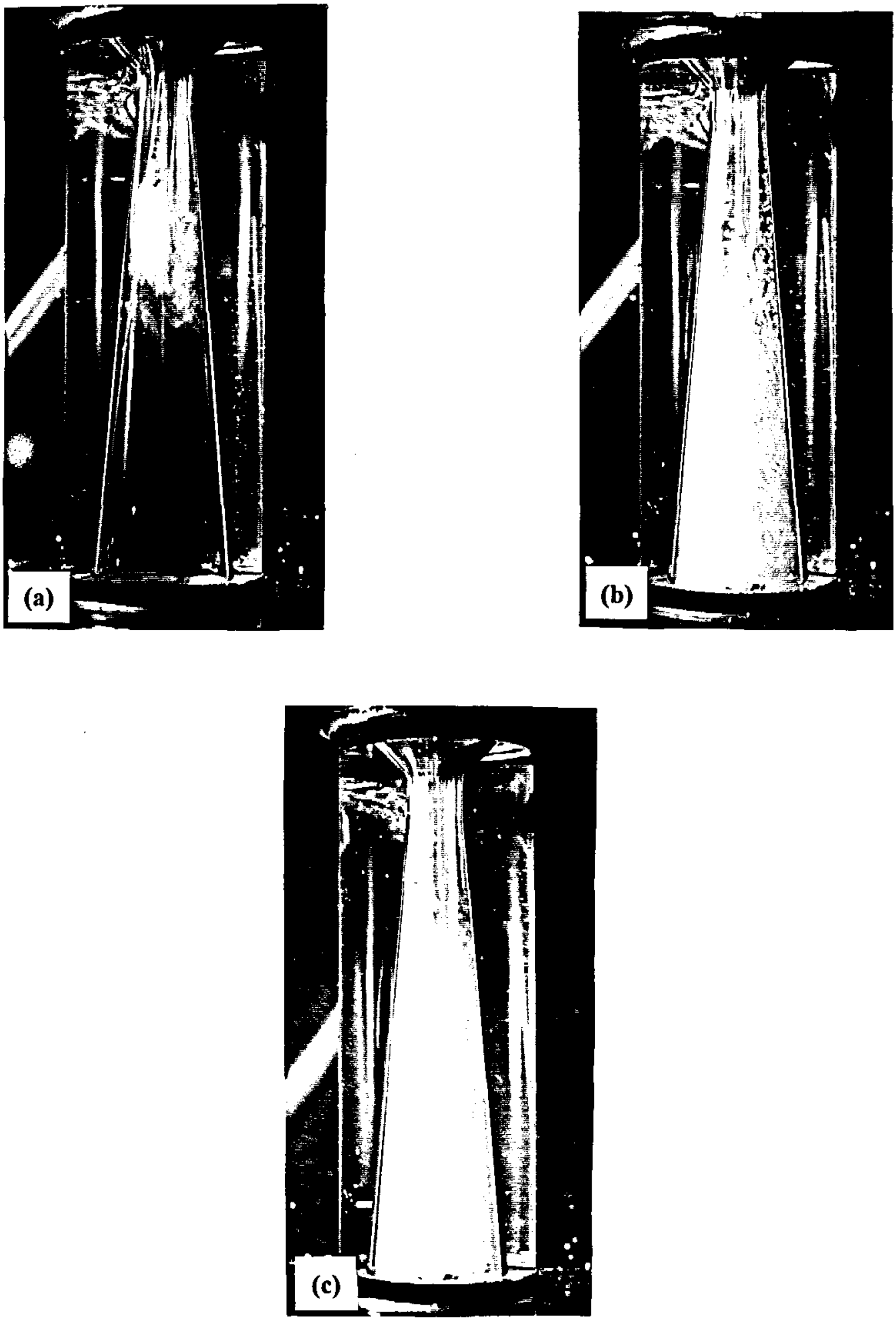

FIGURE 3.7 : Photographs of hydrodynamic cavitation produced in the hydrodynamic cavitation rig under (a) low intensity, (b) medium intensity and (c) high intensity operating conditions

From the cavitation numbers presented in Section 3.2.1.2 and the photographic studies undertaken, it can be concluded that a higher threshold cavitation number is required for the hydrodynamic cavitation rig than for the CAV-OX® chamber.

3.2.1.5 Sound Emission

Sound output is one of the phenomena associated with hydrodynamic and ultrasonic cavitation. The various stages of hydrodynamic cavitation have been described in terms of the noise produced (Ball, et al., 1975):

- **Incipient cavitation** represents the onset of cavitation where the noise consists of light, intermittant, popping sounds.
- **Critical cavitation** is characterised by a light, steady noise which sounds like bacon frying.
- **Incipient damage cavitation** results from the implosion of vapour cavities and is associated with objectionable noise that produces vibration and damage.
- **Choking cavitation** occurs when the pressure at the constriction of the nozzle equals the vapour pressure of the liquid and there is no further increase in discharge when the pressure downstream of the nozzle is decreased at a constant upstream pressure.

The sound levels produced by the CAV-OX® system and hydrodynamic cavitation rig were measured using a sound level meter and an octave filter set as described in Botha (1993) and Chetty (1994). This equipment measures sound in decibels (dB) over the frequency range 31,5 Hz to 31 500 Hz.

(a) CAV-OX® System

The sound levels in the CAV-OX® chamber were recorded at the audible frequency range, i.e.16 Hz to 16 kHz. The maximum sound level was produced in the CAV-OX® chamber was recorded in the divergent section of the nozzle, i.e. the region of bubble collapse. The sound levels emitted in the divergent section of the nozzle were recorded for the operating conditions specified in Table 3.1 (the blanks were determined by replacing the cavitation chamber with a stainless steel pipe) and the results are illustrated in Figure 3.8.

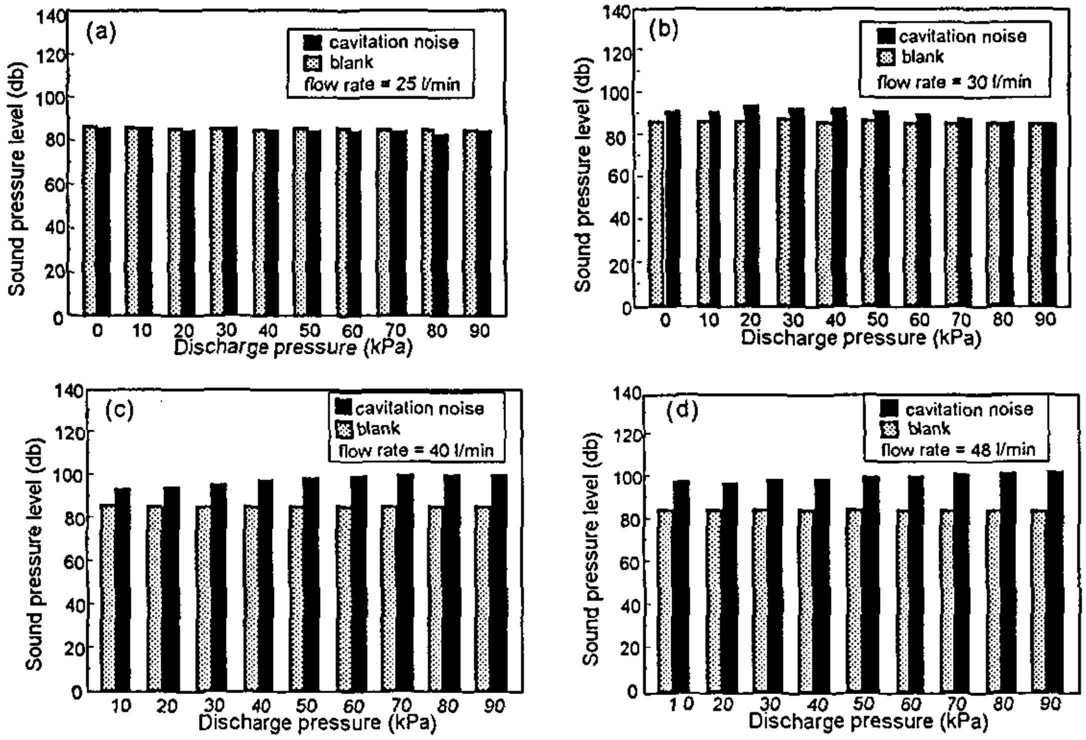

FIGURE 3.8 : Sound pressure levels recorded in the CAV-OX® chamber for different flow rates. The blank was determined by replacing the cavitation chamber with a stainless steel pipe and recording the sound levels at different flow rates

Two features can be observed in these graphs : the sound pressure levels increase with increasing flow rate since more bubbles collapse at a higher flow rate, and the sound pressure levels are a function of the discharge pressure. Increasing the discharge pressure can cause the sound pressure levels to either increase or decrease. An increase in the discharge pressure causes the liquid pressure to increase in the region where bubble collapse occurs. As a result, the bubbles collapse more rapidly and violently and the sound pressure levels increase (Figures 3.8(c) and 3.8(d)). The maximum sound emitted in the CAV-OX® chamber was at the maximum flow rate and discharge pressure (Figure 3.8(d)). Figure 3.8(b) indicates that the sound pressure levels initially increase with the discharge pressure due to an increase in the liquid pressure in the region of bubble collapse. However, further increase in the discharge pressure results in the liquid pressure increasing in the region of bubble growth thus favouring the growth of smaller bubbles which emit lower sound pressure levels upon collapse. An increase in the discharge pressure can also cause an increase in the throat pressure of the CAV-OX® chamber which hinders bubble formation. This was observed for the flow rate of 25 ℓ/min. From Table 3.1, it can be seen that the throat pressure increases from - 94 kPa to - 12 kPa as the discharge pressure increases from 0 kPa to 70 kPa. Consequently, bubble formation is hindered and no sound pressure levels were recorded for this flow rate (Figure 3.8(a)).

(b) Hydrodynamic Cavitation Rig

Sound pressure levels were recorded for the operating conditions in the hydrodynamic cavitation rig at various backpressures (P_{out}) over the frequency range 31,5 Hz to 31 500 Hz. The measurements were recorded at night when the background noise was at a minimum. Figure 3.9 shows the results obtained.

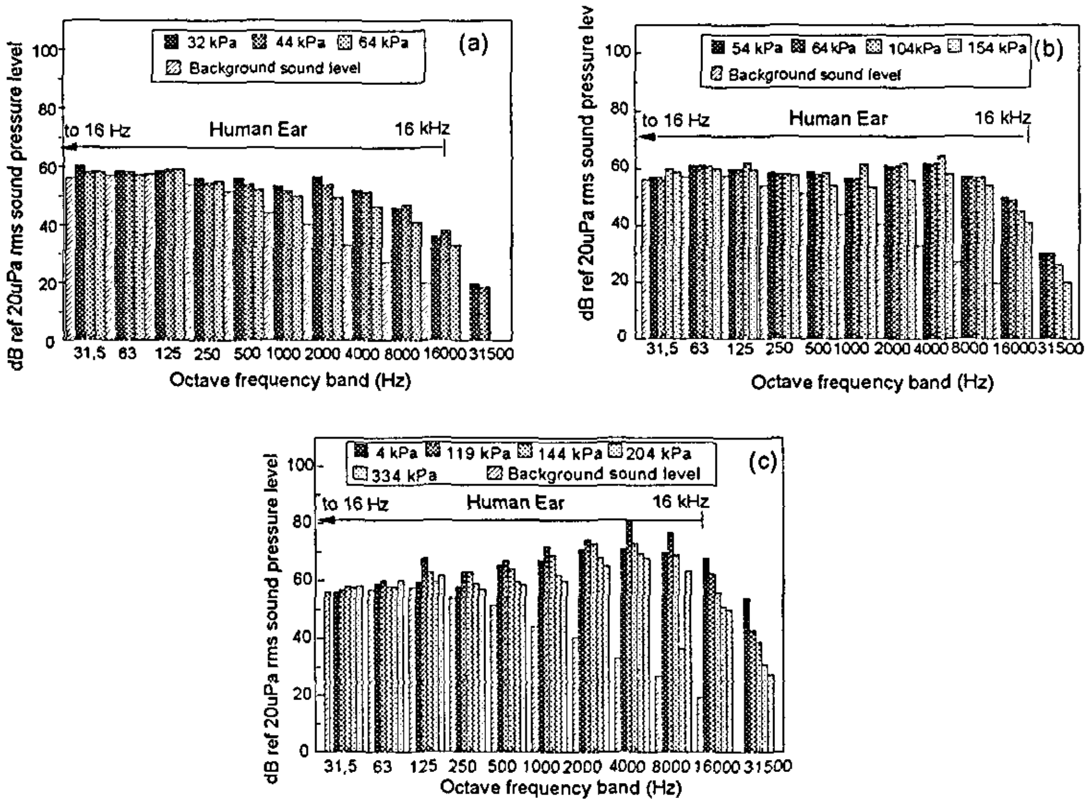

FIGURE 3.9 : Octave frequency band spectra measured in the hydrodynamic cavitation rig for (a) low intensity, (b) medium intensity and (c) high intensity cavitation conditions. The backpressure conditions (outlet absolute pressures) at which the sound levels were recorded for each intensity of cavitation are give in the legend of each graph

The sound levels for the hydrodynamic cavitation rig exhibited a similar trend to those recorded in the CAV-OX® chamber, i.e. the sound levels increase with increasing flow rate. However, it was determined that the noise produced in the cavitation rig in the frequency range of 4 000 to 16 000 Hz was affected by flow rate.

3.2.2 Ultrasonic Cavitation

The ultrasonic bath with a temperature control system (refer to Figure 2.1) was used in the investigation of the degradation of hydantoin compounds by ultrasonic cavitation. Prior to investigating the chemical effects of ultrasonic cavitation on hydantoin degradation, it was necessary to determine the physical characteristics of the bath used.

3.2.2.1 Sound Levels of the Ultrasonic Bath

A sound level meter and octave filter set were used to measure the sound levels at different octave frequency bands (Botha, 1993). The results obtained for the ultrasonic cleaning bath showed that the maximum sound output was at a frequency 31,5 kHz (in the ultrasonic frequency range) which is maximum frequency measurable by the sound meter. The specified frequency of the bath was 38 kHz.

3.2.2.2 Intensity of the Ultrasonic Bath

The intensity of an ultrasonic bath can be estimated by determining the temperature increase of the water sonicated in the bath. The acoustic energy from the ultrasonic waves is absorbed by the liquid in the bath and converted into thermal energy which increases the temperature of the water in the ultrasonic bath (Goswami, et al., 1988). This rate of energy input can be calculated from the initial linear increase in temperature and indicates the amount of energy available to enhance sonochemical reactions. Figure 3.10 illustrates the temperature increase in the water in the ultrasonic bath which was operated for 360 min.

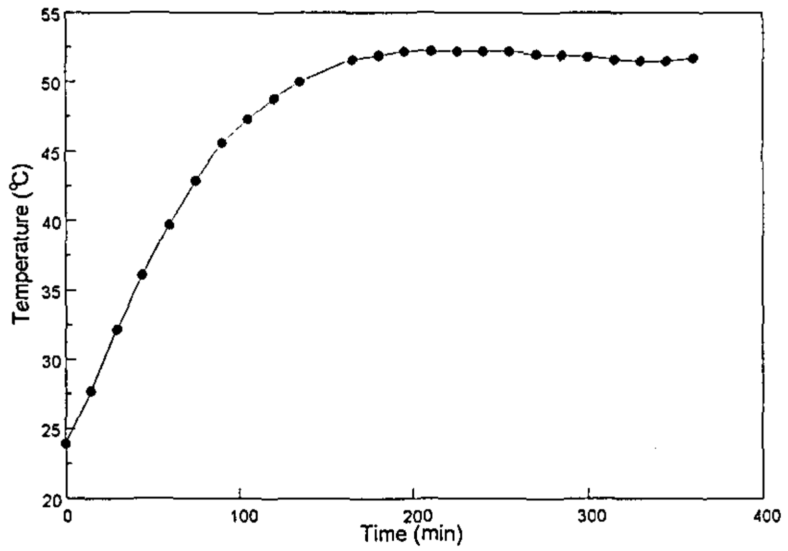

FIGURE 3.10 : Temperature profile of 5 ℓ of water sonicated in the ultrasonic bath for 360 min

The temperature profile in Figure 3.10 indicates that the temperature of the water in the ultrasonic bath increased from 23,9 °C to 52,2 °C within 210 min. After this time, the temperature remained constant. This indicates that the temperature of the water in the ultrasonic bath has to be controlled during experiments thus a temperature control system was established to maintain the temperature of the water in the ultrasonic bath at 25 °C (illustrated in Figure 2.1).

Within 60 min, the temperature of the water in the ultrasonic bath increased from 23,9 °C to 39,7 °C (Figure 3.10). The heat capacity (Cp) of water at 31,8 °C, the average temperature in this temperature range, is 4 177,8 J/kgK(Welty, et al., 1984) therefore the power, Q, required to raise the temperature (by ΔT degrees) of a liquid with a mass flow rate, m, can be calculated from Equation 3.4.

$$Q = mC_p\Delta T \tag{3.4}$$

Substitution of the above values and that for the mass flow rate of the sonicated water (0,0013 kg/s; Schwikkard, 1994) gives a power output of 91,4 J/s.

The intensity of an ultrasonic bath is defined as the energy emitted at the surface of the ultrasonic device (Mason, 1991). The ultrasonic bath used in the experiments contains four piezoelectric transducers (each 55 mm in diameter) bonded to its base; the combined surface area is therefore 9 503 mm^2. Thus, the intensity for the operating conditions of the ultrasonic bath can be calculated by dividing the power (91,4 W) of the ultrasonic bath with the surface area through which the energy was emitted (9 503 mm^2). The intensity of the ultrasonic bath used in the experiments is therefore 9,6 kW/m^2.

Stable cavitation (discussed in Section 2.1) only occurs at intensities of 10 to 30 kW/m^2 whilst transient cavitation (refer to Section 2.1) occurs if the intensity is greater then 100 kW/m^2 (Mason, 1990b). It could therefore be concluded that stable cavitation that occurs in the ultrasonic bath. Sonochemical effects, e.g. free radical formation, microstreaming, etc., result from both stable and transient cavitation (Ratoarinoro, et al., 1992) since, although the temperatures and pressures developed in stable cavities are lower then those in collapsing transient cavities, the lifespan of stable cavities is longer which increases the probability to affect chemical reactions (Mason, 1990b). Therefore, sonochemical effects could be observed using the ultrasonic bath as the promulgator of ultrasonic waves.

Although the intensity of the ultrasonic bath was calculated to be 9,6 kW/m^2, a lower intensity is possible within the reaction vessel. Goodwin (1990a) proposed that, as ultrasonic waves are attenuated at the glass/water interface, the intensity within the reaction vessel could be reduced to 5 kW/m^2. Under these conditions, ultrasonic cavitation may not occur in the reaction vessel (however, the formation of hydrogen peroxide in the ultrasonic bath (see Section 3.3) proved that ultrasonic cavitation occurs). Therefore, it is important to compare the temperature of the water in the reaction vessel is affected through heat conduction from the water in the ultrasonic bath.

3.2.2.3 Temperature Profile of Water in the Ultrasonic Bath and Reaction Vessel

The temperature of the water in the reaction vessel is affected by heat conduction from the water in the ultrasonic bath thus the intensity of ultrasonic cavitation within the reaction vessel cannot be estimated by calorimetry, i.e. as the intensity of water in the ultrasonic bath was determined. However, the temperature of the water in the reaction vessel can be compared to temperature increase of the water in the ultrasonic bath over a period of time when the temperature of the water in the ultrasonic bath is controlled at 25 °C and when it was not controlled (see Figure 3.11).

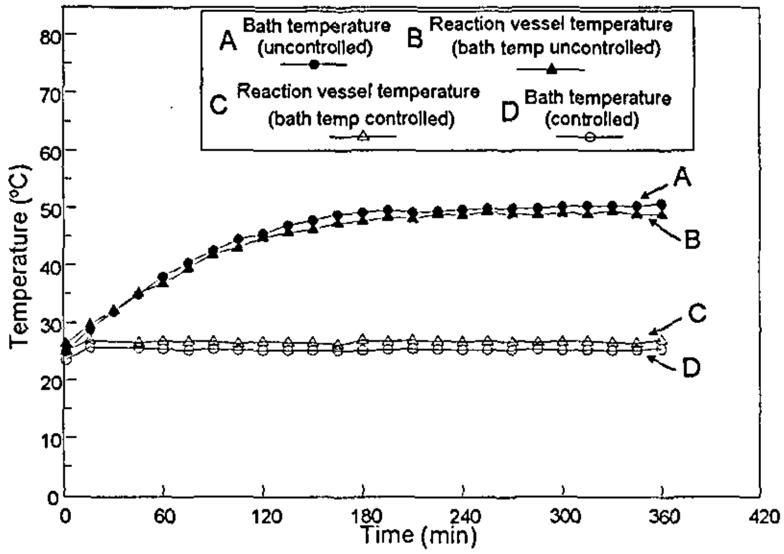

FIGURE 3.11 : Temperature profiles of the water in the reaction vessel and ultrasonic bath sonicated for 360 min when the temperature of the bath was uncontrolled and when the temperature of the bath was controlled at 25 °C

From this figure, it can be seen that the temperature increase of the water in the reaction vessel is less than that in the ultrasonic bath for the uncontrolled cases A and B. Since this temperature increase is an indication of the amount of energy absorbed by the water, it would appear to confirm the observation that the intensity of cavitation in the reaction vessel would be lower than the intensity of cavitation in the ultrasonic bath (Goodwin, 1990a).

Goodwin (1990b) reported that the temperature of the water within the reaction vessel was greater than the temperature of the water in the ultrasonic bath if this latter temperature was controlled, therefore the temperature of a sonochemical reaction must be monitored within the reaction vessel. The actual intensity of cavitation within the reaction vessel could be obtained if the temperature of the water in the reaction vessel could be measured without any external factors acting on it, i.e. conduction by either warm or cold water. The true temperature curve of the water in the reaction vessel (without external factors) would thus lie between graphs B and C in Figure 3.11 as these were influenced by heating through conduction and cooling through conduction respectively.

3.3 CHEMICAL EFFECTS OF CAVITATION

3.3.1 Hydrodynamic Cavitation

The major chemical effect believed to result from hydrodynamic cavitation is the generation of hydroxyl radicals which are proposed to result from the thermal dissociation of water molecules. These hydroxyl radicals can subsequently undergo reactions with organic compounds in solution resulting in degradation products. Free radicals can be detected by various methods which require sophisticated and expensive instrumentation, e.g. magnetic susceptibility, mass spectroscopy and electron spin resonance. However, since hydroxyl radicals can combine to produce hydrogen peroxide, the presence of hydroxyl radicals can be detected by determining the hydrogen peroxide concentration in the system.

Various spectrophotometric methods are available for hydrogen peroxide detection and quatitation (Eisenberg, 1943; Sellers, 1980; Baga, et al., 1988). The first two methods use titanium sulphate and the latter one, copper(II) sulphate and 2,9-dimethyl-1,10-phenanthroline (DMP). These methods were evaluated during the course of the project (Chetty, 1994) and it was found that the $CuSO_4$ / DMP method (Baga, et al., 1988) was the most sensitive of the methods evaluated as it can detect hydrogen peroxide in the concentration range of 10^{-6} mol/ℓ (0,034 mg/ℓ) to $1{,}2 \times 10^{-4}$ mol/ℓ (4,03 mg/ℓ). This method was used to determine the hydrogen peroxide concentration produced in the CAV-OX® chamber, hydrodynamic cavitation rig and ultrasonic cleaning bath.

3.3.1.1 Factors affecting Hydrogen Peroxide Determination in the CAV-OX® system

Prior to the investigation of hydrogen peroxide formation in the CAV-OX® chamber, factors affecting hydrogen peroxide concentration were assessed. Hydrogen peroxide is an unstable compound that decomposes naturally to water and oxygen. The rate of decomposition is dependent on exposure to light (particularly UV) and temperature. Metal ions and organic compounds present in solution can also enhance the decomposition of hydrogen peroxide. Experiments were undertaken to determine the effect of laboratory light, increased temperature and the stainless steel surfaces of the equipment on hydrogen peroxide decomposition.

Solutions of known concentrations of hydrogen peroxide (1,5 mg/ℓ and 0,6 mg/ℓ) were exposed to the various conditions and the hydrogen peroxide concentration monitored at regular intervals. Figures 3.12 and 3.13 illustrate the results obtained as normalised hydrogen peroxide concentration (C / C_o), i.e. the ratio of hydrogen peroxide concentration at time t (C) to the initial hydrogen peroxide concentration (C_o). Rate constants were determined by multipying the gradients of the graphs by the respective initial concentrations, i.e. C_o. Further details are reported in Chetty (1994).

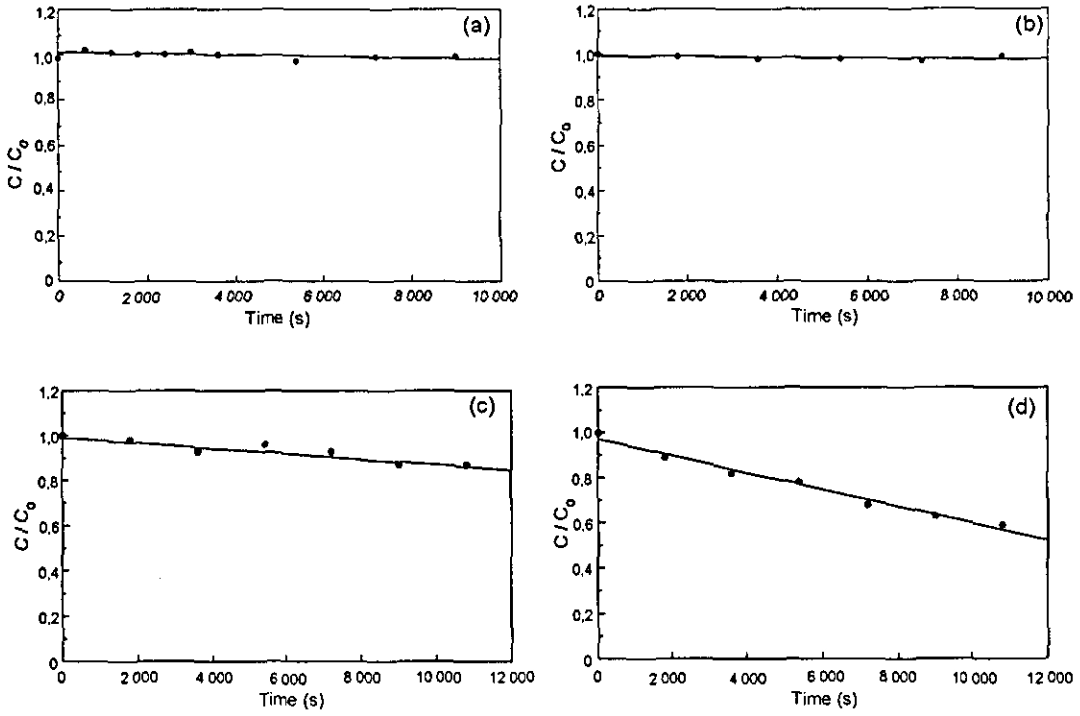

FIGURE 3.12 : Decomposition of hydrogen peroxide solutions (a) exposed to light, (b) at a temperature of 32 °C, (c) in the feed tank of the CAV-OX® equipment, and (d) in the sample port of the equipment. The initial concentration of the hydrogen peroxide solution was 1,5 mg/ℓ

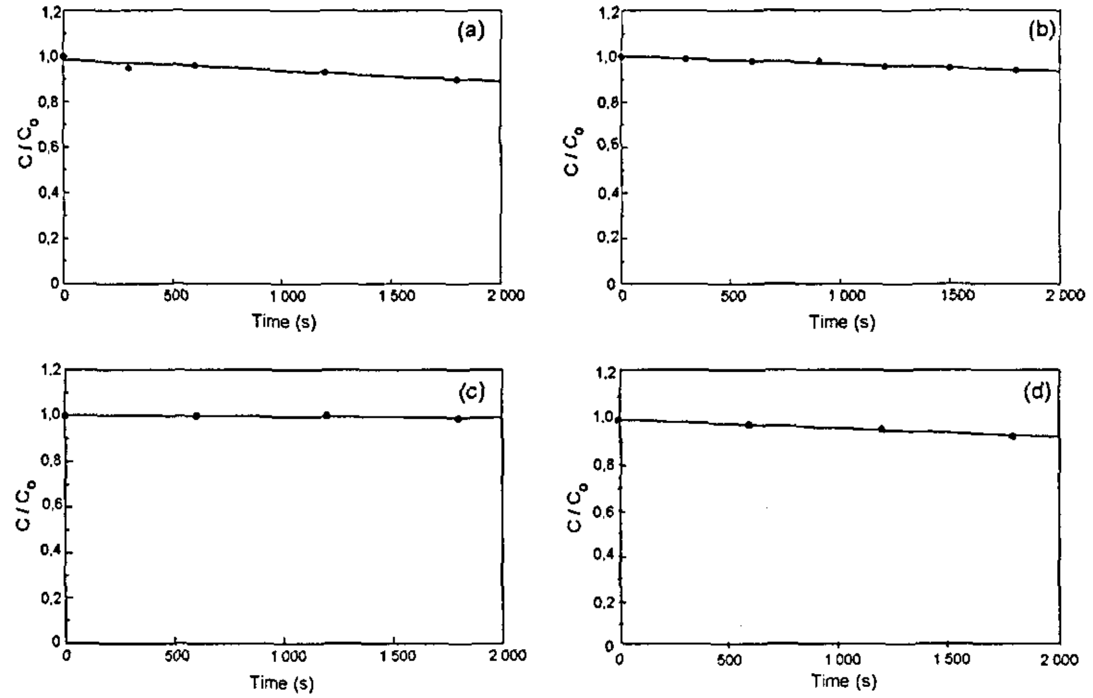

FIGURE 3.13 : Decomposition of hydrogen peroxide solutions (a) exposed to light, (b) at a temperature of 32 °C, (c) in the feed tank of the CAV-OX® equipment, and (d) in the sample port of the equipment. The initial concentration of the hydrogen peroxide solution was 0,6 mg/ℓ

Comparison of Figures 3.12(a) and 3.13(a) indicate that the decomposition rate of the 1,5 mg/ℓ hydrogen peroxide solution is lower than that of the 0,6 mg/ℓ hydrogen peroxide solution which is expected since hydrogen peroxide is more stable at higher concentrations (Snell and Ettre, 1971).

For the 1,5 mg/ℓ hydrogen peroxide solution, there is negligible effect of temperature on the decomposition rate of hydrogen peroxide (Figure 3.12(b)). However, a temperature of 32 °C enhances the decomposition rate of the 0,6 mg/ℓ hydrogen peroxide solution significantly (Figure 3.13(b)). These results indicate that the temperature achieved during operation of the CAV-OX® chamber (32 °C; Chetty, 1994) could affect quantitation of the hydrogen peroxide concentrations produced by hydrodynamic cavitation .

Hydrogen peroxide decomposition is enhanced by the stainless steel surfaces of the CAV-OX® equipment as can be seen in graphs (c) and (d) in Figures 3.12 and 3.13. The decomposition rate of the higher concentration of hydrogen peroxide is greater than for the lower hydrogen peroxide concentration. Hydrogen peroxide decomposition is also increased in the sample port than in the feed tank since the surface area in the sample port is large in comparison to the volume of the solution.

It was demonstrated that the decomposition rate of the 1,5 mg/ℓ hydrogen peroxide solution was enhanced under flow conditions in the CAV-OX® equipment (refer to Figure 3.14). A flow rate of 48 ℓ/min was used since this results in a minimum residence time in the equipment thus minimising the contact time between the solution and the stainless steel surface of the equipment (excluding the feed tank). The decomposition rate of the hydrogen peroxide solution could be decreased under flow conditions in the CAV-OX® chamber if the metal surface of the equipment was passivated with nitric acid prior to operation (Figure 3.14). Chetty (1994) gives further details of these experiments.

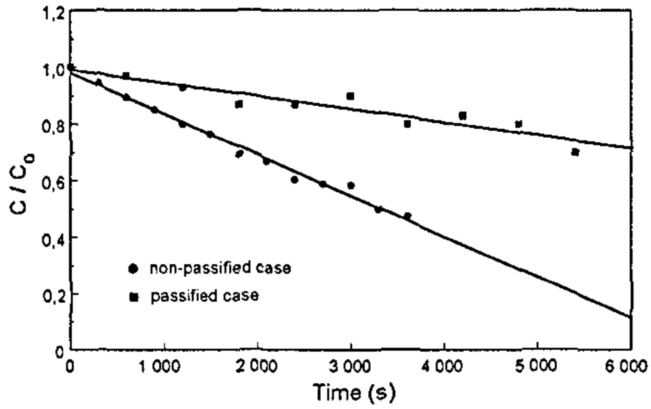

FIGURE 3.14 : Decomposition of 1,5 mg/ℓ hydrogen peroxide solution in the CAV-OX® equipment at a flow rate of 48 ℓ/min

3.3.1.2 Quantitation of Hydrogen Peroxide produced by Hydrodynamic Cavitation

(a) CAV-OX® System

From the preliminary investigations outlined in Section 3.3.1.1, it was concluded that the operating conditions in the CAV-OX® equipment could affect the quantitation of any hydrogen peroxide formed due to decomposition. In order to minimise the decomposition of any hydrogen peroxide produced, the equipment was passivated before experiments were performed.

Some of the operating conditions previously investigated (see Table 3.1) were selected for the evaluation of hydrogen peroxide production in the CAV-OX® chamber and are summarised in Table 3.5.

TABLE 3.5 : Operating conditions selected for the evaluation of hydrogen peroxide production in the CAV-OX® chamber

Operating condition	Flow rate (ℓ/min)	Discharge pressure (kPa)
A	25	0
B	25	70
C	48	18
D	48	70

The above operating conditions were selected on basis of the photographic results (Figure 3.6) and sound levels obtained for these (Section 3.2.1.3). For condition A, few bubbles were produced (Figure 3.6(a)) which emitted no sound on collapse therefore no hydroxyl radicals are expected to be produced for these operating conditions. Similarly, for condition B (Figure 3.6(b)), no bubbles are produced therefore no hydroxyl radicals are expected. Thus, for conditions A and B, no hydrogen peroxide is expected to be detected. However, conditions C and D (Figure 3.6(c) and (d) respectively) produce a large number of bubbles that collapse violently thus are predicted to favour the formation of hydroxyl radicals hence hydrogen peroxide should be detected.

The following experiments were carried out (Chetty, 1994)

- Comparison of the decomposition rates obtained for cavitated and non-cavitated 1,5 mg/ℓ hydrogen peroxide solutions at the operating conditions A, B, C and D specified in Table 3.5 (see Figure 3.15).
- Determination of any hydrogen peroxide formed in reverse osmosis (RO) water and oxygenated RO water cavitated in the CAV-OX® chamber at the operating conditions A, B, C and D.

Figure 3.15 illustrates the decomposition rates for cavitated and non-cavitated hydrogen peroxide solutions.

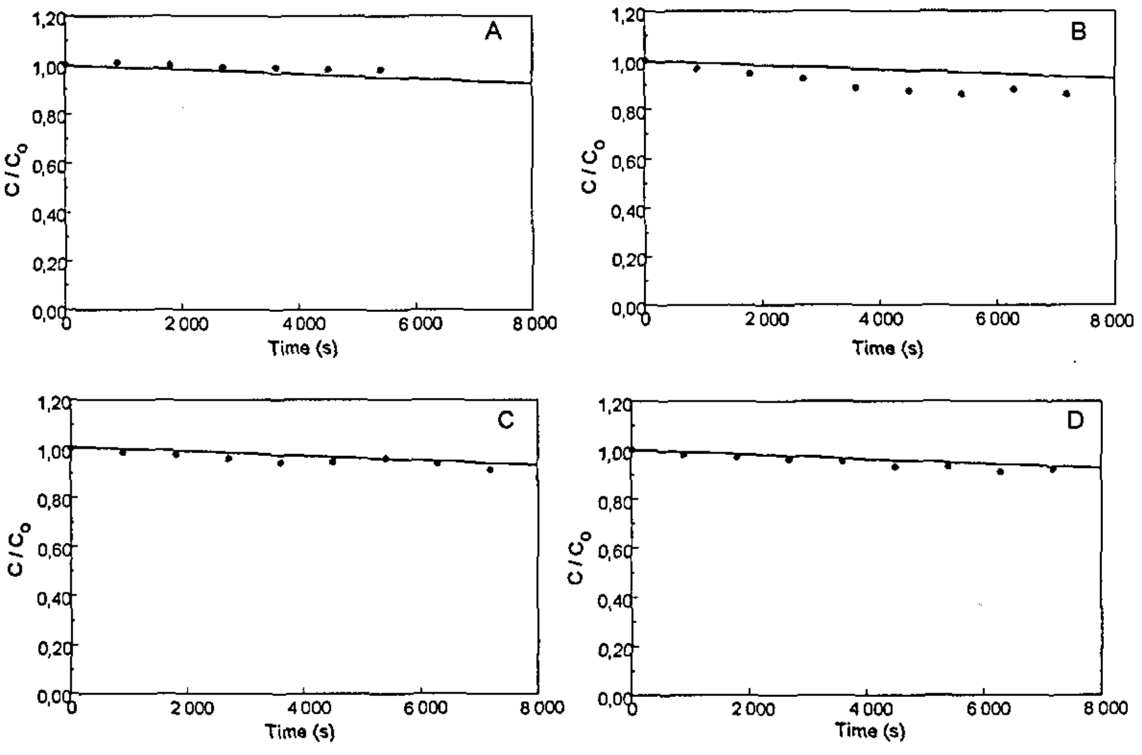

FIGURE 3.15 : Comparison of the decomposition rates for cavitated (indicated by •) and non-cavitated (indicated by —) hydrogen peroxide solutions for the various operating conditions A, B, C and D in the CAV-OX® chamber

It can be seen that there is neither formation nor enhanced decomposition of hydrogen peroxide during cavitation .

Reverse osmosis water was cavitated for 30 min at flow rates of 48 ℓ/min and 25 ℓ/min for varying discharge pressures, i.e. 0 kPa, 14 kPa and 70 kPa, and the amount of hydrogen peroxide in the samples was determined using the copper sulphate / DMP method (Baga, et al., 1988). The absorbance readings ranged between 0,001 and 0,004 (Chetty, 1994) therefore it was concluded that, under the experimental conditions investigated, an undetectable amount of hydrogen peroxide was formed in the CAV-OX® chamber.

The effect of oxygen enhancement on the formation of hydrogen peroxide by hydrodynamic cavitation was investigated by cavitating RO water that contained varying concentrations of oxygen at the most intense cavitation conditions in the CAV-OX® chamber, i.e. a flow rate of 48 ℓ/min and a discharge pressure of 70 kPa. The absorbance readings for the experiments varied betweeen 0,000 and 0,006 (Chetty, 1994). It was therefore concluded that, under the experimental conditions investigated, oxygen does not enhance hydrogen peroxide formation.

(b) Hydrodynamic Cavitation Rig

The formation of hydrogen peroxide by hydrodynamic cavitation in the hydrodynamic cavitation rig was investigated by cavitating 80 ℓ of RO water in the rig for a period of 18 h. Samples were withdrawn at time intervals and the concentration of hydrogen peroxide determined by the copper sulphate / DMP method. It was concluded that an undetectable concentration of hydrogen peroxide was formed within the 18 h duration of the experiment.

3.3.2 Ultrasonic Cavitation

Mason (1991) reports that the energy input for an ultrasonic system is dependant on the size of the ultrasonic bath, type of reaction vessel and the position of the reaction vessel in the ultrasonic bath thus preventing comparison of experimental results from different ultrasonic systems because of the different equipment parameters (ultrasonic bath or probe). One way of comparing the intensity of cavitation in ultrasonic systems is by determining the concentration of hydrogen peroxide formed as a result of the recombination of hydroxyl radicals produced during ultrasonic cavitation (Sehgal, et al., 1982).

3.3.2.1 Hydrogen Peroxide Formation in the Ultrasonic Bath

It has been reported that maximum hydrogen peroxide formation occurs in water saturated with oxygen gas (Mead, et al., 1975). As these experimental conditions would be optimum for the oxidation of organic compounds, the concentration of hydrogen peroxide produced by the ultrasonic cavitation of water saturated with dissolved oxygen over a 24 h period in the ultrasonic bath was determined. The results are shown in Figure 3.16.

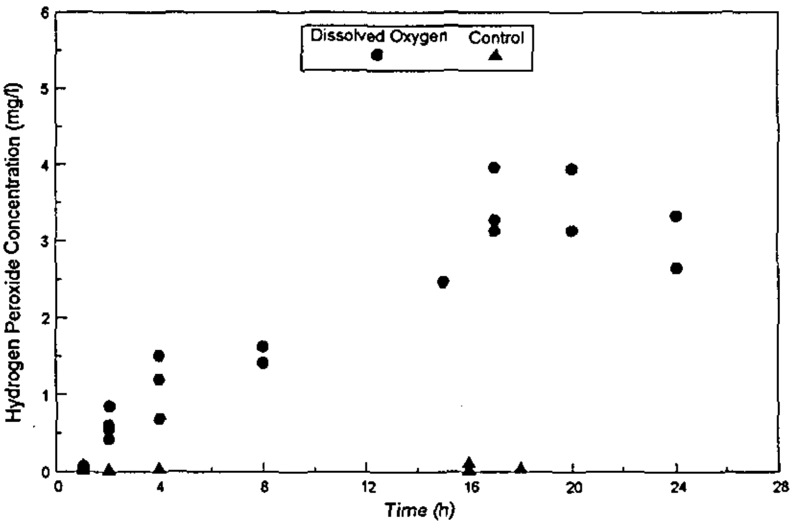

FIGURE 3.16 : Effect of dissolved oxygen on the formation of hydrogen peroxide in water ultrasonically cavitated in the ultrasonic bath. The control represents hydrogen peroxide produced in water in the absence of oxygen

In the absence of oxygen, the concentration of hydrogen peroxide was produced in the water was 0,06 mg/ℓ which is significant since the detection limit for the analytical method is 0,03 mg/ℓ. Since hydrogen peroxide is a product of recombination of hydroxyl radicals formed by the ultrasonic cavitation of water molecules, these results confirm that ultrasonic cavitation occurs in the ultrasonic bath. It is also evident that the presence of dissolved oxygen in solution enhances the concentration of hydrogen peroxide formed, as reported by Mead, et al. (1975). The concentration of hydrogen peroxide increases relatively linearly in the presence of oxygen over the 24 h period investigated to give a maximum concentration of approximately 3,5 mg/ℓ. It must be noted that there is a lack of precision in the results from sonochemical work due to variable acoustic output and other factors (Jennings and Townsend, 1961). This is evident from the large scatter of the experimental data in Figure 3.16.

3.3.2.2 Dissolved Oxygen in the Ultrasonic Bath

As ultrasound has been reported to degas liquids (Mason, 1991), the concentration of dissolved oxygen in water sparged with oxygen for 15 min prior to sonication for 8 h was investigated. Figure 3.17 presents the results obtained.

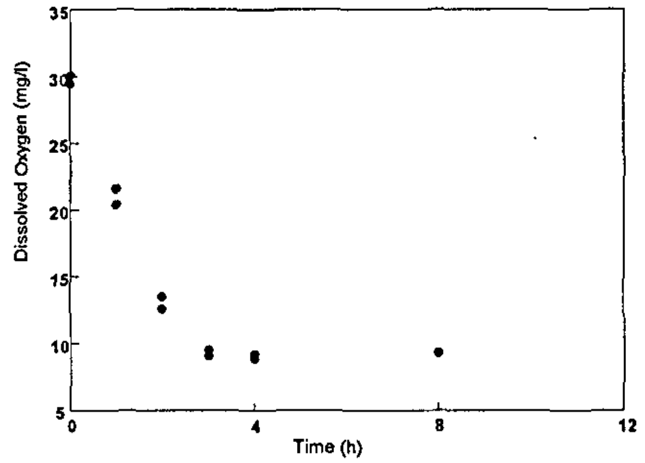

FIGURE 3.17 : Dissolved oxygen concentration in 10 ml water ultrasonically cavitated over 8 h in *the ultrasonic bath*

It can be seen that the dissolved oxygen content in the water decreases from approximately 29,7 mg/ℓ to 9,3 mg/ℓ over 3 h, and then appears to stabilise around this concentration. A dissolved oxygen concentration of 9,0 mg/ℓ was measured in water in equilibrium with air. Therefore, in order to ensure that the hydrogen peroxide concentration increases over time, oxygen gas should be bubbled through the solution being sonicated.

3.3.2.3 Degradation Kinetics of 1-Methylhydantoin

One of the research areas of this project involved the investigation of degradation of hydantoin compounds by ultrasonic cavitation (Schwikkard, 1994) therefore the sonochemical degradation of 1-methylhydantoin was investigated as a function of time in the absence and presence of hydrogen peroxide and oxygen. The results are shown in Figure 3.18.

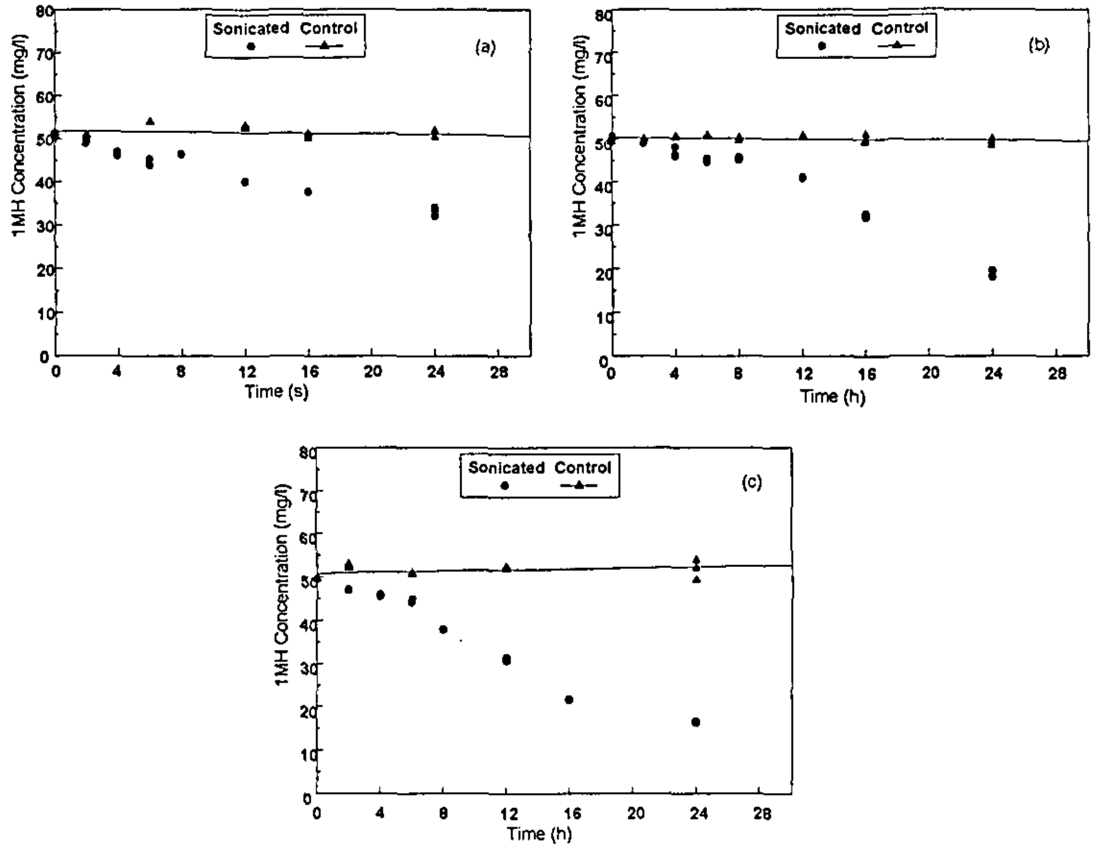

FIGURE 3.18 : Sonochemical degradation of 1-methylhydantoin (1MH) solution (50 mg/ℓ) in (a) the absence of hydrogen peroxide and oxygen, (b) the presence of 1 332 mg/ℓ hydrogen peroxide and absence of oxygen, and (c) the presence of 1 332 mg/ℓ hydrogen peroxide with oxygen saturation prior to sonication. The control solutions were identical unsonicated solutions maintained at a constant temperature

From Figure 3.18, it can be observed that no natural degradation of 1-methyl hydantoin occurs, i.e. ultrasonic cavitation is required for degradation. Therefore, it can be concluded that 1-methylhydantoin can be degraded by ultrasonic cavitation and the rate of degradation is enhanced by the presence of hydrogen peroxide and oxygen as shown in Figure 3.19.

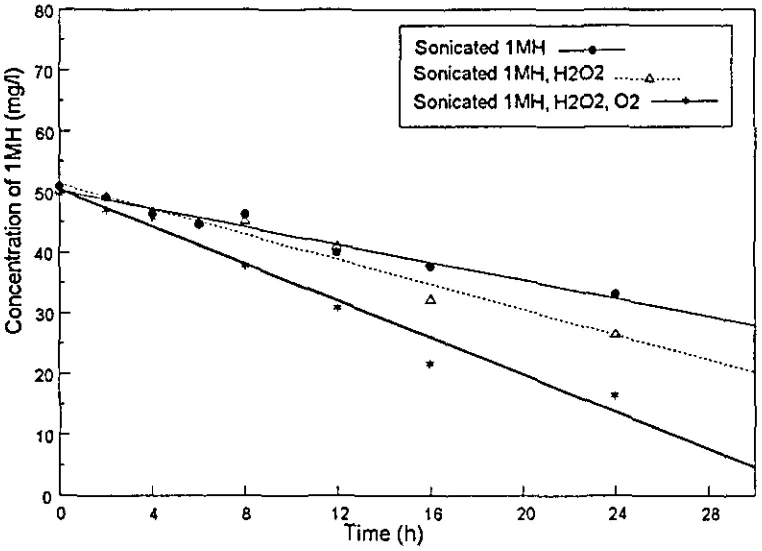

FIGURE 3.19 : **Comparison of the sonochemical degradation conditions for 50 mg/ℓ 1-methylhydantoin**

Approximately 25 to 30 % degradation of 1-methylhydantoin was achieved over 24 h in the ultrasonic bath. Addition of 1 322 mg/ℓ hydrogen peroxide enhances the sonochemical degradation of 1-methylhydantoin to approximately 62 % over 24 h as the concentration of hydroxyl radicals, which are the oxidising species, are increased. The presence of oxygen further increases the concentration of these radicals, as described in Section 2.1, and hence further sonochemical degradation of 1-methylhydantoin (approximately 68 %) occurs. A continuous stream of oxygen during sonication would enable the greatest degree of oxidation of 1-methylhydantoin.

3.3.2.4 Identification of Degradation Products from 1-Methylhydantoin

This section briefly reports the results obtained for the identification of the products resulting from the sonochemical and photochemical degradation of 1-methylhydantoin in the presence of hydrogen peroxide. Schwikkard (1994) gives a more detailed report of the results.

Photochemical degradation of 1-methylhydantoin in the presence of hydrogen peroxide was selected as the technique to produce sufficient quantities of degradation products for collection, separation and identification. As the available ultraviolet (UV) irradiation sources were more powerful then the ultrasonic bath, photochemical irradiation enabled the degradation of larger volumes of more concentrated 1-methylhydantoin solutions in shorter time periods. In addition, analysis by high performance liquid chromatography (HPLC) indicated that similar degradation products were formed for the photochemical and sonochemical degradation of 1-methylhydantoin in the presence of hydrogen peroxide. This is expected since the degradation mechanism for both methods involves oxidation of 1-methylhydantoin by hydroxyl radicals.

A white precipitate was formed during the irradiation of 1-methylhydantoin with a medium pressure mercury ultraviolet light source (Hanovia lamp). A mass spectrum of the precipitate was obtained which indicated the presence of a compound with a molecular weight of 128 g/mol, as well as the presence of a contaminant. It was postulated that the reaction of hydantoin with hydroxyl radicals in the presence of oxygen produces parabanic acid (Pegel, 1993) thus the identical reaction with 1-methylhydantoin would result in 1-methylparabanic acid. Hence, this compound was suspected to be 1-methylparabanic acid (which has a molecular weight of 128 g/mol).

The mass spectrum of the precipitate contains all the required fragmentation patterns reported by Corral, et al. (1979) for 1-methylparabanic acid. Other major peaks on the mass spectrum of the precipitate appear to correspond with those reported for 1-methylhydantoin (Corral et al., 1971). Thus, it was tentively concluded that the precipitate contained 1-methylparabanic acid and 1-methylhydantoin.

The solubility of the precipitate in various solvents was tested for subsequent purification using an open silica gel column. No suitable organic solvent or solvent mixture (water, methanol, ethanol, ethyl acetate, hexane, methylene chloride, propan-2-ol, chloroform, glacial acetic acid and water (1:1), diethyl ether) was found in which the precipitate dissolved significantly for further purification purposes.

The solution of 1-methylhydantoin irradiated in the presence of hydrogen peroxide with the Hanovia lamp was rotavapored to dryness so that the products in solution could be separated and purified for identification purposes. An off-white/slightly yellow, hygroscopic precipitate was obtained. The mass spectrum of this precipitate indicated that it contained a mixture of compounds (two distinct parent compounds with a molecular ion of 256 amu and 146 amu were observed but could not be identified). A peak at 60 amu was also obtained which could possibly could correspond to the molecular ion of urea; this is one of the products (the others being 5-hydroxyhydantoin and glycolic acid) formed in the electroreduction of parabanic acid which also produced an off-white, extremely hydroscopic solid (Dryhurst, et al., 1970).

Urea, oxamide and oxalic acid are possible photochemical and sonochemical degradation products of hydantoin or 1-methylhydantoin which have been identified in literature (Dryhurst, et al., 1970; Ochiai, 1971; Fahr, et al., 1980; Yu et al., 1980; Ienaga, et al., 1988). The UV spectra of these compounds were compared to the UV spectra of the degradation products from 1-methylhydantoin for all the experiments carried out. The urea sample was contaminated therefore could not be used for comparison purposes, and the UV spectrum of oxalic acid did not correspond with the spectrum of any of the degradation products. However, the UV spectrum of oxamide was found to be identical to the spectrum obtained for one of the products formed from the sonochemical degradation of 1-methylhydantoin in the presence of hydrogen peroxide and oxygen. Similar retention times were also observed for oxamide and this product under the same HPLC operating conditions thus supporting the identification of this product as oxamide. However, confirmation of the identity of this product is required.

3.4 BIOLOGICAL EFFECTS OF CAVITATION

One objective of this project was to investigate the effectiveness of hydrodynamic cavitation for the inactivation of raw water bacteria since the potential existed for hydrodynamic cavitation to be used as a simple water treatment process (venturis could be installed in water systems to exploit the existing water head). Ultrasonic cavitation is known to decrease the number of viable bacteria in water and was therefore used a comparative technique.

The effect of both types of cavitation on raw water bacteria (present in water obtained from Umgeni Water's Wiggins Water Treatment Works which was supplied from the Cleremont Pump Station in Durban) was determined using the heterotrophic plate count method. This method does not evaluate the quality of the water after treatment but gives an indication of the efficiency of the treatment process. Plate counts of bacteria were enumerated prior to, and after, cavitation. The results were generally plotted in terms of logarithmic reduction curves (death curves). It was noticed that the death curves of raw water bacteria were non-linear. This effect occurs since raw water contains a mixed population of bacteria, the individual species of which have different death rates. Hence, the initial linear portions of the curves (within 10 min) have been used for comparison between experiments. The death curves also demonstrate a *tailing off* effect where the death rate is reduced. This effect is often evident in work where the surviving colonies are below the 30 colonies per plate limit recommended in Standard Methods (1985).

3.4.1 HYDRODYNAMIC CAVITATION

The objective was to determine whether hydrodynamic cavitation alone could reduce the number of colony forming units of raw water bacteria as quantitated by the heterotrophic plate count (HPC) method. Experiments were performed at three selected operating conditions which represent states of low (A), medium (B) and high cavitation (C) intensity for the hydrodynamic cavitation rig. These operating conditions are described in more detail in Section 3.2 and in Botha (1993).

Figure 3.20 illustrates the concentration of colony forming units in raw water cavitated for 2 h at the various intensities of cavitation in the hydrodynamic cavitation rig. Samples were withdrawn at various time intervals during the experiment. The control in each experiment was raw water which was exposed to identical experimental conditions as the samples except the nozzle was replaced by tubing.

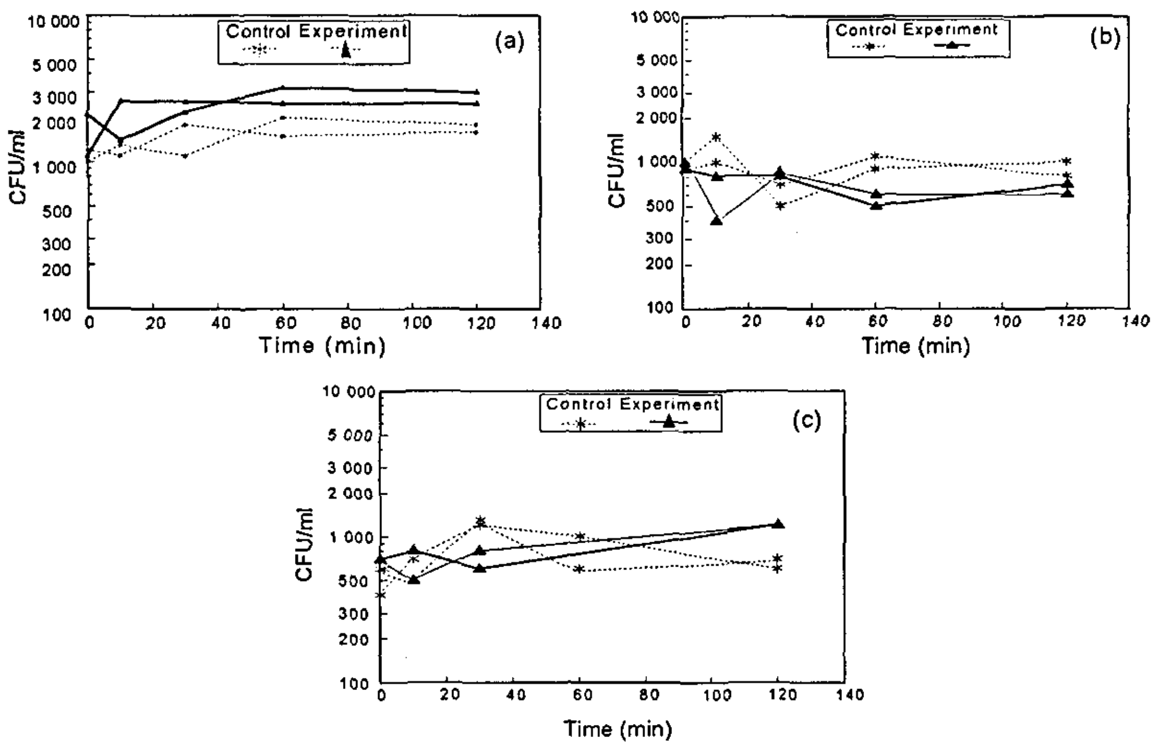

FIGURE 3.20 : Effect of (a) low intensity, (b) medium intensity, and (c) high intensity hydrodynamic cavitation generated in the hydrodynamic cavitation rig on colony forming units in raw water

It is evident from these figures that, whilst there is a slight variation in the bacterial count over the period of the experiment, there is no significant decrease in the concentration of raw water bacteria exposed to hydrodynamic cavitation. The trend in the results is either a constant bacterial count or a slight increase in the counts. This was not considered significant since the increase is less than an order of magnitude. Further experiments in which the cavitation time was increased to 12 h confirmed that there was no enhanced decrease in the bacterial counts of raw water exposed to cavitation.

It was concluded that hydrodynamic cavitation was ineffective as a single process for the inactivation of raw water bacteria since there was no significant effect on the plate counts of raw water bacteria exposed to hydrodynamic cavitation.

Raw water bacteria generally exist in the natural state as aggregates which can be fixed onto the surface of mineral or organic matter or incorporated in human, animal or cell debris. Consequently, bacteria can be protected from inactivation by various disinfecting agents. This has been noted in work with bacterial inactivation by UV irradiation (Qualls, et al., 1983). As hydrodynamic cavitation causes turbulence of the liquid as it passes through the nozzle, it has potential for the dispersion of bacterial aggregates in raw water. In order to determine the degree of dispersion of bacterial aggregates, raw water was cavitated for 2 h in the hydrodynamic cavitation rig. Samples were removed at intervals over the two hour period and the turbidity of the water was measured using nephelometry. In addition, plate counts were performed for each sample in order to assess the relationship between the turbidity of the cavitated water and bacteria concentration. Control experiments were performed using raw water which had been suspended in a bottle inside the feed tank of the cavitation rig to attain the temperature of the samples. The results obtained are presented in Table 3.6.

TABLE 3.6 : Turbidity measurements and plate counts for raw water cavitated at the highest cavitation intensity (ΔP_{nozzle} = 472 kPa) in the hydrodynamic cavitation rig. (-) indicates no analysis

Cavitation time (min)	Turbidity (NTU)		CFU (mℓ)	
	Control	Experiment	Control	Experiment
0	2,3	2,5	1 000	1 100
5	2,5	3,5	(-)	1 400
10	2,5	3,6	(-)	(-)
30	2,6	4,1	700	1 500
120	2,6	4,1	1 000	2 200

The turbidity of the raw water increases over the period of cavitation as a result of dispersion of the bacterial aggregates and the plate counts show a corresponding increase. It was established that the water temperature in the cavitation rig was not responsible for the enhanced plate counts since the plate counts of the control remained constant. It was surmised that the increase in the plate counts was caused by the dispersion of the bacterial aggregates as a result of cavitation since there would be an increase in the number of single or clumped colonies of bacteria in the cavitated water.

Dispersion of bacterial aggregates was qualitatively investigated by photographing samples of cavitated water using scanning electron microscopy. Raw water was sampled prior to cavitation and subsequently after cavitation for 50 h. The samples were treated with standard electron microscopy techniques to prepare stubs for viewing with the scanning electron microscope (Botha, 1993).

Figure 3.21 shows the scanning electron micrographs of non-cavitated (Micrographs 1, 3 and 4) and cavitated (Micrograph 2) water samples. Bacteria exist in raw water as aggregates as illustrated in Micrograph 1. Closer magnification of the bacterial aggregates (Micrograph 3) reveals that the bacteria could be associated with algal cells (the large objects in the micrograph) and debris which provide protection for the bacteria. Micrograph 4 shows the presence of spores (the star-like object and nearby spherical object) which are very resistant to cavitation as well as elongated rod and spherical bacteria. Cavitation of raw water results in dispersion of the bacterial aggregates as is demonstrated in Micrograph 2.

Therefore, it can be concluded that hydrodynamic cavitation generated in the cavitation rig is sufficient to cause dispersion of bacterial aggregates as indicated by the comparison of the turbidity measurements and scanning electron microscopy of cavitated and non-cavitated raw water samples. As a result of this dispersion of bacterial aggregates, the plate counts of bacteria enumerated after hydrodynamic cavitation show a slight increase. However, there is no direct relationship between concentration of colony forming units and the degree of bacterial aggregate dispersion observed with hydrodynamic cavitation of raw water.

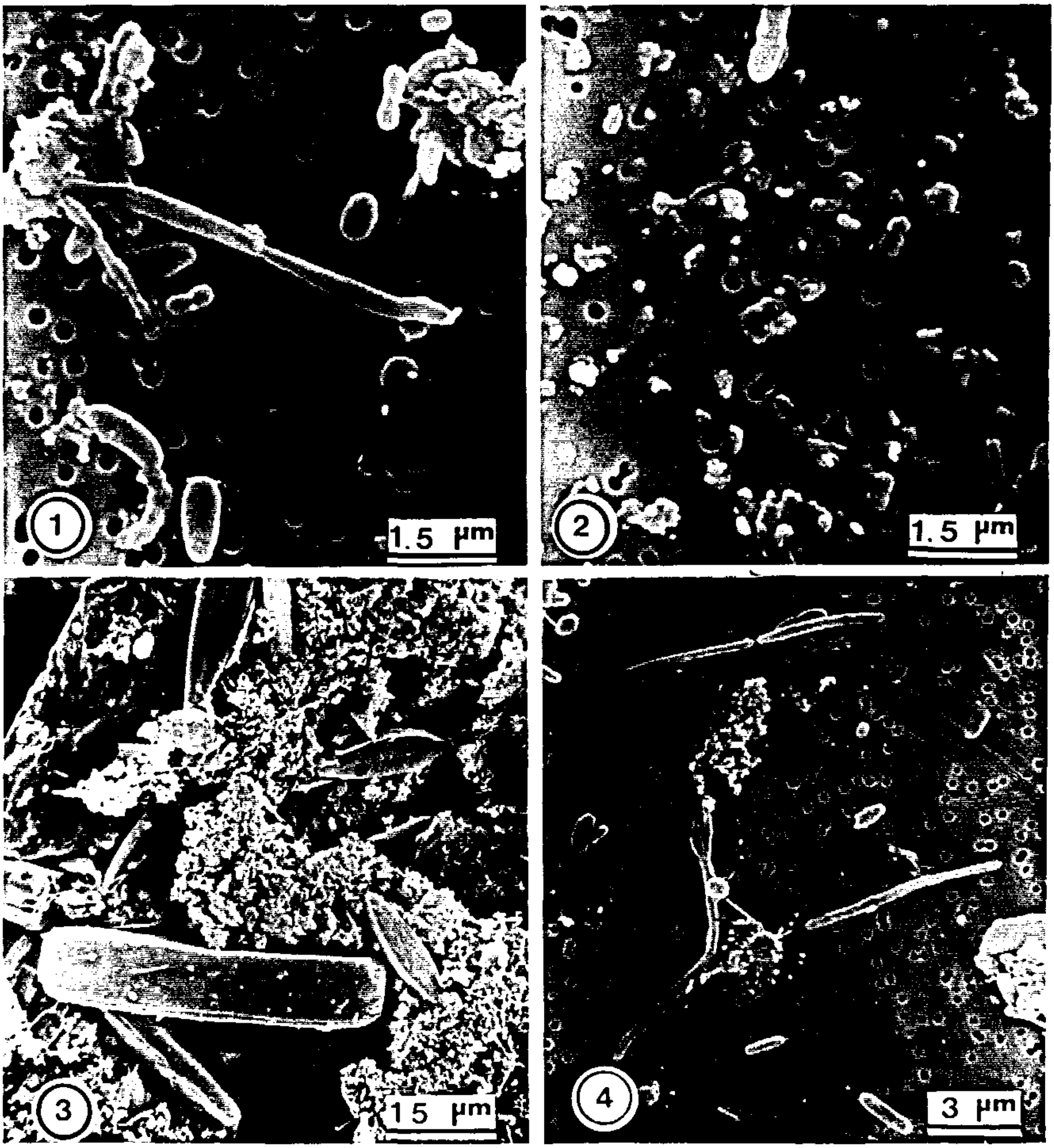

FIGURE 3.21 : Scanning electron micrographs of non-cavitated (Micrographs 1, 3 and 4) and cavitated (Micrograph 2) samples of raw water

3.4.2 ULTRASONIC CAVITATION

Ultrasonic cavitation generated in the ultrasonic bath was investigated for its effect on the numbers of colony forming units of raw water bacteria as quantitated by the heterotrophic plate count method. Samples of raw water were sonicated in the bath at a temperature of 25 °C for 2 h and small volumes were withdrawn from the sonicated samples at various intervals. The control experiments consisted of unsonicated raw water maintained at a constant temperature of 25 °C.

In order to compare results from various experiments that have different initial concentrations of viable bacteria, the results were normalised by dividing by the initial count. It must be emphasised that it is the initial linear portion of the curve which is important when comparing the effectiveness of the various methods used for the inactivation of bacteria in raw water.

Figure 3.22 illustrates the results obtained for the concentration of bacteria in sonicated raw water. The initial results obtained were as colony forming units per mℓ (CFU/mℓ) and are recorded in Botha (1993). However, for the reasons mentioned in the previous paragraph, the results are interpreted in terms of log (N/N_0) where N and N_0 represent the final an initial counts respectively.

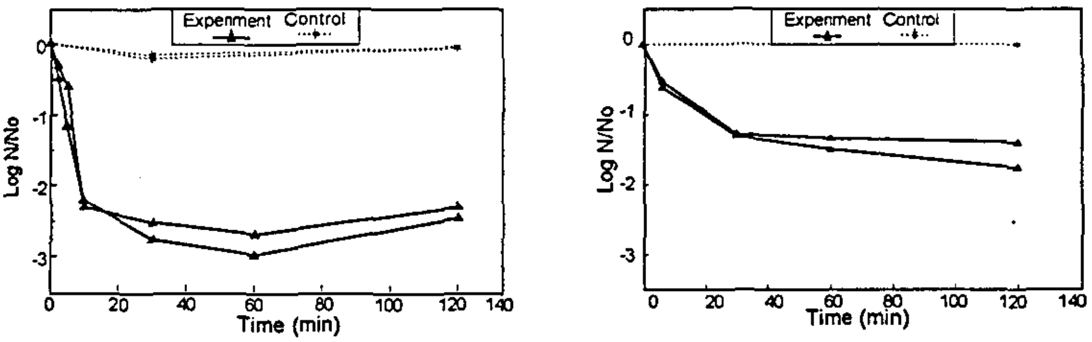

FIGURE 3.22 : Plate counts for raw water sonicated for 2 h in the ultrasonic bath

It can be seen that the cavitation generated by ultrasound results in a decrease in the bacterial count whereas the unsonicated samples (control) indicate no reduction in colony forming units. After 10 min of sonication, there was a log reduction in the bacterial count of between 1 and 2,35 units which corresponds to between 0,1 % and 11 % survival of the bacteria. As the intensity and frequency of ultrasound emitted by the bath has been characterised, it can be concluded that ultrasound of intensity, 9,6 kW/m^2 (Section 3.2.2.1), and frequency, 38 kHz, has an average bactericidal efficiency of 96,2 % for raw water bacteria determined by the heterotrophic plate count method using nutrient agar substrate incubated for 48 h at 37 °C.

Raw water which contained a relatively low initial population of bacteria (1 000 CFU/mℓ) was sonicated for 2 h. Samples of unsonicated and sonicated water were prepared for scanning electron microscopy and photographed. Figure 3.23 illustrates the micrographs obtained for unsonicated (Micrographs 5 and 6) and sonicated (Micrographs 7 and 8) water. As was observed in the micrographs of uncavitated water, a variety of bacteria are present in the unsonicated raw water as aggregates and associated with debris (Micrographs 5 and 6). Dispersion of the bacterial aggregates as well as some disruption of bacterial cells occurs upon sonication as is demonstrated in Micrographs 7 and 8. Comparison of the degree of dispersion caused by hydrodynamic cavitation (Figure 3.21, Micrograph 2) and ultrasonic cavitation (Figure 3.23, Micrograph 7 and 8) indicates that hydrodynamic cavitation is a more effective dispersion method. As result of the low initial bacteria population and thus low turbidity of the sample, the effects of sonication on raw water bacterial aggregates are less pronounced in scanning electron microscopy than that of hydrodynamic cavitation.

It was concluded that ultrasonic cavitation effectively inactivates bacteria as enumerated by the heterotrophic plate count method with the efficiency of inactivation dependent on the intensity and frequency output of the ultrasonic bath. It was concluded from scanning electron microscopy that a possible reason for this is the disruption of bacterial cells by ultrasonic cavitation in addition to their dispersion.

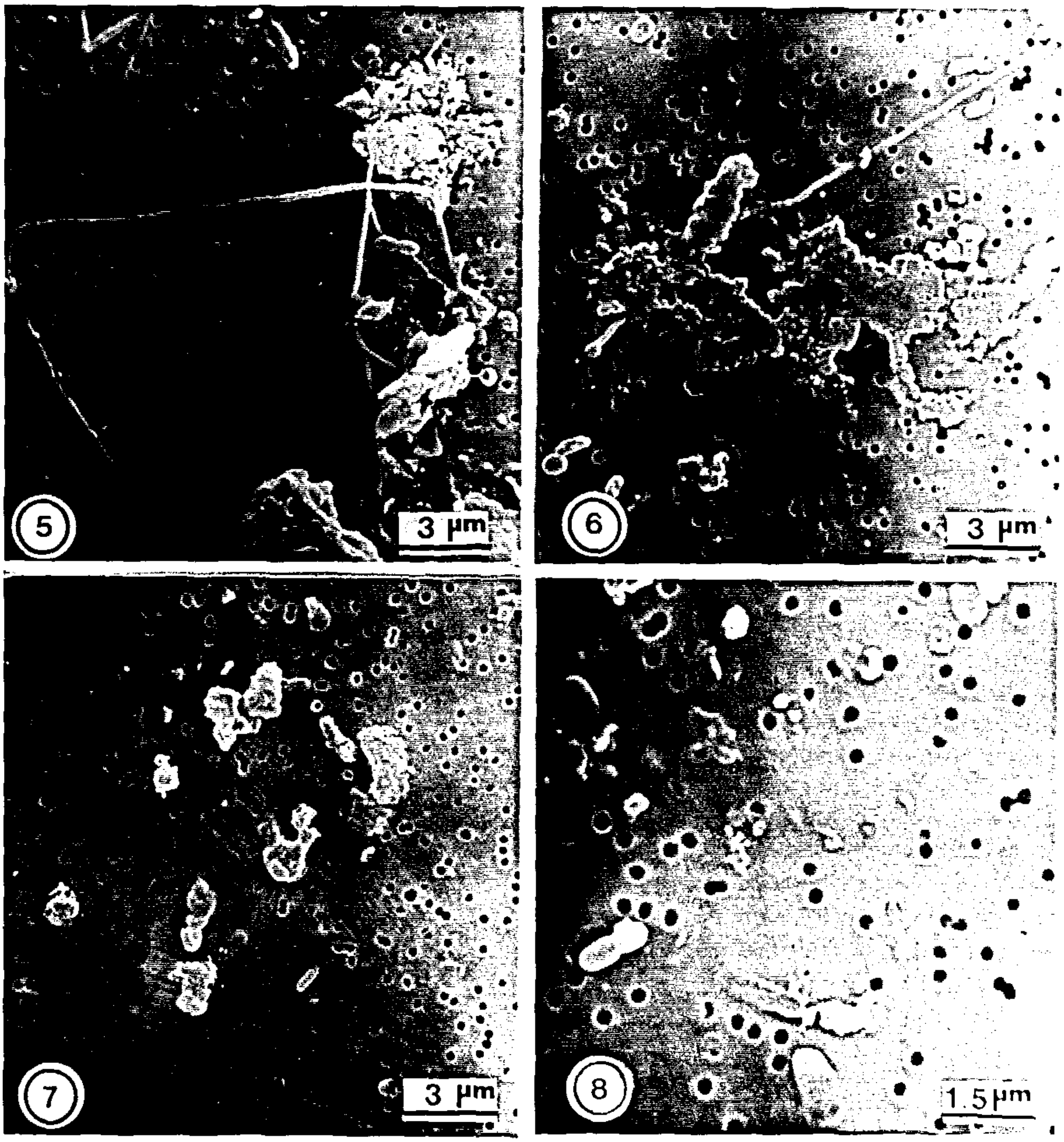

FIGURE 3.23 : Scanning electron micrographs for unsonicated (Micrographs 5 and 6) and sonicated (Micrographs 7 and 8) samples of raw water

3.4.3 CAVITATION AND ULTRAVIOLET IRRADIATION

Ultrasonic cavitation results in dispersion of aggregates and the inactivation of bacteria. It is possible that hydrodynamic cavitation may enhance the inactivation of bacteria by other disinfecting agents since hydrodynamic cavitation disperses bacterial aggregates thus enabling a greater exposure of bacteria to the disinfecting agent. The disinfecting agent chosen in this study was ultraviolet irradiation as it is extremely effective and non-chemical. Both hydrodynamic and ultrasonic cavitation prior to ultraviolet (UV) irradiation were investigated for their effectiveness to enhance the biological effects of UV radiation.

A high pressure mercury lamp with a 254 nm filter was used as the light source. The intensity of the lamp was determined by chemical actinometry to be 0,2 mW/cm^2. Raw water was obtained from Wiggins Water Treatment Plant and cavitated either in the hydrodynamic cavitation rig or in the ultrasonic bath for various periods of time. After cavitation the samples were irradiated with UV light for various time periods before plating and enumeration of viable bacteria. The control for each experiment consisted of uncavitated water that was irradiated with the UV light.

The results obtained for the UV inactivation of the sonicated raw water samples are illustrated in Figures 3.24 and 3.25. It can be seen the figures that ultrasonic cavitation followed by irradiation only appears to have a significant effect on the death rate of bacteria after a sonication time of 10 min (Figure 3.25) which can be attributed to the fact that sonication alone is sufficient to cause inactivation.

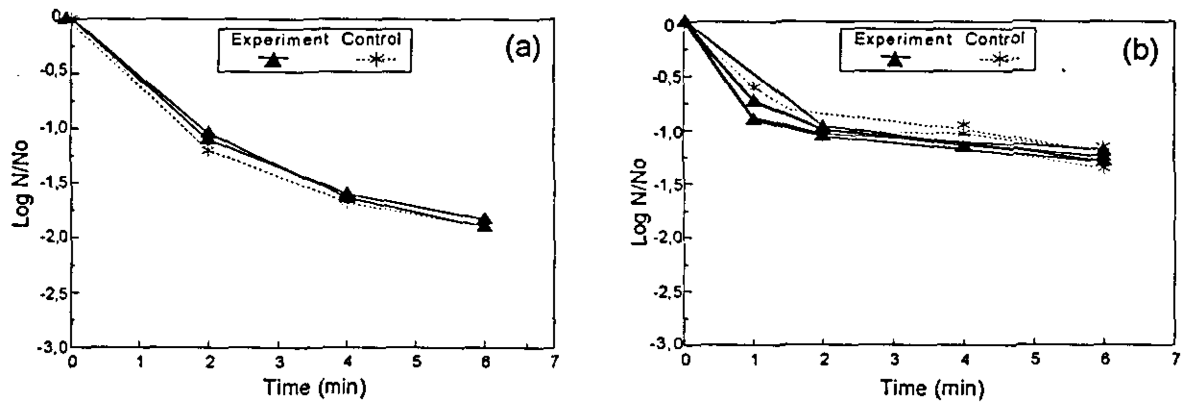

FIGURE 3.24 : Plate counts for raw water sonicated for 1 min prior to UV irradiation

3.4.3 CAVITATION AND ULTRAVIOLET IRRADIATION

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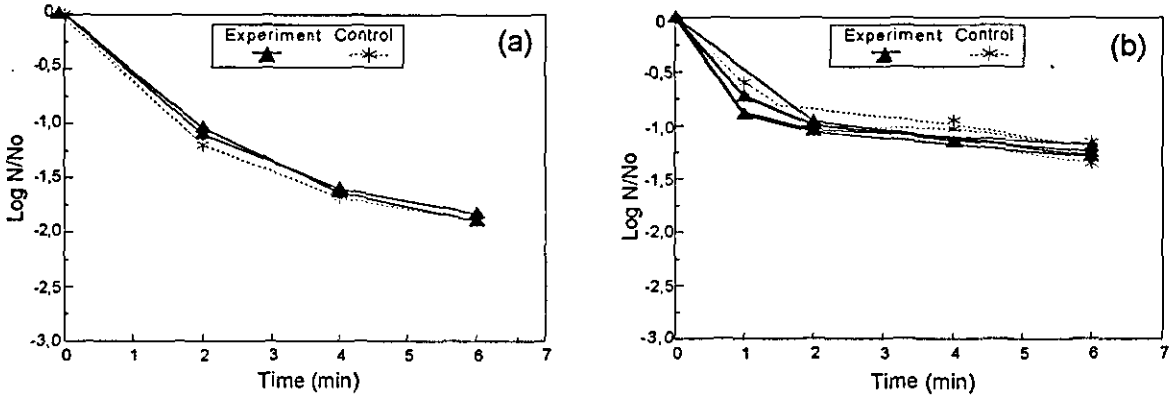

FIGURE 3.24 : Plate counts for raw water sonicated for 1 min prior to UV irradiation

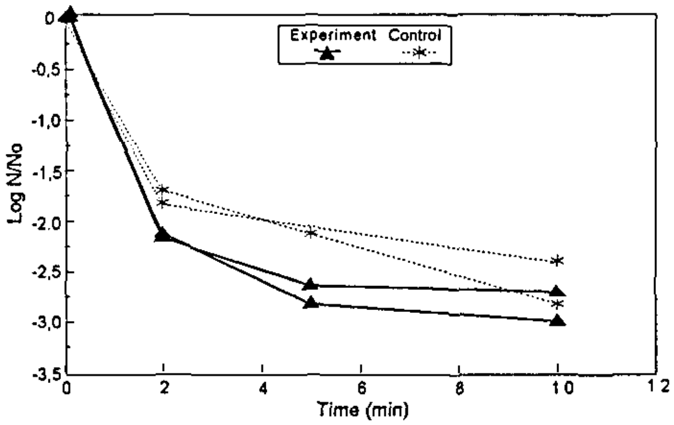

FIGURE 3.25 : Plate count for raw water sonicated for 10 min prior to UV irradiation

Comparison of the control and experimental death curves in Figures 3.24(a) and 3.24(b) demonstrate little enhancement in the inactivation of bacteria by UV in sonicated raw water. Since UV radiation is a potent inactivator of bacteria (refer to Figure 3.26), any effect of sonication on the death rate of the bacteria is insignificant.

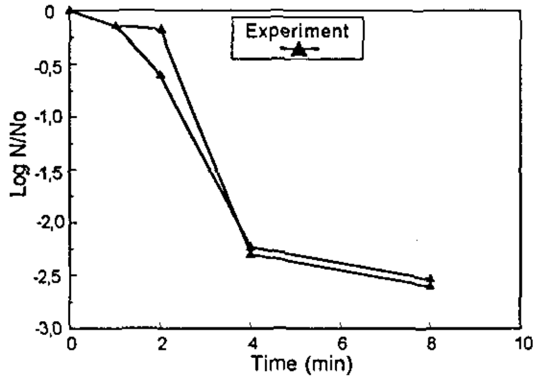

FIGURE 3.26 : Death curve for raw water bacteria irradiated with UV light of 254 nm

The effect of the enhancement of UV irradiation on bacterial inactivation was determined by cavitating raw water in the hydrodynamic cavitation rig at the highest intensity of cavitation for 3 minutes prior to irradiation with UV. Uncavitated raw water was irradiated under identical experimental conditions as the controls. Plate counts were performed before and after cavitation on the irradiated raw water. The results obtained are depicted in Figure 3.27.

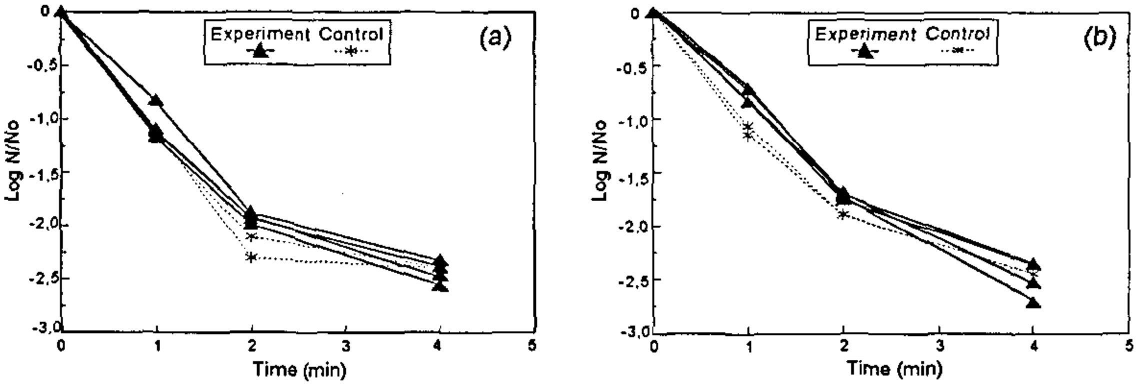

FIGURE 3.27 : Plate counts for raw water cavitated for 3 min *prior to UV irradiation*

It is evident from Figures 3.27(a) and 3.27(b) that there is negligible enhancement on the inactivation of raw water bacteria when hydrodynamic cavitation is used in conjunction with UV. After 2 min of irradiation, there is a log reduction of 2 and 1,7 for Figures 3.27(a) and 3.27(b) respectively. These reductions correspond to an average inactivation of 98,2 % for raw water bacteria exposed to a UV dose of 25,2 mWs/cm^2. These results are consistent with those obtained from low intensity cavitation of raw water followed by UV irradiation.

From the experiments performed it was concluded that there was no significant enhancement by ultrasonic or hydrodynamic cavitation in the inactivation of raw water bacteria by ultraviolet radiation. This could be attributed to the fact that the UV source used in the experiments is very intense and is therefore extremely effective alone for the inactivation of bacteria in raw water (97,5 % inactivation of bacteria is observed for a UV dose of 25,2 mWs/cm^2). Any contribution to the enhancement of the death rate of bacteria by cavitation is therefore observed to be negligible in comparison to the effectiveness of inactivation by UV light. This could be confirmed by using a less intense UV source and repeating the experiments performed using the combination of cavitation, both ultrasonic and hydrodynamic, and ultraviolet light.

Chapter 4

Conclusions

This chapter presents the conclusions obtained from the four areas of research investigated in this project, namely,

☐ The microbiological assessment of hydrodynamic cavitation for the treatment of raw water

☐ The evaluation of hydrodynamic cavitation in the cavitation chamber of the CAV-OX® system

☐ The effect of ultrasonic cavitation on organic pollutants in industrial effluents

☐ The computational fluid dynamics of hydrodynamic cavitation in a venturi

In order to be consistent with the style of this report, the conclusions are discussed in terms of the various effects of cavitation.

4.1 THEORETICAL EFFECTS OF CAVITATION

It was concluded from this investigation that the numerical method using the STAR-CD program is capable of simulating flow conditions up to cavitation, i.e. to indicate the potential of cavitation in a fluid. In addition, using computational fluid dynamics, it is possible to estimate the local velocities at any point within a venturi thus enabling the determination of local cavitation conditions (as defined by a cavitation number) at any point in a fluid.

4.2 PHYSICAL EFFECTS OF CAVITATION

The characteristics of ultrasonic cavitation produced in an ultrasonic cleaning bath and hydrodynamic cavitation produced in the cavitation chamber of a modified CAV-OX® system and a specially-constructed hydrodynamic cavitation rig were investigated.

The physical characteristics of the hydrodynamic cavitation produced in the CAV-OX® chamber and the hydrodynamic cavitation rig were investigated in terms of appearance of bubbles (a phenomenon of cavitation), nozzle flow characteristics, cavitation number (this indicates the intensity of cavitation; the lower the cavitation number, the greater the intensity of cavitation produced) and sound emission. The presence of bubbles, which formed in the throat and collapsed in the divergent section of the chamber, indicated that hydrodynamic cavitation occurred in both systems. The mass of bubbles increased with increasing flow rate, increasing throat pressure and decreasing discharge pressure. From this, it was concluded that the degree (intensity) of hydrodynamic cavitation increases with increasing flow rate and as the pressure drop across the nozzle is increased (this was also observed in the investigation of computational fluid dynamics of hydrodynamic cavitation). This was confirmed by the results for the cavitation numbers for the CAV-OX® chamber and hydrodynamic cavitation rig. Throat cavitation numbers in the CAV-OX® chamber ranged from 0,006 to 0,563 and hydrodynamic cavitation, as indicated by the presence of bubbles, was only observed in the CAV-OX® chamber when the throat cavitation number was less than the threshold cavitation number (which was predicted from extrapolation of literature results to be 0,250 for the CAV-OX® chamber). Cavitation numbers in the hydrodynamic cavitation rig ranged from 0,025 to 0,482; the greatest flow rate and pressure drop across the nozzle resulted in the lowest cavitation number thus confirming that these flow conditions produced the greatest degree of cavitation. Since the collapse of bubbles emit sound, the sound pressure levels determined in the CAV-OX® chamber and hydrodynamic cavitation rig increased with increasing flow rate and pressure drop across the nozzle. The sound pressure levels emitted by the hydrodynamic cavitation rig reached at maximum of 82 dB at 4 000 Hz for the most intense condition of cavitation.

The ultrasonic cavitation produced in a ultrasonic cleaning bath was also characterised in terms of its physical effects. It was proposed that stable ultrasonic cavitation occurs with an intensity of 9,6 kW/m^2 in the ultrasonic cleaning bath. However, this intensity is reduced in the reaction vessel.

4.3 CHEMICAL EFFECTS OF CAVITATION

The chemical characteristics of hydrodynamic cavitation were determined by evaluating the concentration of hydrogen peroxide produced in the CAV-OX® chamber and hydrodynamic cavitation rig. No detectable amount of hydrogen peroxide was produced by the hydrodynamic cavitation of water in the CAV-OX® chamber, even in the presence of oxygen (which enhances hydrogen peroxide production). Similarly, no detectable amount of hydrogen peroxide was produced by the hydrodynamic cavitation (using the most intense cavitation conditions) of water in the hydrodynamic cavitation rig. The minimum detection limit of hydrogen peroxide for these experiments was 0,034 mg/ℓ using the spectrophotometric analytical method of Baga, et al. (1988).

The concentration of hydrogen peroxide produced by the ultrasonic cavitation of water in the ultrasonic cleaning bath was determined to be approximately 0,06 mg/ℓ. This result supports the reports that hydroxyl radicals (which combine to form hydrogen peroxide) are formed during ultrasonic cavitation. Saturation of water with oxygen prior to ultrasonic cavitation (sparged for 15 min prior to sonication) significantly enhanced the concentration of hydrogen peroxide formed from 0,06 mg/ℓ to 3,5 mg/ℓ. It was concluded that continuous sparging with oxygen was necessary in order to maintain the enhancement of the radical reactions in the presence of oxygen.

The degradation of 1-methylhydantoin by ultrasonic cavitation was investigated and it was demonstrated that partial degradation (approximately 25 to 30 %) occurs, possibly due to oxidation by the radical species (especially hydroxyl radicals) that are formed during ultrasonic cavitation. Degradation of 1-methylhydantoin is enhanced by the addition of 1 332 mg/ℓ hydrogen peroxide (approximately 62 % degradation), and further degradation (approximately 68 %) occurs with the addition of hydrogen peroxide and oxygen saturation prior to sonication.

Investigation into the identification of the sonochemical and photochemical degradation products of 1-methylhydantoin in the presence of hydrogen peroxide indicated that similar products were formed. One of the products formed in the photochemical and sonochemical degradation of 1-methylhydantoin in the presence of hydrogen peroxide was tentatively identified as 1-methylparabanic acid. Oxamide was a suspected product in the sonochemical degradation of 1-methylhydantoin in the presence of hydrogen peroxide and oxygen

4.4 BIOLOGICAL EFFECTS OF CAVITATION

As there was no detectable decrease in the colony forming units of raw water bacteria as enumerated by the heterotrophic plate count technique, it was concluded that hydrodynamic cavitation does not inactivate raw water bacteria. However, it was observed from scanning electron micrographs that hydrodynamic cavitation of raw water caused increased dispersal of bacterial aggregates which caused a increase in the turbidity measurements. Consequently, the combination of hydrodynamic cavitation and ultraviolet irradiation was assessed to determine if the dispersal of bacterial aggregates by hydrodynamic cavitation prior to ultraviolet irradiation would enhance bacterial inactivation by ultraviolet light. No significant enhancement in bacterial inactivation was observed when compared with only ultraviolet irradiation. Significant inactivation of raw water bacteria (1,6 to 2 log reduction units) occurred upon ultrasonic cavitation of the water in the ultrasonic cleaning bath.

4.5 SUMMARY OF CONCLUSIONS

The potential of hydrodynamic cavitation for the treatment of raw water without the addition of chemicals has been disproved since hydrodynamic cavitation is not an effective method for the inactivation of bacteria in raw water. Similarly, the application of hydrodynamic cavitation as a single advanced oxidation process is not recommended as the concentration of hydrogen peroxide produced by the hydrodynamic cavitation of water (less than 0,03 mg/ℓ) would be ineffective for the oxidation of organic pollutants in industrial effluents and potable water. These results also invalidate the manufacturer's claims about role of hydrodynamic cavitation in the production of hydroxyl and hydrogen radicals in the CAV-OX® system. From the results obtained during this research project, it was concluded that the function of the hydrodynamic cavitation produced in the cavitation chamber of the CAV-OX® system is to disperse the effluent prior to oxidation with hydrogen peroxide and ultraviolet light. The results obtained for the degradation of 1-methylhydantoin (an organic pollutant in Sasol effluent) by ultrasonic cavitation in the ultrasonic cleaning bath indicate the potential of sonochemistry as an advanced oxidation process for the treatment of industrial effluents. The sonochemical formation of hydroxyl radicals by ultrasonic cavitation can be enhanced for industrial treatment purposes by the addition of hydrogen peroxide and oxygen. The flow conditions, i.e. fluid velocities and pressure drops, which initiate hydrodynamic cavitation in a fluid can be simulated using computational fluid dynamics. However, whilst it has been demonstrated that computational fluid dynamics is a useful tool to indicate the potential of a fluid to undergo cavitation, the numerical simulation of hydrodynamic cavitation which involves two-phase flow using computational fluid dynamics has not been achieved in this project because the flow system is too complex.

Thus, the conclusions resulting from this project can be summarised as follows :

☐ Computational fluid dynamics using the STAR-CD program can be used to determine the flow conditions in a pipe, venturi, etc., which initiate hydrodynamic cavitation.

☐ Hydrodynamic cavitation, which has been characterised in terms of its physical effects in two sets of equipment, does not produce detectable concentrations of hydrogen peroxide thus negating the reports of hydroxyl radical formation, and subsequent hydrogen peroxide production, by hydrodynamic cavitation in the CAV-OX® system (EPA, 1993).

☐ Hydrodynamic cavitation is not effective as a method for the inactivation of bacteria in raw water although it has been used to disrupt bacterial cells (Harrison and Pandit, 1992a, b). However, hydrodynamic cavitation could be used as a means of dispersion in combination with processes such as the CAV-OX® process.

☐ Ultrasonic cavitation in an ultrasonic cleaning bath does produce hydrogen peroxide as well as inactivate raw water bacteria.

☐ Degradation of 1-methylhydantoin can be achieved by ultrasonic cavitation in the ultrasonic cleaning bath. The degradation rate is enhanced in the presence of hydrogen peroxide, and in the presence of hydrogen peroxide combined with oxygen saturation prior to sonication. Similar results are observed for the photochemical degradation of 1-methylhydantoin.

☐ Two degradation products of 1-methylhydantoin have been tentatively identified : 1-methylparabanic acid results from the photochemical and sonochemical degradation of 1-methylhydantoin in the presence of hydrogen peroxide, and oxamide is a suspected product in the sonochemical degradation of 1-methylhydantoin in the presence of hydrogen peroxide and oxygen.

Chapter 5

Recommendations

From the research carried out in this project, the following recommendations can be made :

- ☐ No further investigation into the CAV-OX® process.
- ☐ Further investigation into ultrasonic cavitation on a laboratory and pilot-plant scale for the treatment of industrial effluents.
- ☐ Investigation of the combination of ultrasonic cavitation and ultraviolet treatment using industrial effluents.
- ☐ Investigation of effect of dispersional mixing using hydrodynamic cavitation together with disinfection with chlorine or ozone on the dose of these disinfectants.
- ☐ No further work on the computational fluid dynamics of hydrodynamic cavitation since the detailed flow conditions that occur during cavitation cannot be modelled at present.

Chapter 6

Technology Transfer

6.1 INTERACTION WITH OTHER WRC PROJECTS

Involvement with the University of Potchefstroom for Christian Higher Education and their use of computational fluid dynamics to describe hydrodynamic cavitation in a venturi has resulted in further application of computational fluid dynamics in the Water Research Commission Project No. 648 : *The Application of Computational Fluid Dynamics to Improve the Design and Operation of Water and Wastewater Treatment Works.*

6.2 TECHNOLOGY TRANSFER ASPECTS

Interest in advanced oxidation processes has been shown by Sasol, University of Durban-Westville, Eskom, C G Smith and the Foundation for Water Research :

☐ A report highlighting the industrial uses of sonochemistry for Sasol was prepared for Dr P Stegman **(Annexure A)**.

☐ Assistance has been given to Mr G Lok of Eskom Technology, Research and Investigations who requested information on the uses of sonochemistry in the food and beverage industry.

☐ Technical advice has been given to Mr S Baines of the Physics Department at the University of Durban-Westville.

☐ Dr K J Zeitsch from CG Smith Chemicals, and Dr G Burger and Mr J Buzzard from Illovo Sugar Ltd approached the Pollution Research Group for information on ultraviolet radiation for the sugar industry.

☐ Two representatives (Ms C Stephens and Dr D Newsome) from the Foundation for Water Research (FWR) in the United Kingdom visited the Pollution Research Group in May 1995. The FWR are involved in ultrasonic work and were interested in using ultrasonic cavitation for water treatment.

6.3 PUBLICATIONS

6.3.1 Papers Presented at Conferences and Seminars

☐ S Chetty, F G Neytzell-de Wilde and C A Buckley, *Evaluation of Hydrogen Peroxide and Ultraviolet Radiation of Oxidised Organic Molecules in Industrial Effluents and Potable Water*, 2nd Biennial Conference/Exhibition, Water Institute of Southern Africa, World Trade Centre, Kempton Park, South Africa, 13 - 16 May 1991 **(Annexure B)**

- ☐ G W Schwikkard, *Water Purification by means of Free Radicals*, Sasol Technology Symposium, Rand Afrikaans University, Johannesburg, South Africa, 1 July 1992
- ☐ C J Botha and C A Buckley, *Disinfection of Potable Water - The Role of Hydrodynamic Cavitation*, International Specialised Conference on the Disinfection of Potable Water, Kruger National Park, South Africa, 13 - 18 March 1994
- ☐ C Kaiser, G W Schwikkard and S J Winship, *The Use of Cavitation as an Advanced Oxidation Process for Water Treatment*, Water Institute of Southern Africa (Natal branch) General Meeting, Pinetown, South Africa, 26 July 1995

6.3.2 Poster Presentations

- ☐ C J Botha and C A Buckley, *A Study of Hydrodynamic Cavitation as a Method of Water Disinfection*, Biotech SA '93 : 1st Biotechnology Conference in South Africa - Biotechnology and Development in South Africa, Rhodes University, Grahamstown, South Africa, 31 January - 3 February 1993

6.3.3 Papers in Journals

- ☐ Candace J Botha and Chris A Buckley, *A Study of Hydrodynamic Cavitation as a Method of Water Disinfection*, **Journal of Water Supply Research and Technology - Aqua**, 1995, Vol. 13, No. 2, in print **(Annexure C)**

6.3.4 Theses

- ☐ C J Botha, *A Study of Hydrodynamic Cavitation as a Method of Water Treatment*, MScEng thesis, University of Natal, Durban, South Africa, 1993
- ☐ G W Schwikkard, *An Investigation of the Sonochemical Degradation of Hydantoin Compounds*, MScEng thesis *(cum laude)*, University of Natal, Durban, South Africa, 1994
- ☐ S Chetty, *The Evaluation of the Cavitation Process to Produce Radical Species capable of Oxidising Organic Pollutants in Industrial Wastewaters and Potable Water*, MScEng thesis, University of Natal, Durban, South Africa, 1994

6.3.5 Other

- ☐ As a spin-off from this project, research is being undertaken on the kinetics of hydrogen peroxide formation in the ultrasonic bath by a MScEng student, Sanjeev Jewnarain, at the University of Natal.

6.4 ARCHIVING OF DATA

The data from the project is contained in **Annexures D** to **F** which are available from the Water Research Commission on request.

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ANNEXURE A

REPORT TO SASOL :
THE INDUSTRIAL USES OF SONOCHEMISTRY

by

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July 1995

Annexure to Report to the Water Research Commission on Project No. 388 entitled :
Evaluation of Different Methods to produce Free Radicals for the Oxidation of Organic Molecules in Industrial Effluents and Potable Water (with special reference to CAV-OX®)

Head of Pollution Research Group	:	Professor C A Buckley
Project Leader	:	Ms S J Winship
Project Team	:	Ms C J Kaiser
		Mr S Chetty
		Mr D J Meyer
		Mr G W Schwikkard

Industrial Application of Ultrasound

April 1995
Gavin Schwikkard

Ultrasonic applications with the potential for use at Sasol are discussed in the following sections :

1 Chemical Processing

The application of ultrasonic energy in the chemical processing industry can be classifed into two categories: (a) applications in which ultrasonic methods yield a product superior to that obtained by conventional means (due to a change in reaction path) and (b) applications where ultrasonic energy is used to enhance the rates of conventional unit operations, e.g. solid-liquid extractions (Chendke and Fogler, 1975).

In organic synthesis, the use of ultrasound can reduce reaction time and by-product formation thus increasing the yield (Henglein, 1987). Suslick and Johnson (1984) demonstrated that the use of ultrasound reduced temperature and pressure requirements for formation of transition-metal carbonyl complexes. For the reaction in **Scheme 1**, the use of ultrasound enabled the operating temperature and pressure to be decreased from 160 to 10 °C and from 20,3 to 0,45 MPa respectively, while still giving a comparable yield of the end product.

$$VCl_3.(THF)_3 \rightarrow V(C$$

Scheme 1

Ultrasound can be applied to both homogeneous and heterogeneous chemical reactions. With homogeneous chemical reactions, an increase in reactivity with sonolysis occurs because of the formation of radicals. Sonolysis of water produces hydrogen and hydroxyl radicals which combine to form hydrogen peroxide (Makino et al., 1982). Radical formation has also been reported for the sonolysis of organic solvents. Jennings and Townsend (1961) proposed a reaction scheme involving free radicals for the sonication of carbon tetrachloride and chloroform in water. They reported that the sonication of carbon tetrachloride and chloroform molecules produced free radicals since the dissociation energy required for these molecules was less than that required to split the water molecule (which is known to dissociate during sonication).

For heterogeneous reactions involving mixtures of immiscible liquid phases, sonolysis causes a fine emulsion of the phases and chemical reactions are enhanced due to the increase in interfacial contact area between the phases (Mason, 1990). Davidson et al. (1987) investigated the hydrolysis of wool waxes in sodium hydroxide and reported that the use of ultrasound decreased the reaction time and temperature.

In heterogeneous solid-liquid reactions, the metal can either take part in the reaction or act as a catalyst. The enhanced reactivity can be attributed to an increase in surface area because of the erosion (pitting) of the metal surface which is due either to microstreaming or shock wave generation during cavity collapse (Mason, 1990). Ratoarinoro et al. (1992) investigated the physical and chemical effects of ultrasound on the addition of ethyl malonate to chalcone in toluene using potassium hydroxide as a solid catalyst. With sonication, the initial reaction rate increased by a factor of 10. This increase in reaction rate is due to a decrease in the size of catalyst particles during sonication which corresponds to an increase in surface area thereby increasing the reaction rate.

The ultrasonic enhancement of heterogeneous reactions is greater than that obtained for homogeneous reactions, indicating that chemical applications of ultrasound in industry will be most feasible for heterogeneous solid-liquid reactions, i.e. reactions incorporating a solid phase or catalyst (Bremner, 1986).

Inter-phase mass transfer, especially solid-liquid extractions, is also enhanced by the application of ultrasonic waves. Solid-liquid extraction processes which have showed an increase in extraction rates due to the application of ultrasound are: extraction of soluble matter from cellular solids (e.g. sugar from sugar beets), solvent extraction (oils from oil seeds), extraction of alkaloids from herbaceous and plant-like materials and the leaching of oils (Chendke and Fogler, 1975).

2 Environmental Remediation

Ultrasound can be applied in environmental remediation, for the removal of airborne particles or degradation of low level contaminants (Grinthal and Ondrey, 1992). Acoustic agglomeration can be used to remove pollutant particles from air which are too small (less than 5 um in diameter) to be removed by electrostatic precipitators. Airborne soot in a 15 m^3 chamber were reduced by three orders of magnitude with an ultrasonic transducer, which operated at 21 kHz, in experiments performed at the Institute of Transuranium Elements in Germany; experiments were also scaled up to a 170 m^3 chamber (Grinthal and Ondrey, 1992).

Projects in the USA funded by the Department of Energy (DOE) and the Environmental Protection Agency (EPA) are researching the ultrasonic enhanced decomposition of toxic organics in soil and water (Grinthal and Ondrey, 1992). The results from one project, have shown that ultrasound reduced the time required to destroy 3-chlorobiphenyl in waste water by 75 % (Grinthal and Ondrey, 1992). The reaction was performed at ambient temperature and pressure, and titanium dioxide was used to catalyze the degradation of water molecules into hydroxyl radicals; the hydroxyl radicals react with the halogenated organic compounds decomposing them into carbon dioxide and hydrochloric acid. Ultrasound has been used in research performed at the University of Akron (Ohio) into the treatment of drinking and waste water contaminated with low level (mg ℓ^{-1}) volatile organic compounds (Grinthal and Ondrey, 1992). Ultrasound was shown to destroy seven pollutants, separately and in mixtures (benzene, carbon tetrachloride, 1,2-dichloroethane, methylene chloride, 1,1,1-trichloroethane, 1,1,2-trichloroethylene and toluene). Although the cost of ultrasonic treatment was more then ozonolysis, ultrasonic treatment was more effective in the treatment of certain compounds; 1,1,1-trichloroethane, trichloromethane and carbon tetrachloride (Grinthal and Ondrey, 1992).

The combination of ultrasound and ozone has been used in the treatment of industrial effluent and municipal sewage. The use of ultrasound causes an emulsion, of the suspended particles and dispersed microorganisms, to form. In the treatment chamber, ultrasonic waves prevent the ozone bubbles from coalescing thus ensuring a maximum surface area available for oxidation (Chendke and Fogler, 1975). In a pilot plant processing 76 ℓ d^{-1} of sewage, 60 s of ultrasonic and ozone treatment proved capable of destroying 100 % of the microorganisms, 93 % of the phosphates and 72 % of the compounds containing nitrogen (Chendke and Fogler, 1975).

3 Emulsification

The advantages of ultrasonic emulsification over conventional methods are that an ultrasonic emulsion has particles in the submicrometre range with an extremely narrow particle size distribution. In laboratory studies, the mean particles size of an ultrasonic emulsion was reported to be between 0,18 to 0,37 µm (Chendke and Fogler, 1975). The emulsions are more stable and thus the addition of a surfactant to produce and stabilize the emulsion is not necessary. The energy needed to produce an emulsion is also less than that needed in conventional methods (Chendke and Fogler, 1975). Industrial applications of ultrasonic homogenization are the production of worcestershire sauce, cream type soups, peanut butter and emulsion paint (Chendke and Fogler, 1975).

4 Polymer Chemistry

Prolonged exposure of polymer solutions to ultrasound results in a permanent reduction in the viscosity of the solution. This degradation is due to cavitation. Ultrasound is also used for the initiation of polymerization (Lorimer, 1990). Ultrasonic irradiation, in both batch and continuously stirred reactors, of the suspension polymerization of styrene was found to be an effective method of preventing agglomeration between droplets and the sticking of droplets to the reactor wall. Both of these lead to heat build up and the formation of large masses thus shortening operation times (Hatate et al., 1981 in Lorimer, 1990).

5 Defoaming

Ultrasonic techniques used for breaking foams are mechanical with the advantage that the addition of chemical defoaming agents are not required. Most liquids with viscosities up to 500 cp can be ultrasonically defoamed, however, the exact mechanism of ultrasonic foam disintegation is not entirely understood (Chendke and Fogler, 1975).

6 Ultrasonic Mixing

Reverbatory ultrasonic mixers introduce a high level of ultrasonic energy into a flowing stream for a brief period of time. A typical application is the cleaning of crushed ore which improves the recovery of precious metals from the ore (Hunicke, 1990). Water slurries of 3 ℓ s^{-1} can be treated with a total of 16 kW of ultrasonic energy. Vibrating trays are used for coal and ore beneficiation which can treat slurries with a typical flow rate of 6 kg s^{-1} (mixed with an equal volume of water). The power requirement of this equipment (2 kW) is remarkably low (Hunicke, 1990).

7 Ultrasonic Cleaning

Ultrasonic cleaning equipment is the most widely used ultrasonic industrial application and systems of up to 50 000 ℓ are commercially available (Mason, 1991). An ultrasonic cleaner which contained approximately 7 500 ℓ of heated alkaline-detergent solution and delivered 40 kW of ultrasonic energy was used by the US Navy, from 1968 onwards, to facilitate the disassembling of jet engines since heat and corrosion made the unscrewing of fastening bolts difficult (Hunicke, 1990). The ultrasonic energy was supplied by two banks of immersible transducers and the uniformity of the ultrasonic energy was found to be within 10 % anywhere in the tank.

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ANNEXURE B

EVALUATION OF HYDROGEN PEROXIDE AND ULTRAVIOLET RADIATION OF OXIDISED ORGANIC MOLECULES IN INDUSTRIAL EFFLUENTS

Paper presented by

S Chetty, F G Neytzell-de Wilde and C A Buckley
2nd Biennial Conference/Exhibition, Water Institute of Southern Africa, Kempton Park,
South Africa, 13 - 16 May 1991

Annexure to Report to the Water Research Commission on Project No. 388 entitled :
Evaluation of Different Methods to produce Free Radicals for the Oxidation of Organic Molecules in Industrial Effluents and Potable Water (with special reference to CAV-OX®)

Head of Pollution Research Group	:	Professor C A Buckley
Project Leader	:	Ms S J Winship
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EVALUATION OF HYDROGEN PEROXIDE AND ULTRAVIOLET RADIATION TO OXIDISE ORGANIC MOLECULES IN INDUSTRIAL EFFLUENTS AND POTABLE WATER

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ABSTRACT

The protection of the environment has become an important issue which has implications on industrial operations, specifically the oxidation of organic pollutants in wastewaters. Present methods employ processes to produce a free radical which initiates free radical chain reactions. The use of photolysis for this application has been studied but industrial applications are limited. This preliminary study evaluates the literature of the photocatalytic processes with emphasis on ultraviolet radiation. Current work is concentrated on the production of the hydroxyl radical as an initiator which can be achieved by the photocatalytic decomposition of hydrogen peroxide. It has been reported that cavitation also produces the hydroxyl radical from a water molecule. Effluents containing reactive dyes were treated with UV radiation and hydrogen peroxide. The decolourisation of these effluents was maximised at the UV exposure time of 56 seconds for peroxide concentrations greater than 20 mg/ℓ. Cyanide effluent was also treated and the concentration was reduced from 5 mg/ℓ to under 2 mg/ℓ with 7 mg/ℓ of hydrogen peroxide.

EKSERP

Die beskerming van die omgewing het nou 'n belangrike saak geword en het verwikkelinge op nywerheidse bewerkings gekry. Een van die gebiede wat bepaar daardeur beinvloed is, is die verwydering van organiese besoedelmiddels van nywerheidse gemorste water en drankbare water. Hedendaagse metode maak gebruik van ontwikkelinge wat 'n vrye radikaal oplewer wat 'n vrye radikaal ketting reaksie veroorsaak. Die gebruik van fotolitiese reaksies vir hierdie applikasie is omvattend bestudeer maar nywerheidse applikasies is beperk. Hierdie inleidende studie bereken die letterkunde van die fotokatalitiese ontwikkeling met klem op ultraviolet uitstraaling. Die hoof kenmerk van hedendaagse werk is die oplewering van die hidroxyl radikaal as 'n aanvanger. Dit kan deur die fotokatalitiese ontbinding van die waterstof perokside verrig word. Dit was gerapporteer dat die kavitasie ook die hidroxyl radikaal van 'n water molekule oplewer. Uitstromendes wat reaktiwe kleurstowwe bewat het was met UV uitstraaling en waterstof perokside behandel. Die ontkleuring van hierdie uitstromendes was hoogste by die UV blootstellinge tyd van 56 sekonde vir waterstof perokside konsentrasie groter as 20 mg/ℓ. Cyanide uitstomendes was ook behandel en die konsentrasie was van 5 mg/ℓ tot onder 3 mg/ℓ verminder met 7 mg/ℓ van waterstof perokside.

KEYWORDS

Ultraviolet radiation, hydrogen peroxide, decolourisation, oxidation, hydroxyl radical.

INTRODUCTION

The oxidation of organic compounds in industrial effluents and potable water is becoming increasingly important. Processes that are typically used in industry involves the generation of a free radical which initiates free radical chain reactions resulting in the oxidation of the organic species. These processes use chemical initiators such as hydrogen peroxide, ozone, chlorine and chloride dioxide and/or high energy radiation such as ultraviolet (UV), x-ray, gamma ray and electron beam radiation to produce the free radical initiator .

The use of chlorine to generate free radicals for the treatment of drinking water alters the smell and taste characteristics of the treated water (Mone, 1973). Ozone oxidises the organics by the generation of an oxygen free radical, the predominant products being saturated alcohols and carboxylic acids which build-up after a certain extent of ozonation (Marooka *et al.*, 1988). This can be eliminated by using a stronger oxidising agent. The hydroxyl radical is second only to the fluorine radical in oxidising strength.

Advanced oxidation processes usually refers to the combination of ozone with ultraviolet radiation or hydrogen peroxide or a combination of all three processes to produce the hydroxyl radical. Other processes that also produce the hydroxyl radical are a combination of UV radiation and hydrogen peroxide, a combination of ferrous ion with hydrogen peroxide (Fenton's reagent), the heterogeneous photocatalytic decomposition of water and electron beam radiation. The use of cavitation has been employed in a process to produce the hydroxyl radical by splitting a water molecule.

FREE RADICALS FROM THERMOLYSIS, PHOTOLYSIS OR ELECTRON TRANSFER

A free radical is an atom, a molecule or a complex which contains one or more unpaired electron. Free radicals can exist in the gaseous and liquid phases and the principles are similar in both cases (Codagan, 1973 and Barrow, 1966).

Radicals may be formed by homolytic scission (equal splitting) of co-valent bonds

$$A:B \rightarrow A^{*} + B^{*}$$

where * represents an unpaired electron.

The principle types of reactions are :-

abstraction : $^{*}CH_3 + CH_3CH_2CH_2CH_3 \rightarrow CH_4 + CH_3{}^{*}CHCH_2CH_3$
addition : $Br^{*} + CH_2=CH-R \rightarrow BrCH_2-{}^{*}CH-R$
and combination : $2({}^{*}CH_3) \rightarrow C_2H_6$

The first two reactions are steps that do not eliminate the free radical centre and do not directly give the final products but constitute only steps in that direction. The abstraction step can lead to chain reactions, as in the system of H_2 and Cl_2 :

$$H^{*} + Cl_2 \rightarrow HCl + Cl^{*}$$

$$Cl^{*} + H_2 \rightarrow HCl + H^{*}$$

$H^* + Cl_2 \rightarrow etc.$

The addition step can lead to polymerisation reactions as in the formation of polythene :

$$R^* + CH_2{=}CH_2 \rightarrow R-CH_2-{}^*CH_2$$

$$R-CH_2-\dot{C}H_2 + CH_2{=}CH_2 \rightarrow R-CH_2-CH_2-CH_2-{}^*CH_2$$

Production of Free Radicals

The simplest way to produce radicals is by direct homolysis of co-valent bonds either by thermolysis or photolysis :

$$A-B \xrightarrow[\text{or light}]{\text{heat}} A^* + B^*$$

Another method is to introduce the odd electron from another species in the form of electron transfer via a redox reaction for example Fenton's reaction :

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^- + {}^*OH$$

Photolysis involving radiation in and below UV range have been employed in bond breaking (Cha and Smith, 1972 and Anon, 1990a).

Radical Chain Processes Involved in the Oxidation of Organic Compounds

The liquid-phase oxidation of organic substances occurs by chain-forming and branching reactions but not by combustion. Chain reactions increase the number of free radicals and accelerates the rate of oxidation. Peroxides and hydroperoxides initiate chain reactions by the homolytic rupture of the comparatively weak O-O bond (Emanual *et al.*, 1984). Reactions from bond scission lead to larger molecules or smaller molecules (Semenov, 1958).

Radical Formation by Homolytic Bond Scission Due to Light Absorption

In ordinary chemical reactions, activation energy is supplied by the chance collection in a molecule or pair of molecules, of a large amount of thermal energy. Activation energy can also be acquired through the absorption of a quanta of visible or ultraviolet radiation resulting in photo-chemical reactions. Energy absorption per mole of reaction substance is shown in Table 1 for different wavelengths (Glasstone, 1948).

TABLE 1 : ENERGY ABSORPTION FOR DIFFERENT WAVELENGTHS

Wavelength nm	Colour region	Energy kJ/mol
200	ultraviolet	599
300	ultraviolet	399
400	violet	299
500	blue green	239
600	yellow orange	200
700	red	171
800	near infrared	150

The relationship between wavelength and energy is given by :

$$E = \frac{hc}{\lambda} \tag{1}$$

where

E = energy (J)
h = Planck's constant ($6.626*10^{-34}$ J.s)
c = speed of light (m/s)
λ = wave length (m)

Only light which is absorbed can produce a photochemical change. This is quantified by the absorbance spectrum of the substance. The absorbed radiation affects rotational, vibrational or the electronic energy levels of a molecule. The first two transitions are insufficient to provide activation energy for chemical reaction (above 167 kJ/mol) or for direct bond breaking (209 to 418 kJ/mol). Only electronic transitions are sufficient to break bonds. The absorption of radiation is, however, not necessarily accompanied by chemical reaction.

The electronic spectrum of colourless substances absorbs in the ultraviolet region (less than 400 nm), the energy absorbed will be greater than 299 kJ/mol (Table 1). Such radiations are *likely* to produce a chemical change. The electronic spectrum of coloured substances lie in the visible region (400 to 800 nm) with corresponding energies of 293 to 146 kJ/mol, which is often sufficient to bring about photo-chemical reactions.

The above comments refer to dissociation as the primary stage. A number of secondary processes can follow the primary stage such as, for example, recombination of the products, removal of energy from the light absorbing substance before it has time to react, and chain reactions.

Where the active radiation falls within the banded (discontinuous) spectral region of the absorbing molecule, the primary process is not dissociation, but formation of *excited* or *activated* molecules possessing energy in excess of the normal due to an increase in the electronic energy. The excited molecule may then react when it collides with another molecule, or it may lose its energy if it does not react or combine within a short time (10^{-7} to 10^{-8} s). There is also the possibility of dissociation occurring if there is sufficient energy.

In some cases the reacting substance is unable to absorb radiation directly but a suitable atom or molecule (sensitizer) can absorb the radiation and pass it on to the reacting molecule. Such reactions are called photosensitized reactions.

Bond dissociation energies are given in Table 2 for various common bonds (Johnston, 1968). Any energy acquired by the molecule (by radiation, from electron transfer or by mechanical degradation) can readily be distributed amongst the various modes of molecular excitation, and reaction occurs when the bond to be broken accumulates the necessary amount of energy.

TABLE 2 : DISSOCIATION ENERGY FOR COMMON CHEMICAL BONDS

Bond	Value (kJ/mol)	Compound (s)
O=O	498	O_2
H-H	436	H_2
O-H	464	H_2O
O-O	142	H_2O_2
C-C	347	Organic
C=C	611	Organic
C≡C	837	Organic
C-H	413	Organic
C-N	305	Organic
C-O	358	Organic
C=O	736	Aldehydes
C=O	749	Ketones
C=O	803	CO_2
C=O	1 077	CO
C-F	490	CF_4
C-Cl	326	CCl_4
C-Br	272	CBr_4

Generation of the Hydroxyl Radical Using Hydrogen Peroxide

Effect of ultraviolet light

Hydrogen peroxide is excited by the absorbtion of UV light and dissociates into two hydroxyl radicals ($OH^{\bullet}$). The wavelength of 254 nm is preferred.

Secondary reactions also occur but yields are low and not considered important (Dainton, 1966). The liquid phase reaction involving the decomposition of hydrogen peroxide has been thoroughly investigated.

Photo sensitizers

Organic molecules containing carbonyl groups such as benzophenone ($C_6H_5CO\text{-}C_6H_5$) and anthraquinone ($C_6H_7(CO)_2C_6H_7$) are easily excited by the absorption of UV light. They in turn transfer the energy to the potentially reactive molecules. This technique catalytically produces hydroxyl radicals from peroxide.

The Use of Water for Generation of Hydroxyl Radicals

UV irradiation of water can produce hydroxyl radicals if the wavelength is less than 184 nm. Because of the very short wavelength it is better to use ionizing radiation (Ashmore *et al.*, 1967).

It is alleged that the hydroxyl radical can be produced by controlled cavitation (Chang *et al.*, 1981). Cavitation is caused either by hydrodynamic pressure reduction of a body of liquid or by sonolysis. These processes produce a vapour filled cavity, the violent collapse of which produces instantaneous temperatures up to 2 000 °C and pressures over 100 MPa (Knapp *et al.*, 1970). The high temperatures may cause partial dissociation of some molecules to form reactive hydroxyl radicals. Luminescence due to the photochemical release of energy has been observed. The literature on acoustic cavitation covers a considerable amount of information on chemical effects including the formation of free radicals (Young, 1989). Very little information has appeared in the literature on the use of hydrodynamic cavitation.

Peterson and Zaleiko (1981) have reported on the oxidation of a number of chemicals by hydrodynamic cavitation alone. Oxidation times ranged from 30 minutes to 180 minutes. The use of hydrodynamic cavitation for destruction of microbial cell material in wastewater sludge has also been discussed (Peterson and Zaleiko, 1981).

Should the water molecule dissociate in the absence of scavengers the following could be expected :-

$$H^* + {}^*OH \rightarrow H_2O$$

$$2H^* \rightarrow H_2$$

$$2{}^*OH \rightarrow H_2O_2$$

$$H^* + H_2O \rightarrow {}^*OH + H_2$$

$${}^*OH + H_2 \rightarrow H^* + H_2O$$

Chang *et al.*. (1981) claims the dissociation of water, which has a bond energy of 502kJ/mol., by cavitation does occur. It can be expected that molecules with lower bond energies will also form radicals.

Reactions of the Hydroxyl Radical

Hydroxyl radicals oxidise by *abstraction* of a hydrogen atom from an organic molecule resulting in an organic radical (R^*) :-

$$RH + OH^* \rightarrow R^* + HOH$$

In the presence of oxygen, the organic radical (R*) combines readily with an oxygen molecule to form a peroxy radical ROO*. These organic peroxy radicals are very reactive.

Many *addition* reactions with hydroxyl radicals have been investigated. With vinyl compounds it forms substituted hydroxy ethyl radicals which are the initiating species for addition polymerisation. Similar reactions occur with aromatic molecules to produce more complex molecules for example the formation of m-cresol from toluene (Semenov, 1958 and Bryce-Smith, 1968-1986).

Clearly then, from the above it is necessary to investigate carefully the end products before the techniques used in a process can be recommended for effluent *purification*.

Merz and Waters have indicated that the following compounds are not readily attacked by the hydroxyl radical :-

Carboxylic acids, such as acetic, malonic, maleic and fumaric.
Ketones such as acetone, methyl ethyl ketone.
Amides such as urea, acetamide.

They also list a number of compounds with the products that have been identified (Table 3).

TABLE 3 : PRODUCTS OF OXIDATIONS WITH THE HYDROXYL RADICAL

Substrate type	Substrate oxidised	Products identified
Primary and secondary alcohols	Methyl alcohol	CH_2O
	Ethyl alcohol	CH_3-CHO
Ethers	Diethyl ether	CH_3-CHO
	Dioxan	CH_2O, H-CO_2H, oxalic acid
Amino acids	Glycine	CH_2O
	Alanine	CH_3-CHO
Tertiary alcohols	*tert*-Butyl alcohol	CH_3-CO-CH_3, CH_2O
	tert-Amyl alcohol	CH_3-CO-CH_3, CH_3-CHO C_2H_5-CO-CH_3, CH_2O
Glycols	Ethylene glycol	CH_2(OH)-CHO, CH_2O
Esters	Methyl acetate	CH_2O
	Ethyl acetate	CH_3-CHO
Carboxylic acids	Propionic acid	CH_3-CHO
Amines	Diethylamine	CH_3-CHO
	Triethylamine	CH_3-CHO

CHEMICAL TESTS CONDUCTED TO EXAMINE THE CHARACTERISTICS OF HYDROGEN PEROXIDE AND ULTRAVIOLET RADIATION

Introduction

Tests using UV radiation and hydrogen peroxide were conducted on effluents containing Remazol red and Remazol blue reactive dyes and a sodium cyanide effluent.

Cyanide is a relatively easy inorganic molecule to oxidise. Ritcey (1989) discusses the various processes used to treat cyanide effluent. Although ozone treatment is one of the more successful methods in destroying cyanide effluent it cannot however remove iron cyanide complexes without ultraviolet or ultrasound treatment.

Experimental

The apparatus consisted of three photoreactors connected in series, fitted with low pressure mercury vapour lamps. Each lamp is physically isolated from the fluid in the reactor by a quartz tube which allows 70 to 90 % of short UV rays (predominantly 254 nm) to pass (Mone, 1970). A dosing pump was used to inject hydrogen peroxide into the effluent. The apparatus is depicted schematically in Fig. 1.

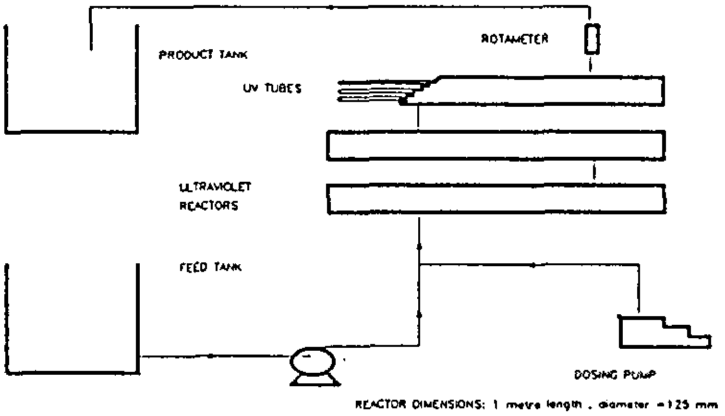

Figure 1. Schematic representation of experimental apparatus

The decolourisation of dyes was determined by ADMI analysis (Allen *et al.*, 1972). The extent to which cyanide concentration decreased was determined with MINTEK cyanide detector sticks. These sticks indicated cyanide concentration in the ranges greater than 2 mg/ℓ, 0,5 to 2 mg/ℓ and less than 0,5 mg/ℓ.

Results and Discussion

Tables 4a and 4b tabulates the results of the tests with Remazol red dye effluent and Remazol blue dye effluents respectively. The effect of hydrogen peroxide concentration and exposure time to UV radiation is shown in Figs. 2 and 3. In all cases complete decolourisation of the effluent could be achieved with less than 100 mg/ℓ of hydrogen peroxide. In both cases the reduction of the ADMI units was greatest at the intermediate retention time of 56 seconds. The reaction products have not been determined. Dyes treated with only hydrogen peroxide showed no reduction in the ADMI value.

TABLE 4a : EFFECT OF H_2O_2 CONC. AND UV RADIATION EXPOSURE TIME ON DECOLOURISATION OF REMAZOL RED DYE EFFLUENT

Flow rate ℓ/min	Retention time seconds	H_2O_2 conc. mg/ℓ	ADMI value	Reduction in ADMI % age
22	81,8	5	223	38,4
		25	85	76,5
		50	100	72,4
		75	44	87,9
		100	35	90,3
32	56,3	0	228	42
		5,9	144	63,4
		11,7	80	79,6
		17,6	79	79,9
		23,4	68	82,7
		58,6	67	83
		46,9	26	93,4
		82	20	94,9
40	45	0	147	59,5
		6,3	106	70,8
		12,5	52	85,7
		21,9	54	85,1
		31,25	66	81,8
		55	65	82,1
		70	73	79,9
		130	76	79,1

Initial dye concentration 5 mg/ℓ

TABLE 4b : EFFECT OF H_2O_2 CONC. AND UV RADIATION EXPOSURE TIME ON DECOLOURISATION OF REMAZOL BLUE DYE EFFLUENT

Flow rate ℓ/min	Retention time seconds	H_2O_2 conc. mg/ℓ	ADMI value	Reduction in ADMI % age
22	81,8	0	128	24,7
		5,6	100	41,2
		11,4	86	49,4
		18,9	80	52,9
		15,9	84	50,6
		45,5	80	52,9
		63,6	84	50,6
32	56,3	0	138	19,3
		2,9	114	33,3
		11,7	86	49,7
		17,6	68	60,2
		20,5	84	50,9
		46,9	90	47,4
		65,6	43	74,9
		93,8	41	76,0
40	45	0	144	19,1
		6,3	114	36,0
		12,5	108	39,3
		15,6	86	51,7
		25	103	42,1
		40	106	40,5
		70	70	60,7
		100	68	61,8

Initial dye concentration 5 mg/ℓ

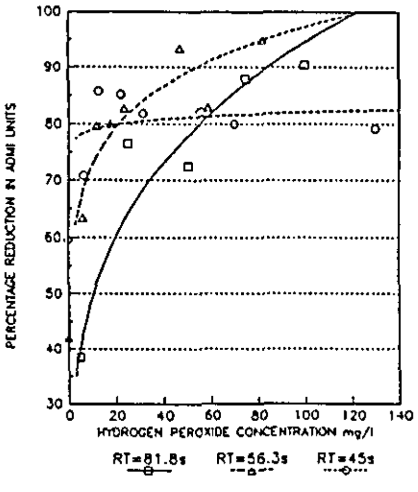

Figure 2. Effect of H_2O_2 conc. on reactive dyes - Remazol Red (F38)

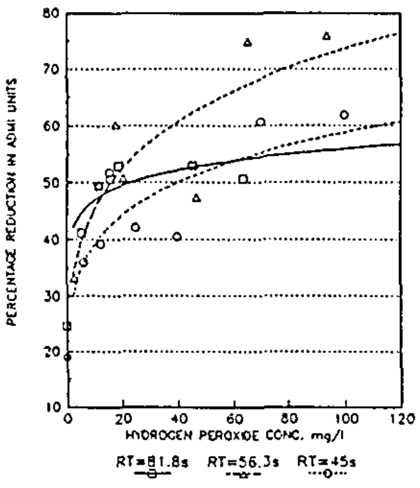

Figure 3. Effect of H_2O_2 conc. on reactive dyes - Remazol Blue (R Special)

The strong oxidation characteristics of the hydroxyl radical is further illustrated by the treatment of the cyanide effluent. The concentration of the effluent is reduced from 5 mg/ℓ to below 2 mg/ℓ by the use of 7 mg/ℓ of hydrogen peroxide. The results of these tests are given in Table 5.

TABLE 5 : RESULTS OF TESTS WITH CYANIDE EFFLUENTS

Conditions	Flow rate ℓ/min	H_2O_2 mg/ℓ	Final cyanide concentration mg/ℓ (CN)
No treatment	3,75		>2
UV only	3,75		>2
H_2O_2 only	3,75	3,8	>2
UV and H_2O_2	3,75	4,9	>2
UV + H_2O_2	3,75	3,0	>2
UV + H_2O_2	3,75	7,0	<2

Initial concentration of cyanide as CN = 5 mg/ℓ

CONCLUSIONS

High energy radiation and strong oxidising agents are being used to achieve complete oxidation of organic pollutants. One such oxidising agent is the hydroxyl radical which can be produced by irradiation of hydrogen peroxide. The hydroxyl radical can also be produced by the splitting of the water molecule. The cavitation process uses this method. Molecules such as glucose have been shown to undergo complete oxidation when treated with the hydroxyl radical. If complete oxidation is not achieved then products need to be identified since toxic compound may be formed. An example is the oxidation of toluene which can produce m-cresol.

Tests conducted with reactive dye effluents indicated that complete decolourisation of the effluent could be achieved with less than 100 mg/ℓ of hydrogen peroxide. Furthermore at concentrations above 20 mg/ℓ of peroxide the decolourisation of the effluent is maximised at the retention time of 56 seconds. Cyanide effluent was also treated with UV radiation and hydrogen peroxide. The cyanide concentration was reduced from 5 mg/ℓ to under 2 mg/ℓ with 7 mg/ℓ of hydrogen peroxide.

ACKNOWLEDGEMENTS

This work was undertaken in terms of a Water Research Commission Project No. 388 entitled *'Evaluation of Different Methods to Produce Free Radicals for the Oxidation of Organic Molecules in Industrial Effluents and Potable Water.'* The initial work was sponsored by Watergroup Africa (Pty) Ltd. who also supplied some of the equipment.

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ANNEXURE C

A STUDY OF HYDRODYNAMIC CAVITATION AS A METHOD OF WATER DISINFECTION

by

Candace J Botha and Chris A Buckley
Journal of Water Supply Research and Technology - Aqua, 1995, **13**(2), in print

Annexure to Report to the Water Research Commission on Project No. 388 entitled :
Evaluation of Different Methods to produce Free Radicals for the Oxidation of Organic Molecules in Industrial Effluents and Potable Water (with special reference to CAV-OX®)

Head of Pollution Research Group :	Professor C A Buckley
Project Leader :	Ms S J Winship
Project Team :	Ms C J Kaiser
	Mr S Chetty
	Mr D J Meyer
	Mr G W Schwikkard

DISINFECTION OF POTABLE WATER - THE ROLE OF HYDRODYNAMIC CAVITATION

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ABSTRACT

With the quality of water declining due to pressures from the increasing demand on water resources and the controversies regarding the use of commonly used disinfectants in water treatment processes, it is necessary to research new water treatment processes. The CAV-OX® process involves the combination of ultraviolet radiation, the addition of hydrogen peroxide and hydrodynamic cavitation. This technology is based on the production of hydroxyl radicals by hydrodynamic cavitation and by photolysis of hydrogen peroxide. As disinfection by both hydrogen peroxide and ultraviolet radiation has been extensively researched, a hydrodynamic cavitation rig was built to evaluate hydrodynamic cavitation in terms of bacterial inactivation for disinfection.

INTRODUCTION

Young [1] describes cavitation as the formation and activity of bubbles (or cavities) in a liquid. A vapour cavity can form anywhere in a flowing liquid where the local pressure is reduced to that of the liquid vapour pressure at the temperature of the flowing liquid. Four kinds of cavitation-generating mechanisms have been described : **Hydrodynamic cavitation** resulting from pressure variations in a flowing liquid due to the geometry of the system; **ultrasonic/acoustic cavitation** in which sound waves create pressure variations; **optic cavitation** which is produced by photons of high intensity (laser) light and **particle cavitation** which is produced by a proton rupturing a liquid [1].

In hydrodynamic cavitation the state of a fluid that is near to, or cavitating, can be defined by Equation 1 :

$$\sigma_c = \frac{P - P_V}{0{,}5\rho v^2} \qquad (1)$$

where :

σ_c = cavitation number
P = local fluid static pressure (Pa)
Pv = saturated vapour pressure at fluid temperature (Pa)
ρ = fluid density (kg/m^3)
v = local fluid velocity (m/s)

Cavitation numbers are used to describe the susceptibility of a flow to cavitate. The lower the cavitation number the more intense the cavitation. When the local pressures are lower than the saturated vapour pressure, cavities, consisting mainly of gases which have come out of solution, form in the liquid [2]. The presence of nuclei such as submicroscopic gas bubbles or solid non-wetted particles can result in the occurrence of cavitation at pressures higher than the vapour pressure of the fluid. The bubbles collapse upon entering regions where the local pressure is higher than the vapour pressure of the liquid. The collapse causes noise, vibration and extensive pitting of boundary materials in the regions of bubble collapse [3]. It has been predicted that, during the implosion of ultrasonically induced bubbles, instantaneous localised temperatures from 2 273 K to 5 000 K and pressures from 101 MPa (1 000 atm) to 101 325 MPa (10^6 atm) can result [4,5]. In the most recent work predictions of temperatures above 50 273 K have been made [6]. The intense temperatures and pressures exhibited by bubble collapse are proposed to result in the thermal dissociation of water into short-lived, highly reactive hydrogen and hydroxyl radicals [7]. Peterson and Zaleiko [4] maintain that hydrodynamic cavitation alone is effective in producing these radicals from water. Ultrasonic cavitation, which produces noise, chemical reactions and luminescence, has been widely researched. Webster [8] notes that ultrasonic cavitation accelerates chemical reactions e.g. the hydrolysis of esters and initiates reactions e.g. the decomposition of water :

$$H_2O \rightarrow H^\bullet + {}^\bullet OH$$

The products of the above reaction are then responsible for secondary reactions involving dissolved substances. The predominant secondary reactions are :

$$\begin{aligned} {}^\bullet OH + {}^\bullet OH &\rightarrow H_2O_2 \\ H^\bullet + H^\bullet &\rightarrow H_2 \end{aligned}$$

Hydrogen peroxide has been detected in a sonicated solution of potassium iodide [9].

Light emission has been observed during ultrasonic and hydrodynamic cavitation. This phenomenon is believed to occur during bubble collapse. Jarman and Taylor [10] found that the intensity of luminescence from hydrodynamic cavitation was two orders of magnitude less than that recorded in ultrasonic cavitation.

Ultrasound is used extensively in biology to destroy or rupture cells, to homogenise solutions and to clean instruments. Possible mechanisms for cell disruption are shear stresses resulting from turbulent flow and high velocity gradients [5,11], and cavitation forces involving mechanical stresses combined with free radical reactions [11]. The local effects of cavity collapse producing cavitation forces include local heating, electrical discharges, sonoluminescence and free radical formation [5] . Apart from these physical factors, cell size [12], cell shape [11], stage of cell development [11] , species of cell [13] and bond strengths between bacterium and media [13] are considerations which have been proposed to affect the efficiency of disruption and inactivation of microorganisms. Ultrasound has also been used to disrupt cells for the extraction of intracellular constituents, for the dispersion of bacterial aggregates [14] and to inactivate bacteria in water and effluent [15].

The application of hydrodynamic cavitation for bacterial inactivation and disruption has not been studied extensively. Peterson and Zaleiko [4] claim that hydrodynamic cavitation generated in a nozzle ruptures the cell wall, releasing the internal material that may be subsequently oxidised by free radicals. Hydrodynamic cavitation has been used by Harrison [16] and Harrison and Pandit [17,18] to disrupt yeast and bacterial cells in order to obtain intracellular material. The extent of disruption was monitored by soluble protein release. Hydrodynamic cavitation is known to produce forces such as pressure fluctuations, shock waves, stresses and extreme temperatures. Based on this, the potential for cell destruction akin to that achieved by ultrasonic cavitation exists.

Peterson and Zaleiko [4] devised a treatment process which combines hydrogen peroxide, hydrodynamic cavitation and ultraviolet radiation. The basis of the technology is the production of hydroxyl radicals by hydrodynamic cavitation of water and by the photolysis of hydrogen peroxide. Little experimentation has been undertaken to determine the effect of the cavitation nozzle alone, without the effects of hydrogen peroxide and ultraviolet radiation except on sucrose, phenol, activated sludge and raw sewage. The effect was monitored in terms of reduction in chemical oxygen demand [4].

The CAV-OX® process (Magnum Water Technology, USA) employs ultraviolet radiation, hydrogen peroxide and hydrodynamic cavitation to photolyse and oxidise organic compounds present in water at mg/ℓ concentrations to nondetectable levels [19].

The system is being investigated for the treatment of volatile organic compounds primarily trichloroethene, benzene, toluene, ethylbenzene and xylenes [19]. Hydrogen peroxide is added to the contaminated groundwater which is then pumped through a cavitation nozzle, followed by ultraviolet radiation (Figure 1). The removal efficiencies of contaminants are reported to range from 20 % to 99 %. No analysis was undertaken using the nozzle alone. Hydrodynamic cavitation produced in a nozzle is used *to generate hydroxyl radicals and hydrogen atoms which combine to form hydrogen peroxide and molecular hydrogen* [19] .

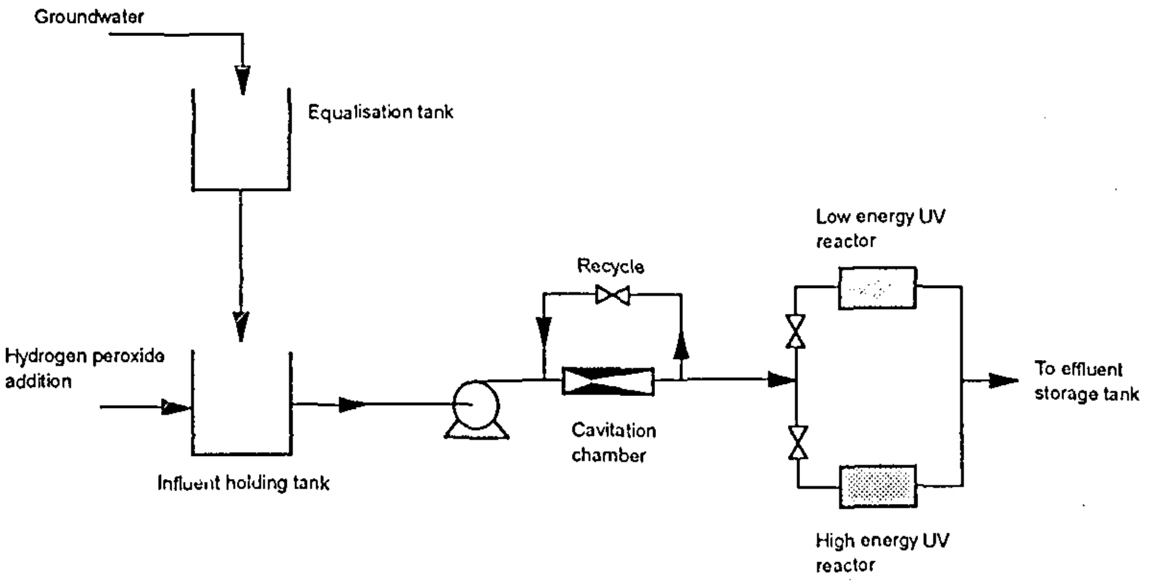

Figure 1 : CAV-OX® system [19] **used in the oxidation of volatile organic contaminants**

The University of Natal was approached to evaluate the CAV-OX® system for use in water treatment. As the bactericidal effects of hydrogen peroxide and ultraviolet radiation are well known, it was decided to assess the efficiency of hydrodynamic cavitation alone. It was recognised that the potential energy in distribution pipes could be harnessed to generate cavitation with the installation of a nozzle. This would then allow water to be treated at source, perhaps several times along the distribution system and possibly at the tap, making potable water readily available.

The experimental programe involved the evaluation of :

- the bactericidal efficiency of hydrodynamic cavitation alone using heterotrophic plate count (HPC) analysis, and
- the analysis of hydrogen peroxide as an indication of free radical formation.

MATERIALS AND METHODS

The Hydrodynamic Cavitation Rig

A hydrodynamic cavitation rig (Figure 2) was constructed in order to both intensify cavitation and to facilitate a large range of operating conditions. The cavitation nozzle was installed 10 m above the free liquid surface in the feed tank. This provided a reduced pressure at the outlet to the nozzle.

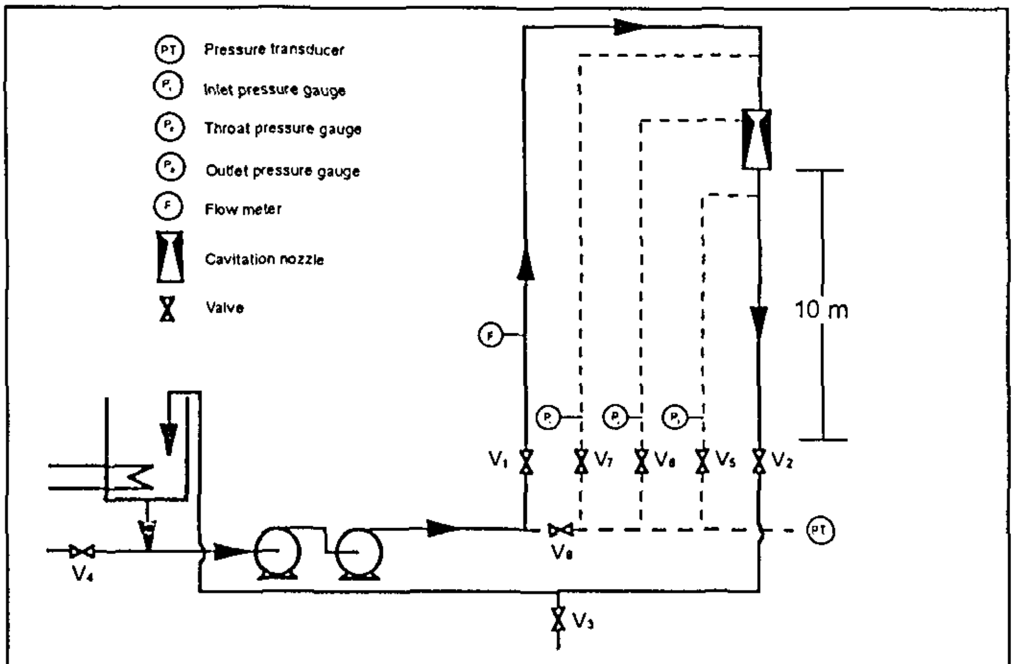

Figure 2 : Process instrumentation diagram of hydrodynamic cavitation rig

Figure 3 shows the dimensions of the Perspex replica of the nozzle originally supplied with the CAV-OX® unit.

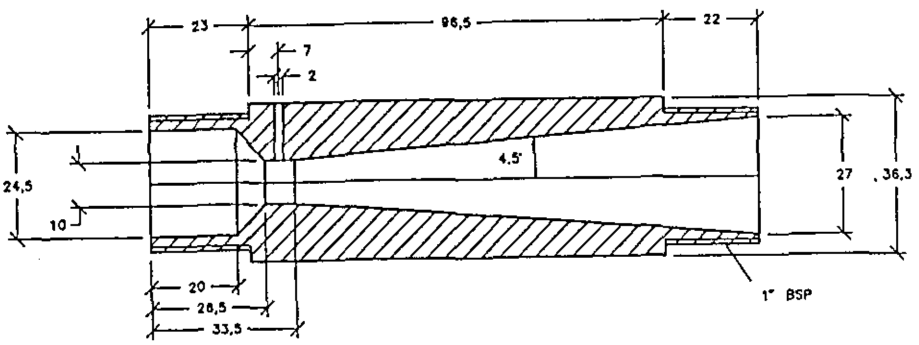

Figure 3 : Dimensions of cavitation nozzle (mm)

Hydrogen Peroxide Analysis

The concentration of hydrogen peroxide produced in the hydrodynamic cavitation rig was determined by a method based on the reduction of copper (II) ions by hydrogen peroxide in the presence of excess of 2,9-dimethyl-1,10-phenanthroline (DMP) to form the copper (I)-DMP complex [20]. This method can detect hydrogen peroxide concentrations from 0,034 mg/ℓ to 4,08 mg/ℓ. The concentration of copper (I)-DMP complex is determined directly by spectrophotometric measurement at 454 nm, and is related to the concentration of hydrogen peroxide. A volume of 80 ℓ of reverse osmosis permeate was poured into the feed tank and cavitated at the highest intensity achieved by the rig. Samples were withdrawn from the sample port at various intervals over an 18 h period. The sample was added to a 10 mℓ volumetric flask containing DMP and copper sulphate solution and the absorbance measured. The concentration of hydrogen peroxide was determined from the calibration curve. The blank consisted of reverse osmosis permeate containing no hydrogen peroxide.

Heterotrophic Plate Count Analysis

Raw water (80 ℓ) was obtained from Wiggins Water Treatment Plant in Durban and poured into the feed tank of the cavitation rig. An initial sample was taken from the feed tank in a sterile sample bottle. Cavitation was initiated at the selected operating conditions and samples were collected from the sample port over 2 h. The samples were then appropriately diluted [21], plated using nutrient agar and incubated at 37 °C for 48 h. As a control raw water was pumped through the system with the cavitation nozzle replaced by an open tube. Raw water from a river or dam was selected for use in HPC analysis as it contains a wide variety of naturally occurring species of bacteria. The HPC of water prior to and after cavitation enable the assessment of the efficiency of the cavitation rig. This test, does not provide an indication of the quality of the water but, rather it constitutes the initial test in the assessment of the efficiency of the process.

RESULTS

Hydrodynamic Cavitation

The feed tank was filled with water and all valves were open and the pumps engaged. The inlet pressure was 487 kPa, the flow rate was 124 ℓ/min and the outlet pressure was 15 kPa. Valve 2 (Figure 2) was then incrementally closed and at various stages the inlet, outlet, throat pressure and flow rate were recorded. Where the lines are horizontal, cavitation occurs at a constant flow rate. This procedure was followed for various inlet pressures which were set using valve 1 (Figure 2). The difference between the inlet and the outlet pressure was calculated and plotted against the measured flow rate (Figure 4). As the pressure drop across the nozzle is reduced, the intensity of cavitation is decreased until cavitation ceases to occur. This occurs when the flow rate is reduced by increasing the back pressure (outlet pressure). These conditions cause the throat pressure to be raised above the vapour pressure of the liquid and bubble formation ceases.

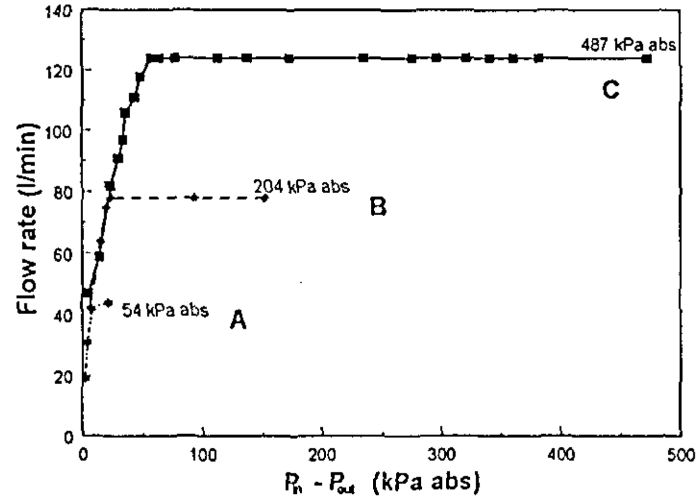

Figure 4 : Selected operating conditions showing inlet pressures of 54; 204; and 487 kPa corresponding to pressure drops across the nozzle of 22; 152; and 472 kPa respectively

In Figure 4 it is evident that the lower the inlet pressure, the smaller the pressure drop across the nozzle and the lower the intensity of cavitation. Conditions A, B and C show increasing intensities of cavitation. The cavitation numbers (Equation 1) were calculated for each of these conditions. The cavitation number at condition A was 0,482, condition B was 0,258, and condition C was 0,025. The lower the cavitation number the more intense the cavitation.

A Perspex box, filled with water, was fitted to the nozzle for photography of condition C and the condition of no cavitation. Figure 5 (a) shows the condition of no cavitation where no bubbles are evident. As cavitation begins the bubbles appear at the throat of the nozzle and gradually extend to fill the entire divergent portion of the nozzle. Figure 5 (b) cavitation of the highest intensity achieved by the cavitation rig where bubbles appear as a white mass in the divergent portion of the nozzle.

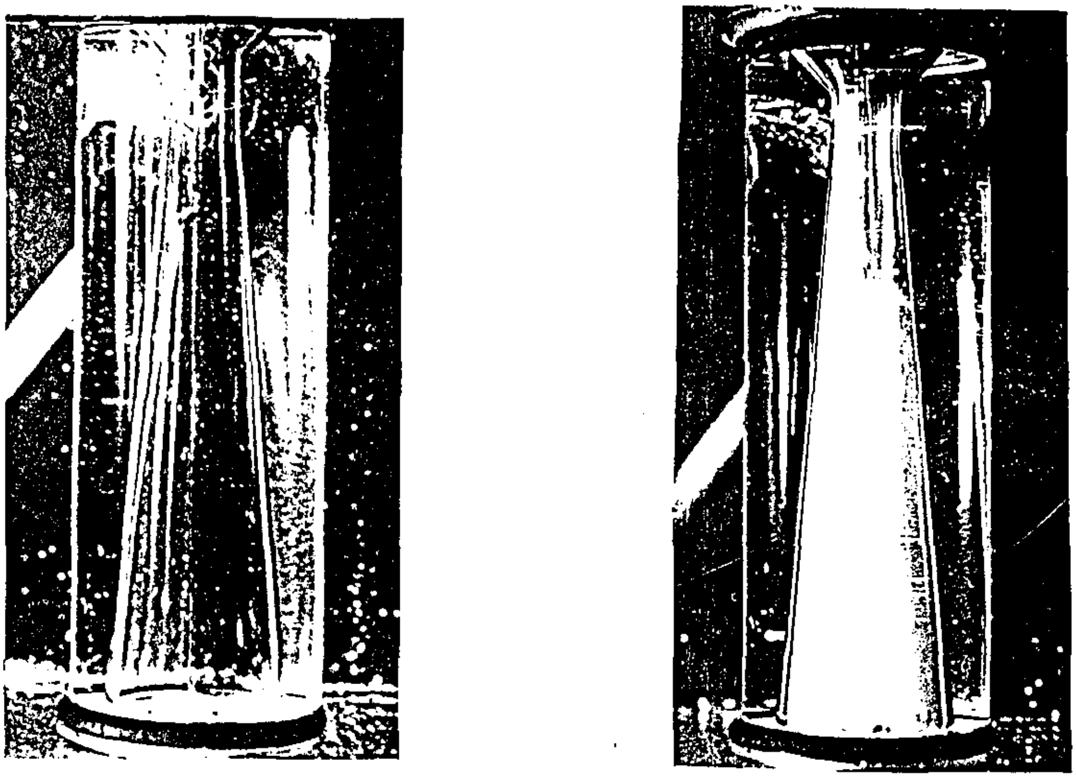

Figure 5 : Photographs showing no cavitation (a), and intense hydrodynamic cavitation generated in a nozzle (b)

Production of Hydrogen Peroxide

Hydrogen peroxide was not detected in hydrodynamically cavitated reverse osmosis permeate as there was no significant difference between the absorbance measurement of the blank and the cavitated water. It was concluded that any hydrogen peroxide produced was below the detection limit of 0,034 mg/ℓ using the method by Baga et al. [20] and was assumed to be negligible.

As a comparison, the hydrogen peroxide produced by an 8 ℓ KERRY Pulsatron (38 kHz) ultrasonic cleaning bath was monitored using the method by Baga et al.[20]. Based on the calibration curve it was found that sonication (1 h) of reverse osmosis permeate produced approximately 0,1 mg/ℓ of hydrogen peroxide.

Cavitation of Raw Water Bacteria

Figures 6 (a), (b), and (c) show the results of hydrodynamic cavitation (at three intensities) while Figure 6 (d) shows the results of a 12 h period of cavitation.

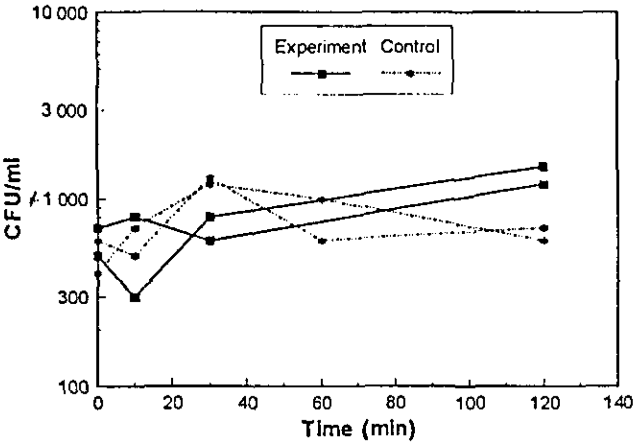

Figure 6 (a) : Raw water exposed to low intensity cavitation

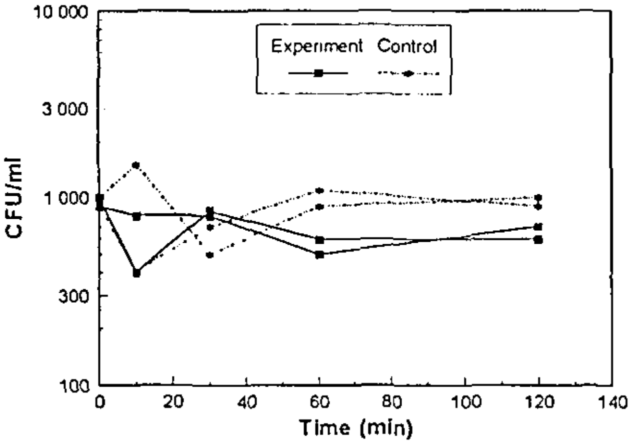

Figure 6 (b) : Raw water exposed to medium intensity cavitation

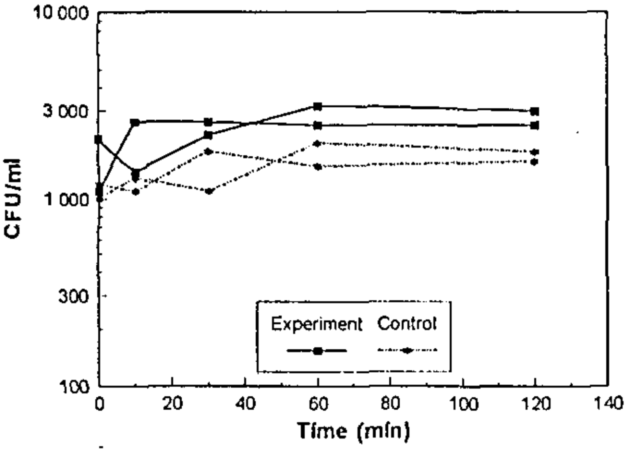

Figure 6 (c) : Raw water exposed to high intensity cavitation

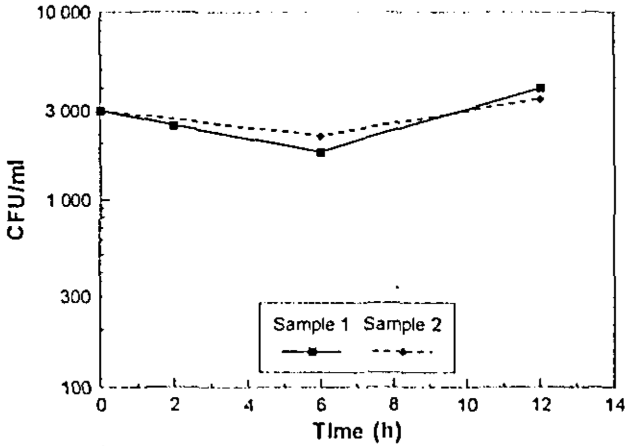

Figure 6 (d) : Raw water exposed to 12 h of the high intensity cavitation

Figures 6 (a), (b), and (c) show that there is no significant reduction in the concentration of colony forming units over the 2 h period for cavitation conditions A, B or C. Figure 6 (d) shows that no reduction in CFU/mℓ occurred after 12 h of hydrodynamic cavitation. The data from the cavitated samples in the above figures show general trends either indicating a slight increase in CFU/mℓ over time or a maintenance in CFU/mℓ. The increases do not constitute an order of magnitude difference and therefore are not considered significant. Any increase in count could be due to the dispersion of aggregates of bacteria as shown in studies of turbidity and scanning electron microscopy [22]. Hydrodynamic cavitation in isolation is therefore not effective in the inactivation of heterotrophic bacteria.

As a comparison the effect of ultrasound on raw water bacteria was undertaken by sonication of 25 mℓ of raw water and HPC analysis at various intervals. Treatment with ultrasound resulted in a decrease in CFU/mℓ whereas the non-sonicated control indicated no reduction in CFU/mℓ (Figure 7). Based on the experiments it can be concluded that ultrasound at an intensity of 18,3 mW/cm^2

(183 W/m^2) and a frequency of 38 kHz has a bactericidal efficiency of on average 96,2 % for heterotrophic plate count bacteria in raw water.

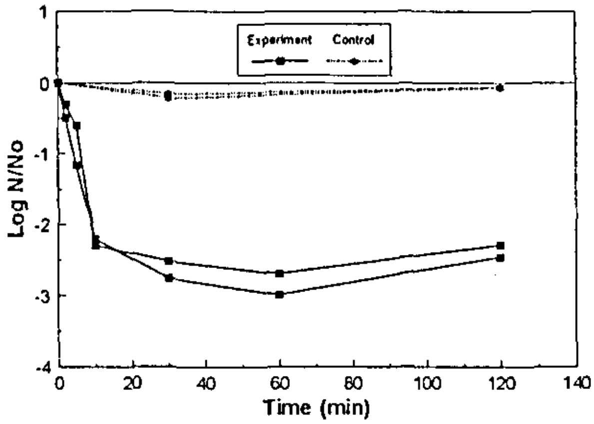

Figure 7 : Inactivation of raw water bacteria by ultrasound

DISCUSSION

The objective of this project was to evaluate the potential of hydrodynamic cavitation for water treatment with the inactivation of raw water bacteria as the primary aim. Ultrasound was used as a comparison. Several points emerged from the experiments undertaken.

Raw Water and Heterotrophic Plate Count Analysis

The choice of raw water for experimentation as opposed to the conventional procedure of the inoculation using a selected indicator microorganism e.g. *Escherichia coli* proved successful. Various authors [13,23] note the greater resistance in susceptibility of naturally occurring bacteria to disinfection than laboratory cultured species. Bacteria which occur in rivers and streams often exist in a resistant, stationary state, as spores or protected by association with debris. Consequently, these bacteria require a greater dose of disinfectant than laboratory cultured bacteria. In addition, the use of model indicator species to determine the water quality after a disinfection process can lead to the conclusion that the process produces water safe for human consumption. However, the pathogens that occur in contaminated and polluted water are often resistant to the disinfection doses applied to eliminate indicator species. Watkins [24] notes that often a false sense of security is obtained when indicator species are used for the assessment of the efficiency of a disinfection process. For these reasons it is advantageous to initially determine the efficiency of a process using a general population of bacteria thus the HPC was selected to determine the efficiency of bacterial inactivation by hydrodynamic cavitation. In this application, the changes in bacterial counts are more important than the absolute numbers of bacteria. The application of HPC using raw water is favourable as it is a simple and inexpensive form of pilot-plant evaluation which can save time and materials should the pilot-plant prove unsuccessful.

Hydrodynamic Cavitation

Cavitation numbers are used to describe the susceptibility of a flow to cavitate. The lower the cavitation number the greater the intensity of cavitation. The cavitation numbers produced by the cavitation rig ranged from 0,5 to 0,03. Harrison and Pandit [17] report cavitation numbers ranging from 2,79 to 0,99 (using Equation 1), and note that cavitation occurrs at numbers less than 1,0 to 2,5. Based on cavitation numbers the hydrodynamic cavitation produced in this cavitation rig is substantial.

Hydrogen Peroxide Production

A concentration of 0,1 mg/ℓ of hydrogen peroxide was produced from the sonication (1 h) of reverse osmosis permeate in the ultrasonic bath, supporting the theory that cavitation results in the formation of hydroxyl radicals which subsequently combine to produce hydrogen peroxide. In contrast, no hydrogen peroxide was detected during hydrodynamic cavitation of reverse osmosis permeate.

Inactivation of Raw Water Bacteria

Heterotrophic plate counts were used to monitor changes in the concentration of viable colony forming units in cavitated and non-cavitated raw water. At least an order of magnitude decrease is required before the inactivation method is considered to be effective. Exposure of raw water bacteria to ultrasound resulted in a 2 decade reduction in CFU/mℓ.

The hydrodynamic cavitation produced in this cavitation rig is substantial and it can be concluded that cavitation alone does not inactivate bacteria in raw water and therefore does not have potential to be used as a single process in water treatment.

Comparison of Ultrasonic and Hydrodynamic Cavitation

Cavitation is the common phenomenon exhibited by both the ultrasonic bath and the hydrodynamic cavitation rig. The results of the two forms of cavitation; i.e. hydrogen peroxide production and efficiency of bacterial inactivation, differed. Apparent differences between the processes include :

a) **Scale** : Smaller volumes (40 mℓ) were exposed to ultrasound than to hydrodynamic cavitation (80 ℓ). Direct comparison of the results of the two forms of cavitation is therefore not possible.

b) **Residence time** : The ultrasonic bath provides continuous treatment of small volumes of water whereas the cavitation rig limits the effective treatment period to the time (milliseconds) in which the water passes through the cavitation nozzle. This factor is one of the major differences between the two cavitation processes.

c) **Initiation of cavitation** : Ultrasonic cavitation is initiated by alternating compression and rarefaction of the liquid in response to ultrasonic waves. Hydrodynamic cavitation is initiated by the pressure drop across the nozzle.

d) **Bubble size** : Bubble sizes (radii) resulting from ultrasonic cavitation at intensities of 1 MHz and 50 kHz have been reported to be 4μm and 80μm respectively [25]. The bubbles generated during hydrodynamic cavitation are visible and can be described as a *cloud of vaporous cavities* whereas no bubbles or clouds of bubbles were observed during ultrasonic cavitation.

e) **Hydrogen peroxide** : A concentration of 0,1 mg/ℓ of hydrogen peroxide was detected from sonication of reverse osmosis permeate indicating the formation of hydroxyl radicals and subsequent reaction to form hydrogen peroxide. Hydrogen peroxide was not detected by using the Cu (II) - DMP method during hydrodynamic cavitation of reverse osmosis permeate. It can be concluded from this that the concentration of hydrogen peroxide generated during bubble collapse was less than the lower detection limit of the analysis (0,034 mg/ℓ). As a result of the scale and the residence time, a relatively small volume of permeate is exposed to hydrodynamic cavitation for milliseconds and any hydrogen peroxide which formed in the nozzle would have been diluted in the reverse osmosis permeate (80 ℓ). An unreasonable number of passes through the system would be required, during which time any hydrogen peroxide would either decompose or react.

f) **Bacterial inactivation** : Ultrasonic cavitation inactivated bacteria whereas hydrodynamic cavitation was unsuccessful in inactivating bacteria. The ultrasound and hydrodynamic results are not directly comparable because of differences in residence time, equipment scale and possibly the form of cavitation.

Evaluation of Water Treatment Technologies

The water industry is constantly evaluating water treatment processes. In the evaluation of systems it is important to inform people of the ineffective processes as well as the effective ones. The application of hydrodynamic cavitation for the treatment of potable water is one such a case. The experiments undertaken in this study indicate that an undetectable concentration of hydrogen peroxide was produced by hydrodynamic cavitation using the method by Baga et al. [20], and that no reduction in the viability of raw water bacteria was achieved. Based on these results it can be concluded that hydrodynamic cavitation alone is not a feasible process for disinfection of potable water.

SUMMARY AND CONCLUSIONS

The project was designed to determine whether hydrodynamic cavitation could be used for disinfection of raw water. Raw water was used as the inoculum as it was considered most representative for a water treatment project. The absolute numbers of colony forming units was of secondary importance compared to the change in the CFU/mℓ which is used to determine the efficiency of a process.

Hydrodynamic cavitation can rupture cells [17,18] but was not successful in the inactivation of naturally occurring raw water bacteria as determined in this investigation. Had hydrodynamic cavitation proved to be successful in the inactivation of raw water bacteria, the ease of installation would have made this an attractive prospect for water treatment by exploiting the existing potential energy in pipelines of water distribution systems. Ultrasonic cavitation was not only used for comparison, but more importantly as a control. Hydrodynamic cavitation produced in the cavitation rig was determined to be unsuitable as a single process for the inactivation of raw water bacteria.

The conclusions of this work can be summarised as follows :

- Raw water used in the heterotrophic plate count analysis provides an assessment of the efficiency of the hydrodynamic cavitation process.
- In this study, hydrodynamic cavitation did not inactivate bacteria present in raw water.
- Hydrodynamic cavitation did not produce sufficient hydrogen peroxide for oxidation and therefore cannot be described as a major contributer to free radical production.
- Hydrodynamic cavitation alone is an inappropriate technology for inactivation of bacteria and hence for disinfection.

ACKNOWLEDGEMENTS

The authors of this paper would like to thank the Water Research Commission, Diarec Diamonds and Umgeni Water for their contribution in this project.

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