

DISINTEGRATION OF SLUDGE USING OZONE-HYDRODYNAMIC CAVITATION

by

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Abstract

In our study we applied hydrodynamic cavitation and ozonation both separately and combined, to determine the synergistic effect of these two technologies for sludge disintegration. A 2 mm orifice was used as a cavitation device. Ozone was injected after cavitation at a concentration of 35 mg/L at a flow of 3 Lpm. The sludge was subjected to treatment for 90 minutes in all three cases. In a final step, combined ozone and cavitation was applied to disintegrate the sludge for 10 hours. It was found that the combination of ozonation and cavitation exhibited higher sludge disintegration capacity than the individual technologies applied alone. About 31% of VSS was reduced by the combined system, whereas 19% was reduced by ozone and only 4% was reduced by cavitation alone after 90 minutes of treatment. Soluble chemical oxygen demand (SCOD) was increased by approximately 1600 mg/L in the combined system, which was much higher than the individual effect observed with either ozone or cavitation alone. About 75% of this SCOD was found to be biodegradable. In the combined system, soluble TOC increased by approximately 1.5 times the amount released by ozone alone, indicating higher release of organic matter from biomass. Only cavitation did not show any significant release of soluble total organic carbon (TOC) compared to the other treatments. In combined application, soluble biochemical oxygen demand (BOD) increased to 420 mg/L, which was significantly higher than the increase of BOD due to the application of ozone alone which was 260 mg/L. Based on the SCOD, it was found that a maximum of 50% of the sludge could be solubilised in 10 hours of combined treatment. It was also found that with ozone-cavitation, approximately 26% of the total sludge phosphorus was released to the solution after 10 hours, although most of the release occurred within the first 2 hours. Within the operating conditions applied, cavitation itself was not sufficient for the disintegration of sludge, although better disintegration was found in combined application at higher inlet pressure. In the case of ozonation alone, higher disintegration was obtained at longer ozonation time.

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Abbreviations

AOP	Advanced oxidation process
BOD	Biochemical oxygen demand
COD	Chemical oxygen demand
EPS	Exocellular polymeric substances
SCOD	Soluble chemical oxygen demand
SRT	Solids retention time
TCOD	Total chemical oxygen demand
TOC	Total organic carbon
TSS	Total suspended solids
VFA	Volatile fatty acid
VSS	Volatile suspended solids
WAS	Waste activated sludge
WWTP	Wastewater treatment plant

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Dedication

To my family and friends.

Chapter 1: Introduction

1.1 Background and motivation

The norm for urban wastewater treatment in North America is the conventional activated sludge process due to its capability of providing robust treatment of municipal wastewater with generally well understood and predictable performance. In the last century, the activated sludge process was a legacy due to the easy availability and the minimal cost of the energy and resources. As a result, a large development has been made in this sector without considering the problem associated with the requirement of larger footprint, higher energy requirement and also the value of recoverable material in the untreated wastewater. But in this 21st century the world is facing decreasing land availability and higher energy costs. Another problem in activated sludge plants is the production of large quantities of byproduct sludge or biosolids. The cost of treating and disposing of this excess sludge is up to 50 to 60% of the plant operating cost (Egemen et al., 1999). In large cities, disposal of these large quantities of excess sludge produced by wastewater treatment plants has become a major political and economic challenge. By reducing the production of these large quantities of excess sludge, significant cost, energy and land savings can be realized.

Some of the common ways to handle the excess sludge produced in activated sludge plants are landfill disposal, agricultural application, incineration, etc. But today the disposal of sludge in landfills is being phased out by the establishment of new rules and regulations. Similarly agricultural disposal is also heavily regulated. Incineration is not popular at all due to its high operation and management cost and also because of restrictions by national and local guidelines as well as the public. Anaerobic digestion is the most common method used to reduce sludge. In anaerobic digestion approximately 30-40% volatile solids reduction is achieved at a retention time of 20-30 days.

Several disintegration technologies have been introduced to minimize sludge production in treatment plants. These can be classified as mechanical (Baier and Schmidheiny, 1997; Hogan et al., 2004; Wood et al., 2009), chemical (Chiu et al., 1997), and thermal (Dereix et al., 2006)

methods. Disintegration helps to release the cell contents by destroying the cell wall and helps to increase the biodegradability of the sludge. With the present level of knowledge none of these disintegration technologies can be used to process large volume of waste and also most of these technologies failed to degrade the more complex particulates completely. These processes can be used together with conventional processes to increase the removal efficiency of volatile material present in the residues (Beltran et al. 1999; Engwall et al., 1999; Kitis et al., 1999; Mastin et al., 2001). The efficacy of the conventional method depends on the conditioning achieved reached by the pre-treatment stages. So the selection of proper pre-treatment technology is important (Gogate and Pandit, 2004).

Among all these methods, chemical methods based on ozone have been successfully used with conventional biological treatment processes to achieve a zero sludge yield (Deleris et al., 2002; Goel et al., 2004; Huysmans et al., 2001; Sakai et al., 1997; Salhi et al., 2003; Yasui et al., 1996; Yasui and Shibata, 1995). Almost all the other disintegration methods, including ozone, have been studied to improve methane production in anaerobic digestion.

In the case of ozonation, an ozone reactor is used in the treatment process. A part of the activated sludge is ozonated in an ozone reactor to kill the microorganisms in the sludge and oxidize a portion of the organic substances. Part of the organic matter is mineralized by the biological treatment and results in the reduction of sludge production. The whole process is schematically presented in Figure 1.

Ozone oxidizes pollutants in two forms in water i.e. molecular ozone and/or hydroxyl radical (OH^\cdot) generated from the decomposition of ozone (Staehelin and Hoigné 1982). Less ozone decomposition is desirable for disinfection, while generation of hydroxyl radical (OH^\cdot) is expected for oxidation of micropollutants as these are much more reactive compared to the ozone molecule itself. But ozonation alone can't produce sufficient hydroxyl radical (OH^\cdot). To enhance the production of hydroxyl radical (OH^\cdot), many efforts have been made to explore advanced oxidation processes (AOPs). Ozone /hydrogen peroxide and ozone/ultrasound are commonly used technologies in ozone based AOPs (Kang and Hoffmann, 1998).

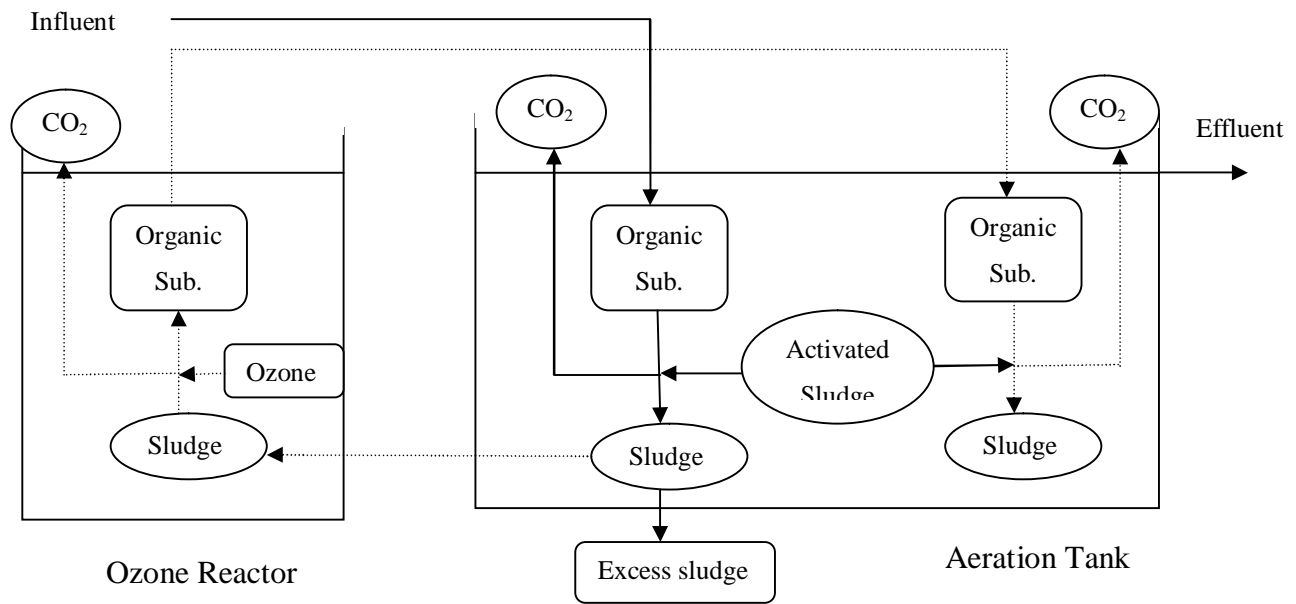


Figure 1: Application of ozone for sludge reduction (Kamiya and Hirotsuji, 1998)

Cavitation in the form of ultrasound has also been used widely for disintegrating the sludge. There are two types of cavitation used i.e. acoustic cavitation and hydrodynamic cavitation. Cavitation is defined as the growth, formation and subsequent collapse of cavities in a fluid over a very small period of time (milliseconds) that releases high energy (Suslick, 1990). Among these techniques, acoustic cavitation has been studied and applied for disintegration purposes in the form of ultrasound. (Gogate and Kabadi, 2009). The problems involved with acoustic cavitation are its high energy requirement and also difficulties involved with scaling up. On the other hand hydrodynamic cavitation is less energy intensive compared to acoustic cavitation and also can be applied at a larger scale. But there is not enough knowledge available about application of hydrodynamic cavitation for sludge disintegration (Kang and Hoffmann, 1998).

Hybrid techniques, involving two or more disintegration technologies, have become popular due to their higher efficiencies. In general, in hybrid techniques a mechanical technology is coupled with a chemical process. The efficiency of the chemical treatment can be improved significantly from this combined application. Combined application helps to overcome the problem of one technique by using another. Jyoti and Pandit (2004) have applied ozone in combination with acoustic and hydrodynamic cavitation for water disinfection and found that the disinfection

efficiency of the ozone was increased significantly due to the synergistic effect of cavitation and ozone. The aim of our study was to evaluate the combined performance of ozone and hydrodynamic cavitation for sludge disintegration.

1.2 Thesis organization

The whole thesis has been organized into five chapters. Background and Motivation of this research is discussed in chapter 1: Introduction which is followed by chapter 2: Literature Review where the literature related to the application of ozone and cavitation is discussed. This chapter also contains the hypothesis and the specific objective of the thesis. Chapter 3: Materials and Methods describes the experimental set up and test methods used to achieve the objective of the thesis. The results of the experiments are presented and discussed in chapter 4: Results and Discussion. Finally the key conclusions reached from this research are summarized in chapter 5: Conclusions.

Chapter 2: Literature Review

2.1 Introduction

Wastewater treatment (WWTP) has developed a lot over the last few decades. From a small system, it has become a huge industry now. The most common method to treat the wastewater is the activated sludge process, where treatment is done by utilizing different microorganisms under different operating conditions. Although a significant improvement has been achieved in wastewater treatment, still the generation of sludge or biosolids has remained problematic. Primary and secondary clarification are the two unit operations which generate sludge in a wastewater treatment plant. Sludge recovered from the primary clarifier is typically readily degradable compared to the secondary sludge generated from biomass which is more resistant to degradation. A significant portion of money is spent to treat and dispose of this sludge in WWTPs.

To reduce the amount of sludge as well as to improve the sludge quality, different disintegration technologies have been applied in the sludge treatment process. Disintegration technologies help to fragment the cell wall and release the intracellular compounds by the application of different physical or chemical methods. Disintegrated sludge can be used in both aerobic and anaerobic biological processes as a substrate. Disintegrated sludge can be further treated in one of the following ways.

- Anaerobic digestion can be improved as well as accelerated by first applying disintegration to waste sludge. Disintegration helps to accelerate the hydrolysis process by disrupting the cell walls and releasing the organic matter inside the cell, which is the limiting step in the digestion process (Lehne et al., 2001).
- Disintegrated sludge improves biomass production in an anaerobic digestion process and it improves phosphorus recovery and the nutrient removal processes by transferring the activated sludge solids into the liquid phase (Grübel and Machnicka, 2010).
- In a wastewater nitrogen removal treatment process, disintegrated sludge can be used as a source of carbon for denitrification (Lehne et al., 2001).

- Disintegrated sludge can be applied to reduce sludge bulking and foaming in an activated sludge treatment process by breaking up the filamentous structure and larger flocks (Muller, 2000).

Some of the common disintegration processes are given in Table 1. All the methods have been developed with a common goal to achieve partial or complete lysis of the cell, which means the destruction and release of the organic matter inside in the bacterial cell. Extracellular polymeric substances may also be degraded by these disintegration techniques (Neyens et al., 2004).

Table 1. Different methods of disintegration

Physical	Chemical	Thermal	Biological
Cavitation (Hydrodynamic/Acoustic)	Alkaline/Acid hydrolysis	Microwave	Aerobic digestion
Homogenizer	Use of enzymes	Autoclave	Anaerobic digestion
Stirred ball mills	Ozone	Steam heating	

In this chapter, we critically analyze two disintegration technologies i.e. cavitation and ozone and their applicability in wastewater treatment, both individually and in combination.

2.2 Cavitation

Cavitation is defined as the phenomena of the formation, growth and subsequent collapse of microbubbles or cavities occurring over an extremely small interval of time (milliseconds), releasing large quantities of energy (Lorimer and Mason, 1987; Shah et al., 1999; Suslick et al., 1990). Release of highly reactive free radicals, generation of hot spots, continuous cleaning as well as increase in the surface area of solid catalysts, enhancement in the mass transfer rate due to turbulence generated, etc. are some of the important effects of cavitation (Adewuyi, 2001; Pandit and Moholkar, 1996; Pestman et al., 1994; Shah et al., 1999; Suslick et al., 1990; Thompson and Doraiswamy, 1999). Based on the mode of generation, cavitation can be classified into four types viz. acoustic, hydrodynamic, optic and particle. Among these, acoustic and hydrodynamic cavitation have been found to be effective in bringing about the desired chemical changes whereas optic and particle cavitation have been used for single bubble

cavitation which is not able to bring the required chemical changes. The destruction/oxidation by cavitation can be explained by free radical attack (Nagata et al., 2000) and pyrolysis (Kang and Hoffmann, 1998). The degree of destruction depends on the cavitation intensity as well as on the characteristics of the pollutant substrate being oxidized. (Gogate and Pandit, 2004).

2.2.1 Acoustic cavitation

In acoustic cavitation, high frequency sound waves, usually ultrasound, are used to generate cavities. Normally the frequencies of the sound waves are between 16 KHz and 100 MHz. Bubbles and cavities are generated and collapsed by using alternate compression and rarefaction cycles of the sound (Lorimer and Mason, 1987; Shah et al., 1999; Suslick et al., 1990).

Different types of instruments have been used for acoustic cavitation. Figure 2 illustrates some of the commonly used acoustic cavitation devices. The systems with higher dissipation areas are more energy efficient (Gogate et al., 2001, 2003). Multiple frequencies/multiple transducers have been found to be more beneficial than the equipment using a single frequency (Gogate et al., 2001, 2003; Hua et al., 1995; Sivakumar and Pandit, 2002; Thoma et al., 1997). A newly developed ultrasonic horn vibrating in the radial direction was found to be a promising device for medium to large scale application for its improved energy dissipation ability due to its larger irradiating area (Dahlem et al., 1998, 1999). More work needs to be done to find out the behaviour of this instrument under high frequency and high dissipation conditions.

Higher frequencies of operation are suitable for the destruction of pollutants up to an optimum value which depends on the characteristics of the pollutant (Hua et al., 1995; Hung and Hoffmann, 1999). Very few investigations have been made on the destruction of pollutants using higher frequencies as it's difficult to operate at frequencies greater than 200 kHz. Running a sonochemical reactor at higher frequencies in continuous operation at a larger scale is difficult as it causes erosion of the transducer surface. Power requirement increases with frequency and this can make the process uneconomical due to the fact that a large amount of supplied energy will be used only for the generation of the cavities. Multiple frequencies produce more intense cavitation than single frequency operation and results in higher yield of transformation but with minimal

problems of operation (Moholkar et al., 1999). With an increase in cavitation activity, larger volumes of effluent can be treated effectively (Gogate et al., 2003; Sivakumar and Pandit, 2002). Ultrasonic probes with higher irradiating surface areas are more energy efficient as they ensure the uniform dissipation of energy (Gogate et al., 2001).

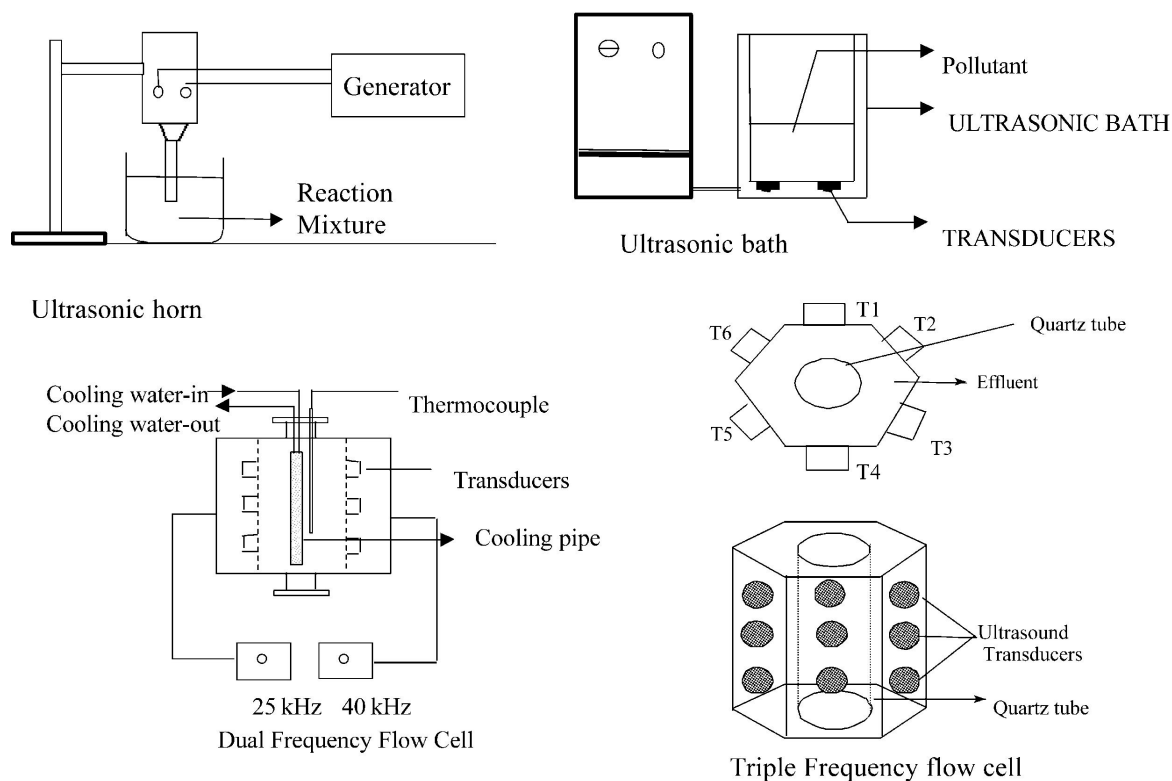


Figure 2: Commonly used acoustic cavitation devices (Gogate and Pandit, 2004).

The performance of a sonochemical reactor is also affected by the physicochemical properties of the medium such as vapour pressure, surface tension, viscosity, presence of impurities, etc. These liquid properties affect the cavitation inception, the number of cavities generated and also the initial size of nuclei. The minimum power required for the onset of cavitation is defined as cavitation inception. The cumulative pressure/temperature pulse generated due to cavitation is the product of the total number of cavities and pulse generated from the collapse of a single cavity. Thus it is advisable to produce a large number of cavitation events in a reactor with smaller cavitation nuclei (Gogate, 2002; Gogate and Pandit, 2000a).

To enhance the cavitation effect, pre-treatment may be applied to a waste stream to dilute the pollutant concentration, as a lower initial concentration of pollutant increases the rate of sonochemical degradation. However, an optimum value should be selected as it has a negative effect on the power density (Sivakumar and Pandit, 2001). Presence of gases (oxygen, ozone), aeration or addition of catalyst can increase the degradation by a sonochemical reactor (Hung and Hoffmann, 1998; Ingale and Mahajani, 1995; Mason, et al., 1996; Nagata et al., 2000; Pandit et al., 2001; Seymour and Gupta, 1997; Shirgaonkar and Pandit, 1998; Sivakumar and Pandit, 2002). However the presence of a catalyst can also interfere with the propagation of the sound waves. Thus, optimization of catalyst concentration is required (Gogate et al., 2002). Temperature is another important factor, as the rate of bubble destruction is inversely proportional to the temperature (Sivakumar and Pandit, 2002; Suslick et al., 1997).

Several researchers (Bhatnagar and Cheung, 1994; Catallo and Junk, 1995; David et al., 1998; Dewulf et al., 2001; Francony and Petrier, 1996; Gogate et al., 2001; Gonze et al., 1999; Nagata et al., 2000; Peters, 2001; Price et al., 1994; Weavers et al., 2000; Yoo et al., 1997) have applied sonochemical reactors in the wastewater sector for the degradation of various compounds at different scales of operation. Most of the works have been done at laboratory scale. Prior to application at full scale, more research is needed on both the design parameters for scaling up and also the feasibility of using transducers at high energy dissipation.

Another important matter is that model pollutants are used in most of the studies and degradation rates may not be the same when applied to the real wastewater sample that contains many components. Peters (2001) has studied the sonolytic degradation of 1,2 dichloroethane in both deionized water and in natural samples and observed the complete destruction of the material. On the other hand, a study conducted by Commenges et al. (2000) did not find ultrasonic irradiation technology to be effective for the removal of chemical oxygen demand (COD) and toxicity when applied to a paper mill effluent. So there is still uncertainty about the applicability of this technology for real wastewaters.

2.2.2 Hydrodynamic cavitation

In hydrodynamic cavitation, liquid passes through a hydraulic device such as an orifice, venturi, valve, etc., to generate the cavitation (Gogate and Pandit, 2001). Among all these devices, an orifice plate offers the greatest flexibility in terms of the selection of different plate configurations with different diameters and different configurations of the orifices (Gogate, 2002). Cavitation normally occurs in high a velocity region. Figure 3 illustrates a flow through a pipe restriction. At the vena contracta the flow area decreases and consequently the velocity increases according to the continuity equation and in turn the pressure decreases according to the Bernoulli equation. At lower flow rates the pressure remains well above the vapor pressure.

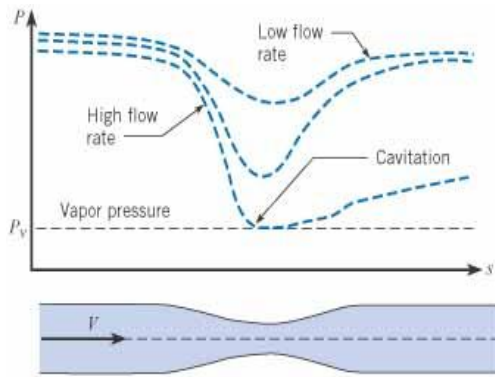


Figure 3: Flow through pipe restriction.

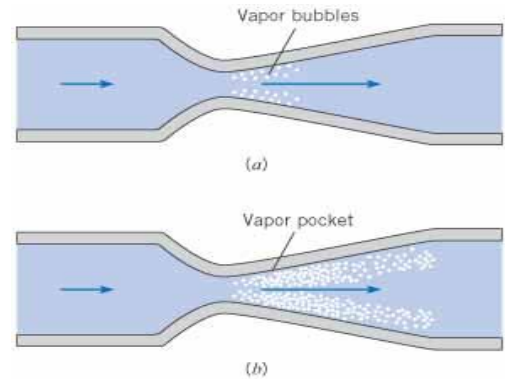


Figure 4: Formation of vapor bubbles a) low flow b) higher flow.

However when the flow rate is high, the pressure can decrease to the liquid vapor pressure and the liquid starts to boil. At that point bubbles generate and cavitation is started. Turbulence, viscosity and the presence of contaminant gases can affect the onset of cavitation. The pressure recovery occurs beyond the vena contracta which causes the bubbles to collapse as shown in Figure 4a and produce noise. When the flow is further increased, as shown in Figure 4b, the zone of bubble formation is extended, although the local pressure is still equivalent to the vapor pressure. When the bubbles collapse, the local temperature and pressure might increase up to $10^3 - 10^4$ K and $10^2 - 10^3$ bar respectively, due to the compression effects upon its internal gases. This may cause water to dissociate into H^\cdot and OH^\cdot radicals. The hydroxyl radical is a very powerful oxidant that is capable of oxidizing most compounds. Processes that generate hydroxyl radicals are commonly known as advanced oxidation processes (AOP). Thus, cavitation can be

viewed as an AOP where bubbles behave like a micro-reactors when they collapse (Benito et al., 2005).

2.2.3 Factors affecting hydrodynamic cavitation

A schematic diagram of the hydrodynamic cavitation process is shown in Figure 5. The top box shows the parameters that induce the pressure pulse. Cavitation takes place due to the pressure pulse created by certain nuclei. The cavitation process can be viewed as the sum of individual isolated cavities or as interacting bubble clouds. The latter is more realistic especially when dealing with large bubble densities. The number and size of bubbles, as well as the collapse temperature, can be estimated both experimentally and theoretically. The reaction location has a great impact on the chemical activity of the system. Thus it is necessary to find out the effective location and the kind of cavitation necessary to enhance a desired reaction (Arrojo and Benito, 2008).

Different parameters affect hydrodynamic cavitation, specifically the number of cavities formed and the collapse conditions. The collapse conditions are defined by the temperature and pressure reached at the collapse of cavities. The parameters that affect the cavitation are shown in Figure 6. Some of the important parameters are discussed below.

2.2.3.1 Cavitation number

Cavitation number is an important dimensionless parameter in hydrodynamic cavitation which is defined as follows (Gogate and Pandit, 2000b):

$$C_v = \frac{P_2 - P_v}{1/2 \rho v_0^2} \dots\dots\dots (2.1)$$

Where P_2 is the recovered pressure downstream, P_v is the vapor pressure of the liquid, v_0 is the velocity of the liquid at the orifice and ρ is the density of the liquid.

Under ideal conditions cavitation occurs when $C_v < 1$. In a model simulation Gogate and Pandit (2000b) showed that cavities generated at $C_v > 2$ do not collapse. The pressure pulse generated under these conditions will not have any desirable chemical effects, though it may contribute a little physical or mechanical effect to cavitation set up.

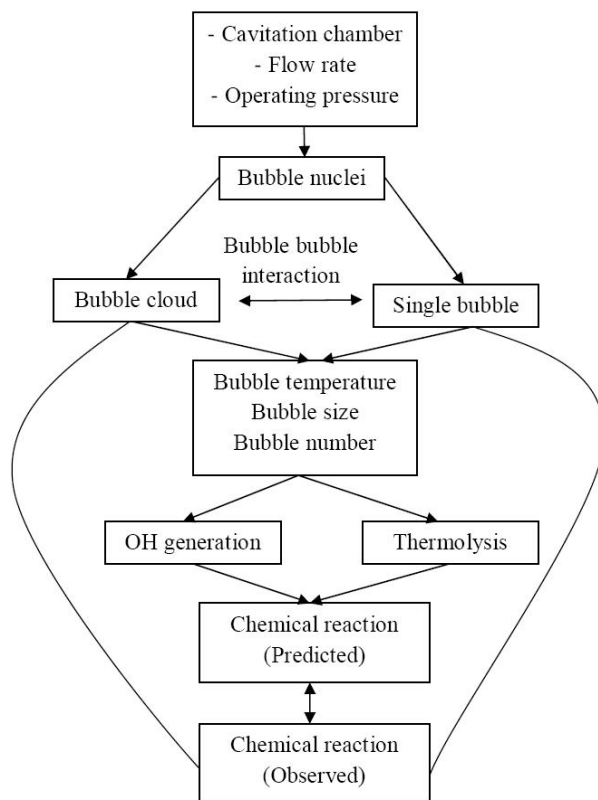


Figure 5: Basic theoretical scheme of hydrodynamic cavitation as an AOP (Arrojo and Benito, 2008).

Vichare et al. (2000) also found a higher liberation of iodine from the decomposition of potassium iodide at low cavitation number. The number of cavities generated and cavitation events are high at lower cavitation number while the intensities due to cavity collapse are low. Sivakumar and Pandit (2002) have also reported a higher degradation of rhodamine B at lower cavitation number. It is also to be noted that cavitation can also take place at $C_v > 1$ due to the presence of dissolved gases or suspended particles (Gogate and Pandit, 2000b). Cavitation number increases with an increase of the orifice hole diameter and is impacted by the flow geometry (Vichare et al., 2000; Yan and Thorpe, 1990). Braeutigam et al. (2010) showed that the

optimal value of C_v decreases with an increase of pipe diameter and it is also reciprocally correlated with the velocity of the fluid.

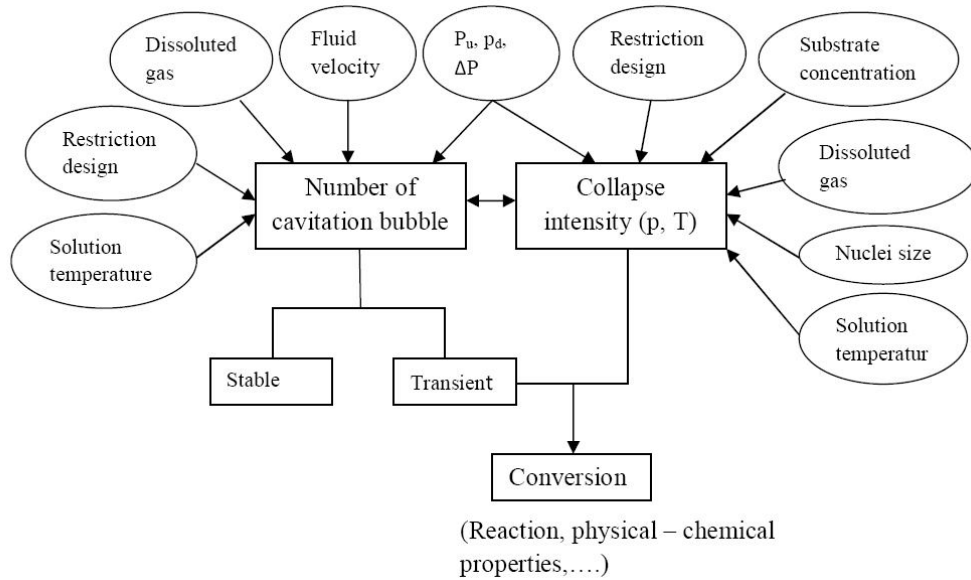


Figure 6: Overview of the effective parameters in hydrodynamic cavitation (Braeutigam et al., 2010).

2.2.3.2 Inlet pressure

Inlet pressure plays an important role in cavitation. With an increase of inlet pressure, the downstream pressure also increases, which causes a higher permanent pressure drop across the orifice. As a result, a high pressure pulse is generated due to the more violent collapse of cavities (Gogate and Pandit, 2000b). Cavitation effects are observed when the inlet pressure reaches a certain minimum pressure which is known as the cavitation inception threshold value (Kumar and Pandit, 1999; Shirgaonkar and Pandit, 1998). Collapse pressure increases with a further increase of inlet pressure due to single cavity collapse, whereas the number of cavities generated goes on decreasing with increasing pressure, thereby resulting in an optimum inlet pressure in hydrodynamic cavitation (Gogate, 2002). Gareth and Danver (1996) reported in their study that cell disruption with an orifice plate increases up to a certain pressure, then decreases. Other studies also confirmed the existence of an optimum pressure where it was shown that iodine liberation was maximized at that pressure by using aqueous KI decomposition as a model

reaction (Shirgaonkar and Pandit, 1997). Senthil Kumar et al. (2000) and Vichare et al. (2000) both have shown that the degradation of KI increases with an increase of upstream pressure up to a certain discharge pressure in a hydrodynamic cavitation system with orifice plates.

2.2.3.3 Diameter of the constriction

The diameter of the constriction affects the cavitation inception number, which increases with increased diameter (Yan and Thorpe, 1990). The cavitation starts at a higher cavitation number when a larger diameter constriction is used. A higher magnitude pressure pulse is generated with an extent range of cavitation at the same cavitation number with larger diameter holes (Gogate, 2002). Gogate and Pandit (2000b) have also confirmed in a model simulation that at constant percentage of free area occupied by orifice holes and at a constant inlet pressure, the pressure pulse generated in cavitation increases with an increase of hole diameter. It should also be kept in mind that the number of holes decreases with an increase of hole diameter, which in turn, causes a decrease in the number of cavities generated. Vichare et al. (2000) have shown that the liberation of iodine decreases with an increase of diameter of the holes at a constant free area, whereas Sivakumar and Pandit (2002) have reported that the destruction of rhodamine B increases with an increase of hole diameter. It may be that the degradation of iodine requires lower cavitation intensities whereas destruction of complex rhodamine B requires higher cavitation intensities. Thus, optimization is required for both the number and size of the holes depending on the required cavitation intensities for the target pollutant.

2.2.3.4 Physicochemical properties of the liquid and the initial size of nuclei

The effects of the physicochemical properties of the liquid and the initial size of nuclei on cavitation are similar to those in acoustic cavitation. The lifetime of a cavity increases with an increase in the initial cavity size (R_0) at a constant intensity (I) and frequency (f). The number of cavities generated decreases with an increase of initial cavity size, which also pushes the maximum radius ratio (R_{\max}/R_0) to a lower value. The magnitude of the pressure pulse generated is inversely proportional to the initial cavity size, as more violent collapse may happen in the case of a smaller cavity (Gogate and Pandit, 2000a). The effects of all the liquid properties are

not the same and also these properties affect the cavitation in more than one way. For example the generation of cavities becomes more difficult when the surface tension of the liquid is higher, and this eventually increases the threshold pressure for cavitation. On the other hand, more violent collapse occurs at higher surface tension of the liquid. The collapse pressure of the cavities is also affected by the presence of dissolved gases (Gogate and Pandit, 2000b). Senthil Kumar et al. (2000) found that the degradation of aqueous KI solution was much higher initially due to the presence of dissolved gases. After 15-20 minutes when all the dissolved air was liberated by degasification, the true kinetics of KI degradation were observed. The effect of the dissolved gases on cavitation yield cannot be generalized due to the difference in physicochemical properties of the gases. Hart and Henglein (1985) observed that iodine formation from KI solution varied when different gases such as argon, nitrogen or oxygen were used as the dissolved gases. Effects of some physicochemical properties on hydrodynamic cavitation reactors are summarized in Table 2.

2.2.3.5 Percentage of free area for the flow

To quantify the effect of free area on the cavitation intensity a parameter called α is introduced which is the ratio of the total perimeter of the hole to the total area of the opening.

$$\alpha = \frac{\text{Total Perimeter of the holes}}{\text{Total area of opening}} = \frac{n \times 2\pi (d_h/2)}{(d_h/2)^2} = 4/d_h \dots\dots\dots(2.2)$$

Where n and d_h are the number and diameter of the holes. Sivakumar and Pandit (2002) have observed that the degradation of rhodamine B increases with an increase of α value. Vichare et al. (2000) also observed a similar trend for iodine liberation, except with a different order of magnitude. This was due to the fact that a higher value of collapse pressure is required for rhodamine B degradation compared to the decomposition of KI. It was also observed that a plate with a larger number of holes produced a higher rate of degradation with the same α value, which was also confirmed by Kumar and Pandit (1999) in a bubble dynamics model. On the

other hand cavity collapse pressure decreased with an increase of free flow area (Gogate and Pandit, 2000b). Thus for a certain flow area, an orifice plate with a larger number of holes with a small diameter will give a better cavitation effect, as a larger number of cavities experiences higher turbulence due to the increase of shear layer.

Table 2. Effect of physicochemical properties of liquid on hydrodynamic cavitation reactors
(Gogate, 2002)

Liquid properties	Effect	Favorable condition
Dissolved gas A. Solubility B. Polytropic constant and thermal conductivity	Gas content, nucleation, collapse phase Intensity of cavitation events	Low solubility Gases with higher polytropic constant and lower conductivity (monatomic gases)
Liquid vapor pressure	Cavitation threshold, intensity of cavitation, rate of chemical reaction	Liquid with low vapor pressure
Viscosity	Transient threshold	Low viscosity
Surface tension	Size of the nuclei (cavitation threshold)	Low surface tension
Bulk liquid temperature	Intensity of collapse, rate of the reaction, threshold/ nucleation, almost all physical properties,	Optimum value exists, generally lower temperatures are preferable
Surfactants and electrolytes	Cavitation threshold, reaction kinetics	Case study of each system is necessary to ascertain the exact nature of the effect
Solid constituents	Cavitation threshold/ nucleation, attenuation of sound intensity	Low concentration
Immiscible liquid phase	Interfacial cavitation, number of bubbles per unit volume, reaction kinetics	Depends on the nature of the system

Another parameter called β_0 is also used. This is the ratio of total flow area or total area of holes to the cross sectional area of pipe. Sivakumar and Pandit (2002) observed that the degradation of rhodamine B increased with a decrease of β_0 value. Cavitation yield is inversely proportional to the free area offered to the liquid medium (Gogate and Pandit, 2000b). In the case of KI decomposition Vichare et al. (2000) also obtained similar results. If plates having the same β_0

values are compared, the plate with the smaller hole size will give higher cavitation yield due to higher turbulence frequency (f_T) and cavitation intensity.

$$f_T = v/l \dots\dots\dots(2.3)$$

$$l = 0.08 (d_h + d_p)/2\dots\dots\dots(2.4)$$

Where l is the scale of turbulence, d_h and d_p are the diameters of the hole and pipe respectively and v is the fluctuating component of mean velocity. Table 3 shows the optimum set of operating conditions for hydrodynamic cavitation reactors.

Table 3. Optimum operating condition for hydrodynamic cavitators (Gogate, 2008)

Property	Favorable condition
Inlet pressure into the system/rotor speed depending on the type of equipment	Use increased pressures or rotor speed but avoid super-cavitation by operating below a certain optimum value
Physicochemical properties of the liquid and initial radius of the nuclei	The guidelines for selecting the physicochemical properties so as to achieve lower initial sizes of the nuclei are similar to those used for the sonochemical reactors
Diameter of the constriction used for generation of cavities e.g. hole on the orifice plate	Optimization needs to be carried out depending on the application. Higher diameters are recommended for applications which require intense cavitation whereas lower diameters with a large number of holes should be selected for applications with reduced intensity
Percentage free area offered for the flow (ratio of the free area available for the flow, i.e. cross-sectional area of holes on the orifice plate to the total cross-sectional area of the pipe)	Lower free areas must be used for producing high intensities of cavitation and hence the desired beneficial effects

2.2.4 Overview of the work done in recent years

Although hydrodynamic cavitation is more energy efficient, more flexible and offers greater potentiality for scaling up than acoustic cavitation, this technology has not been applied in wastewater treatment extensively (Gogate and Pandit, 2004). It has been reported that hydrodynamic cavitation has been applied for the degradation of several organic compounds

such as rhodamine B (Sivakumar and Pandit, 2002; Wang et al., 2008), p-nitrophenol (Kalumuck and Chahine, 2001), alachlor (Wang and Zhang, 2009) and for the decolorization of dye effluent (Sivakumar and Pandit, 2002) by using an orifice plate, cavitating jet, etc. Shirgaonkar and Pandit (1998) have demonstrated the effect of cavitation by using a high speed and high pressure homogenizer for release of enzymes/proteins. They observed that protein release was much higher at 10000 rpm compared to 5000 rpm as the cavitation inception occurred at 8000 rpm in a high speed homogenizer (Kumar and Pandit, 1999). Save et al. (1994) studied hydrodynamic cavitation based on throttling valves for yeast cell disruption and noted that extension of cell disruption increased with an increase of treatment time and number of passes. It was also found that, depending on the time of exposure, the activities of the enzyme released from the cell remained unaltered (Save et al., 1997). Thus it is important to control both the cavitation intensity and time of treatment for the desired level of treatment. Partial disruption of *E. coli* cells was investigated by Balasundaram and Pandit (2001), using hydrodynamic cavitation. It was reported that there was selective release of periplasmic and cytoplasmic enzymes relative to the total soluble protein as a function of cavitation intensity.

Hydrodynamic cavitation has great potential in water disinfection due to its capability to generate highly reactive free radicals and turbulence. The mechanism involved in disinfection of microorganisms by cavitation is thought to involve the following effects (Gogate and Kabadi, 2009).

- a) Mechanical effect: Associated with the generation of currents, shear stresses and turbulence due to liquid circulation.
- b) Chemical effect: Generation of free hydroxyl radicals.
- c) Heat effect: Hot spot generation due to high local pressure and temperature.

It has been observed that in hydrodynamic cavitation, chemical and thermal effects play supporting roles to mechanical effects in microbial disinfection. Jyoti and Pandit (2004) applied ozone and hydrodynamic cavitation to bore well water and found this technique much more effective in water disinfection compared to other individual physical-chemical techniques including ozonation, hydrodynamic cavitation and acoustic cavitation.

Cavitation can also be used as supplementary technique to a conventional biological oxidation process to increase substrate biodegradability or to reduce toxicity by degrading biorefractory materials (Gogate and Kabadi, 2009). It can also be used with an anaerobic digestion process to improve the digestibility of the sludge by solubilising it. Machnicka et al. (2009) combined hydrodynamic cavitation with anaerobic digestion and showed that biogas production increased up to 131% with the addition of 30% of volume disintegrated sludge in the fermentation process. They used a 1.2 mm nozzle for the generation of cavitation. It was also reported that soluble COD increased by 284 mg/L after application of cavitation for 90 minutes, showing evidence that the organic matter and polymer in the activated sludge was transferred from the solid phase to the liquid phase. Hydrodynamic cavitation was shown to improve phosphorus removal and recovery in the form of struvite by solubilizing phosphorus and ammonium nitrogen, as well as potassium, magnesium and calcium cations from the solid phase to the liquid (Grübel and Machnicka, 2010; Machnicka et al., 2009). Similar results were obtained when this technology was applied to the foam collected from a full scale enhanced biological nutrient treatment removal plant (Grübel and Machnicka, 2010). Huang et al. (2009) demonstrated that dewaterability of sludge can be improved by applying hydrodynamic cavitation.

2.3 Hydrodynamic vs acoustic cavitation

Acoustic cavitation in the form of ultrasound has been observed capable of removing a wide variety of contaminants from water. Significant research has been done in this field compared to hydrodynamic cavitation, but most of the studies have been done at laboratory scale. Scale-up is a big issue in acoustic cavitation compared to hydrodynamic cavitation. Designing large scale acoustic cavitation equipment involves information from a variety of fields compared to the hydrodynamic cavitation. Hydrodynamic cavitation reactors offer versatility and ease of operation. Several studies have proven that hydrodynamic cavitation is much more energy efficient and effective than acoustic cavitation (Gogate and Pandit, 2005; Gogate and Kabadi, 2009; Jyoti and Pandit, 2004; Kalumuck and Chahine, 2001; Save et al., 1997).

2.4 Ozone

Ozone is a very powerful oxidizing agent which reacts strongly with compounds containing multiple bonds rather than the single bond species. This is mainly due to the fact that there is no easy pathway to oxidation with single bonded functionality. The practical action of ozone is often dependent on how it reacts with pollutants rather than simply gaining the electron (except in the case of simple ion oxidation). It implies that whether ozone will oxidize a substrate in a reasonable time frame depends mostly on the kinetic factors rather than thermodynamics of ozone-induced oxidation (Gogate and Pandit, 2004).

Static mixers, packed and plate columns, jet reactors, countercurrent bubble columns, agitated vessels etc., are used to transfer ozone into water (Bowers et al., 1973; Glaze, 1987; Martin and Galey, 1994). Ozone transfer efficiency depends on the interfacial area of contact and also on the time of contact. To increase the contact area, small pore size ozone diffusers using porous glass, porous disks, ceramic membranes etc., are used and by increasing the liquid depth of the reactor, a longer contact time is achieved between the gas and water (Ciardelli and Ranieri, 2001; Janknecht et al., 2001; Ledakowicz et al., 2001; Picard et al., 2001). There is always a possibility of plugging of a porous diffuser by the suspended solids and also by oxidized precipitates which eventually reduced the ozone transfer rate. Side stream injectors can be used to avoid plugging and these can also operate at higher gas flow and higher mixing efficiency without bubble channelling problems. They are also subject to corrosion, bumping and lower contact time. Martin and Galey (1994) used static mixers in their study and observed an increasing mass transfer coefficient with decreasing water flow rate and increasing gas flow rate. It has also been reported that ozone transfer efficiency in static mixers increases with an increase in the pressure drop or a decrease in gas/liquid ratio and that transfer is independent of ozone loading (de Traversay et al., 2001). As static mixers are not used frequently with wastewater, more studies are required to calculate the energy requirement, as the pressure drop would be higher due to the suspended solids and other effluent properties compared to water containing microorganisms.

The degree of degradation achieved by ozonation depends on different parameters such as pH, temperature, contact time and interfacial area, ozone partial pressure, presence of catalyst,

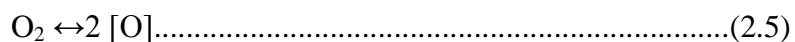
concentration of ozone in the gas, type of carrier gas (air/O₂), etc. At high pH values ozone reacts with almost all the organic and inorganic matter present in the medium (Beltran et al., 1992; Beltran et al., 1994; Staehelin and Hoigne, 1982). The solubilities of ozone and oxygen in water are shown in Table 4. It has been found that the solubility of ozone decreases with an increase in temperature, which may result in low degradation due to a limitation in the amount of ozone available for reaction (Beltran et al., 1994). Wu and Wang (2001) reported that the degradation of azodyes increased with temperature. This was similar to the findings of previous studies conducted by Meijers et al. (1995) which demonstrated an increase in degradation of diuron with an increase of temperature from 5 to 20⁰ C. Longer contact time and larger interfacial area are expected to increase ozone activity. Use of contactor or static mixer might be effective. The extent of degradation increases with an increase in ozone partial pressure which also increases the cost of ozone generation. The best approach is to ensure maximum transfer of ozone into the solution (Beltran et al., 1992, 1993; Ledakowicz et al., 2001).

Table 4. Solubility of ozone and oxygen in water (Rice, 1980)

Temperature (⁰ C)	Ozone solubility (mg/L)	Oxygen (from air) solubility (mg/L)
0	20	6.9
2	10	6.6
20	8.92	4.3
28	1.5	3.7

2.4.1 Ozone generation

Ozone is formed by combining two oxygen fragments, generated by rupturing the stable oxygen molecule, with another oxygen molecule.



In nature, ozone is generated by sunlight passing through the oxygen in the atmosphere. Artificially, ozone can be generated by passing a high voltage electrical discharge, high or low electrical frequencies or high energy radiation through air. Ozone is also produced as a

byproduct from the operation of welding equipment, the generation of electrical power, UV lights, electrostatic copying machines and from other electrical devices. Commercially, ozone must be generated at the site of use due to its short half life. The generation of ozone is energy intensive, as most of the power supplied to generate ozone is utilized to produce light, sound and preliminary heat rather than to produce ozone (Rice, 1980). Approximately 4 to 8% of ozone is produced in air or oxygen with very low energy efficiency (5-10%). Ozone generation requires an absolutely dry input gas stream (Glaze, 1987).

2.4.2 Ozone in water treatment

Ozone is used for the treatment of wastewater as well as for the disinfection of water. As a powerful oxidant, ozone is used to oxidize a variety of contaminants present in water and wastewater. Some of the applications of ozone in water treatment are listed in Table 5. Ozone is also used to increase the biodegradability of organic compounds. In wastewater treatment plants ozone can be used as a pre-treatment before the bio-digestion and also can be used in the recycle loop to reduce the overall sludge production in the plant.

Table 5. Application of ozone in water treatment (Rice, 1980)

Bacterial disinfection
Viral inactivation
Oxidation of soluble iron and/or manganese
Decomplexing organically bound manganese (oxidation)
Color removal (oxidation)
Taste removal (oxidation)
Odor removal (oxidation)
Algae removal (oxidation)
Removal of organics (oxidation)
Suspended solids removal (oxidation)
Increased biodegradability of dissolved organics

Several researchers (Ahn et al., 2002; Boehler et al., 2006; Deleris et al., 2002; Kamiya and Hirotsuji, 1998; Lee et al., 2005; Nagare et al., 2008; Sievers et al., 2004; Yeom et al., 2002) have studied the potential of ozone to reduce wastewater treatment plant sludge production by installing an ozonation tank in a recycle line. In almost all the applications, activated sludge was taken from the bioreactor and then after ozonation, returned back to the aeration tank. Sakai et al.

(1997) and Yasui et al. (1996) achieved zero sludge production by ozonating a small part of the returned sludge in the system without negatively affecting the effluent quality. Ozonation of sludge before digestion can improve the digestibility of the sludge by disrupting the floc and cell walls (Ahn et al., 2002; Bernal et al., 2005; Bougrier et al., 2006, 2007; Carballa et al., 2007; Chu et al., 2007; Manterola et al., 2008; Richard Jr. et al., 2008; Yeom et al., 2002; Zhao et al., 2007). Weemaes et al. (2000) reported that methane production increased by a factor of 1.8 and the digestion rate was accelerated by a factor of 2.2 using ozone pre-treatment before anaerobic digestion. Ozone pre-treated sludge can also be used as a possible source of carbon for denitrification (Ahn et al., 2002; Lee et al., 2005; Sakai et al., 1997; Yeom et al., 2002; Zhao et al., 2007). Nagare et al. (2008) and Tsuno et al. (2008) reported that biological nutrient removal was not affected due to the reduction of the sludge treated by ozone. Kamiya and Hirotsuji (1998) reported the existence of a threshold ozone concentration value to achieve the yield reduction and also showed that intermittent ozonation is much more effective than continuous ozonation with the added benefit that it also reduces the required ozone dose.

2.5 Research scope and objective

Although hydrodynamic cavitation offers higher energy efficiency as well as higher yield potential than acoustic cavitation, the implementation of this technology at a large scale is still lacking. So far only one commercial process known as CAVOX, 1994 has been developed by Magnum Water Technology Inc., California, which applies hydrodynamic cavitation along with UV irradiation and hydrogen peroxide to degrade benzene, ethyl benzene, toluene, xylenes, phenol, pentachlorophenol, cyanide, atrazine. The effectiveness of this technology has been shown in different case studies operated at pilot scale for a variety of chemicals. But the applicability of this process needs to be tested for real wastewater as well as for complex mixtures. Although cavitation offers immense potential for the degradation of pollutants present in wastewater, much work needs to be done as most of the studies available in this area are from small scale experiments using model reactions (Process, 1994).

Ozone alone has seen limited application due to its high production cost as well as its short half life, though it has been successfully used for sludge reduction in WWTPs. Due to the low

solubility of ozone; it has a poor gas-liquid mass transfer efficiency which makes the overall process uneconomical. These problems can be overcome by applying ozone along with other techniques. Jyoti and Pandit (2004) have reported that synergistic application of hydrodynamic cavitation and ozone for water disinfection resulted in reduced ozone requirements and significantly improved disinfection efficiency. Our hypothesis is that combined application of hydrodynamic cavitation and ozonation on sludge will improve the disintegration capacity of ozone and will also reduce the ozone requirement. Based on this hypothesis the specific research questions of this project were.

- Does the combined application of cavitation and ozonation improve the disintegration of sludge?
- Does cavitation enhance the disintegration capacity of ozone?
- How does inlet pressure affect the performance of ozone hydrodynamic cavitation in sludge disintegration?

Chapter 3: Materials and Methods

3.1 Waste activated sludge

Waste activated sludge (WAS) was collected from the University of British Columbia, Vancouver wastewater treatment pilot plant facility. The UBC pilot plant consists of two parallel trains known as train A and train B. Train A was operating as a membrane enhanced biological phosphorous removal process and train B was a simplified University of Cape Town (UCT) enhanced biological phosphorous removal process with secondary clarification. WAS was collected from train B. Both trains received domestic wastewater from the UBC campus. Raw wastewater was pumped into three large storage tanks which were followed by a common circular primary clarifier. The solids retention time (SRT) of the plant was 20 days. Train B had an anaerobic zone, an anoxic zone and an aerobic zone which was finally followed by a secondary clarifier. The anoxic and aerobic recycle ratios were 1:1, relative to the influent flow rate (Monti, 2006). WAS was collected from the aerobic zone. First WAS was collected in a wasting tank and then the required amount of sludge was pumped into the experiment tank.

3.2 Experimental program

In this study, hydrodynamic cavitation and ozone were initially applied to the aerobic WAS and finally the combined effect of hydrodynamic cavitation and ozonation was evaluated for sludge disintegration. The experimental setup is shown in Figure 7. Aerobic WAS of 25 L was pumped from the wasting tank into a 120 L tank. The setup consisted of a 120 L tank, a positive displacement pump (Moyno 332, ½ hp, 208 VAC), a cavitation device, an ozone injector, control valves (V_1 , V_2) and pressure gauges (P_1 , P_2). The diameter of the main line was 19 mm and discharged well below the liquid level in the tank to avoid air induction. A hard acrylic tube was used after the injector for visual inspection. A mixer was used in the tank to ensure proper mixing. An ozone generator (VMUS 08, Azco Industries Limited, Surrey, BC, Canada) was used for ozone generation from pure oxygen. A 6.35 mm tube was connected to the injector from the ozone generator. Temperature and pH were not controlled. The samples were collected from the tank and duplicate measurements were made for all the samples.

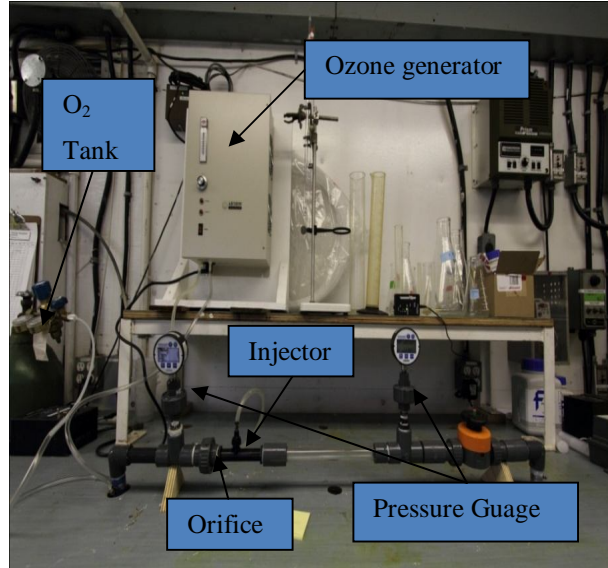
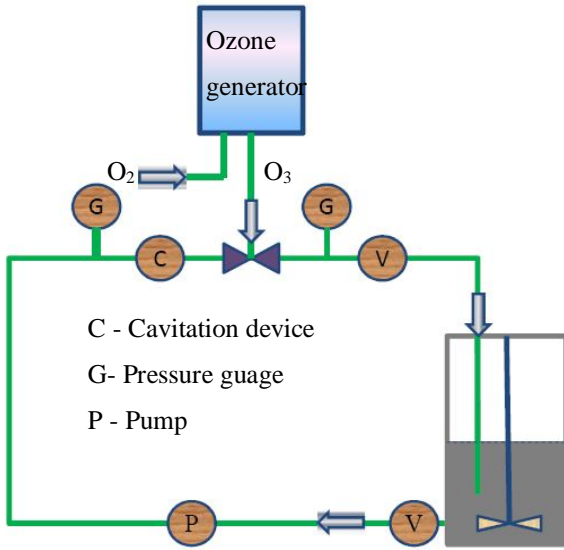


Figure 7: Ozone-hydrodynamic cavitation.

3.2.1 Hydrodynamic cavitation

In the first stage of the study, the individual effect of cavitation for sludge disintegration was evaluated. In this case, the ozone injector was taken out from the system. A 2 mm single orifice plate was used as a cavitation device. The inlet pressure was selected as 515 kpa as this was the maximum pressure achievable with the available pump and the flow rate was 4.9 Lpm. Both valves were kept open. The whole experiment was run for 90 minutes and samples were collected from the tank at 0, 2, 4, 6, 10, 20, 30, 40, 60 and 90 minutes.

3.2.2 Ozonation

In the second stage of the study, the effect of ozone for sludge disintegration was evaluated. In this case, the ozone generator discharged at 3 Lpm with an ozone concentration of 35 - 40 mg/L. The flow rate of the sludge was 4.9 Lpm. The orifice plate was taken out from the system. The experiments were run for 90 minutes and the samples were collected from the tank after 0, 2, 4, 6, 10, 20, 30, 40, 60 and 90 minutes.

3.2.3 Ozone hydrodynamic cavitation

In the third and final stage of the study the combined effect of ozone and hydrodynamic cavitation for sludge disintegration was evaluated. In this case, the ozone generator discharged at 3 Lpm with an ozone concentration of 35 mg/L at two different inlet pressures 515 Kpa and 275 Kpa. The experiments were run for 90 minutes initially and the samples were collected at 0, 2, 4, 6, 10, 20, 30, 40, 60 and 90 minutes. Later on, the experiments were run for 10 hours to achieve the maximum possible sludge disintegration. The inlet pressure used for this case was 515 kpa. Samples were collected in every 30 minutes for the first 3 hours and then every hour for the rest of the experiment.

3.3 Ozone generator

The amount of ozone generated by the ozone generator was evaluated from time to time following the Standard Methods (APHA et al., 2005). Ozone was generated by using pure oxygen (Figure 8). Two 2 L Erlenmeyer flasks containing 2 L of 20 g/L potassium iodide (KI) solution were kept in series for trapping the ozone. The ozone generator discharge was bubbled through the solution for a specified time at a measured flow rate. The flasks were kept sealed except for inlets and outlets for gas flow. Then 10 mL of solution was diluted up to 100 mL by using distilled water. After that 5 mL of 2 N H₂SO₄ were added to the solution. Then the solution was titrated by using 0.005 N Na₂S₂O₃ until the light yellow color appeared. After that starch indicator was added and the titration was continued until the blue color disappeared. The ozone generation rate was calculated by using the following formula:

$$\text{Ozone dose (mg/L)} = \frac{(A+B) \times N \times 24 \times \text{DF}}{T} \dots\dots\dots(3.1)$$

Where:

A = mL Titrant for trap A,

B = mL Titrant for trap B,

N = normality of Na₂S₂O₃,

T = Ozonation time, min, and

DF = Dilution factor.

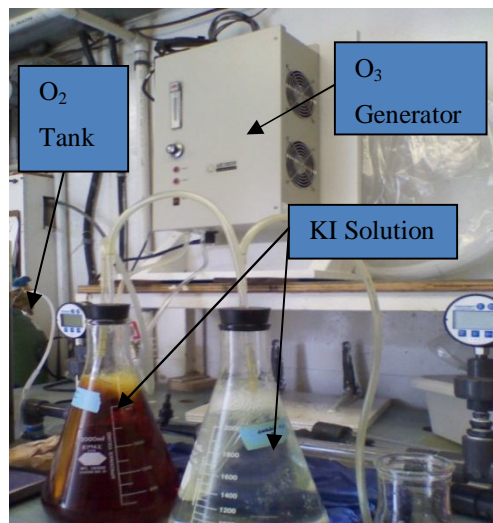
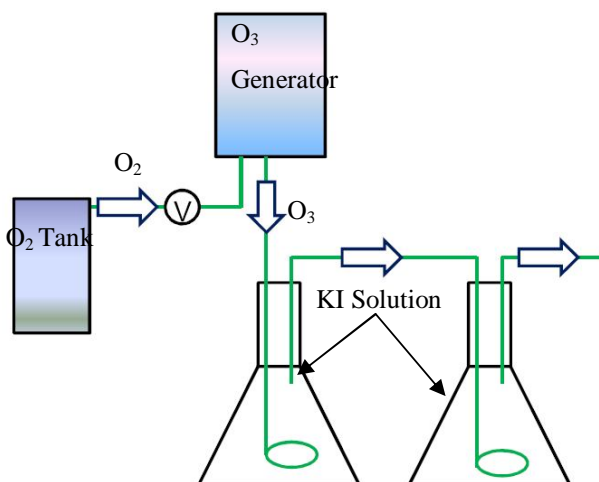


Figure 8: Generation of ozone.

3.4 Characterization of sludge samples

Sludge samples were analyzed for total and volatile suspended solid content (TSS/VSS), Chemical Oxygen Demand (COD), readily biodegradable COD, soluble total organic carbon, total and ortho-phosphate, volatile fatty acids, ammonium nitrogen, nitrate+nitrite nitrogen, soluble Biochemical Oxygen Demand (BOD) and temperature. The samples were first centrifuged at 24900 rcf for 10 minutes using Thermo IEC multi centrifuge, and then filtered through a 0.45 μm membrane filter to separate soluble fractions from particulate fractions. The analytical methods for the analysis are described below. More details can be found in Standard Methods (APHA et al., 2005).

3.4.1 Total and volatile suspended solids (TSS/VSS)

TSS and VSS were measured according to the Standard Methods (APHA et al., 2005). Specified volumes of well mixed samples were filtered through glass micro fibre filter paper (WhatmanTM 934 AHTM) and then the residues retained on the filter papers were dried overnight at 105⁰ C, weighed, transferred to 550⁰ C, heated for an hour and weighed again. TSS and VSS were calculated using the following equation:

$$\text{TSS (mg/L)} = (X - Y) \times 10^6 / V \dots\dots\dots(3.2)$$

$$\text{VSS (mg/L)} = (X - Z) \times 10^6 / V \dots\dots\dots(3.3)$$

Where,

X = Mass of the filtered sludge dried at 103⁰ C,

Y = Mass of the aluminium dish containing glass fiber filter, and

Z = Mass of the filtered sludge dried at 550⁰ C.

3.4.2 Total and soluble chemical oxygen demand (COD)

The closed reflux, colorimetric method was used for determining the total and soluble COD described in Standard Methods (APHA et al., 2005). For COD analysis, samples were added to a previously made reagent which was prepared in accordance with Standard Methods (APHA et al., 2005). The reagent was made by mixing 2.7 mL of sulfuric acid reagent with 1.2 mL of digestion solution. The digestion solution was made by adding 10.217 g of K₂Cr₂O₇ and 167 mL of H₂SO₄ in 1 L of distilled water for high range of COD (20-900 mg/L). For low range (0-20 mg/L) COD 2.27 g of K₂Cr₂O₇ was used. Low range reagents were used for the samples collected for the first 20 minutes and high range reagents were used for the rest. The samples were analyzed by using HACH DR2800 Direct Reading Spectrophotometer.

3.4.3 Volatile fatty acids

All the samples were analyzed for VFA by using gas chromatography (GC). Soluble samples were preserved in 2 mL glass vials. A drop of 10% H₃PO₄ was added as preservative to each vial. All the soluble samples were analyzed in an HP 6890 Series gas chromatograph with a flame ionization detector (FID). The operating specifications of the GC used for the analysis are described in Table 6.

3.4.4 Ammonium nitrogen

Approximately 8 mL of 0.45 µm membrane filtered samples were preserved by adding two drops of 5% v/v H₂SO₄. Ammonium nitrogen was analyzed by using the automated phenate method

according to the Standard Methods NH₃-N (APHA et al., 2005). A Lachat Quik-Chem 8000 flow injection analyzer was used for the analysis.

Table 6: Operating specifications of the gas chromatograph.

Column	HPFFAP 25 m x 0.32 mm x 0.25 µm film
Carrier Gas	Hydrogen (H ₂) Carrier, 68 kpa (10 psi) Head Pressure
Injection Temperature	180 ⁰ C
Detector Temperature	250 ⁰ C
Oven Initial Temperature	80 ⁰ C
Oven Final Temperature	200 ⁰ C
Oven Temperature Program Rate	12 ⁰ C/min

3.4.5 Nitrate+nitrite nitrogen

Approximately 8 mL of 0.45 µm membrane filtered samples were preserved by adding two drops of 0.10% phenyl mercuric acetate to analyze nitrate+nitrite nitrogen. Samples were analyzed according to the cadmium reduction flow injection method described in Standard Method 4500-NO₃ I⁻ (APHA et al., 2005) by using a Lachat Quik-Chem 8000 flow injection analyzer.

3.4.6 Total and ortho-phosphate phosphorus

To determine the total phosphate, 5 mL of digestion reagent was added to 1 mL of unfiltered sample. To make the digestion reagent, 200 mL of concentrated H₂SO₄ was slowly added to 350 mL of distilled water in a large beaker and then 134 gm of K₂SO₄ was added and stirred. When the solution became cool, distilled water was added up to 1L volume. Phosphorus was determined after block digestion according to the Standard Method 4500 P H (APHA et al., 2005) by using Lachat Quik-Chem 8000 flow injection analyzer. The digestion was done at 135⁰ C for the first 300 minutes and at 375⁰ C for next 180 minutes.

Approximately 8 mL of 0.45 µm membrane filtered samples were preserved by adding two drops of 0.10% phenyl mercuric acetate to analyze ortho-phosphate. Preserved samples were analyzed

according to the Standard Methods 4500 P G (APHA et al., 2005) by using Lachat Quik-Chem 8000 flow injection analyzer.

3.4.7 Total organic carbon (TOC)

For TOC analysis, approximately 10 mL of filtered sample were preserved by adding two drops of 10% HCL. Samples were subsequently analyzed according to the high temperature combustion method described in Standard Methods 5310 B (APHA et al., 2005) by using a IL 550 TOC-TN analyzer (CA).

3.4.8 Biochemical oxygen demand (BOD)

The BOD₅ concentrations of the initial samples and samples after 90 minutes of treatment with both ozone and ozone-hydrodynamic cavitation were measured according to Standard Methods (APHA et al., 2005). For the initial samples, 50 mL of filtered sample were added to a 300 mL BOD bottle which was then filled with dilution water, made according to the method described in 5210 B in Standard Methods (APHA et al., 2005). Then the dissolved oxygen (DO) was measured initially and the bottle was incubated in a 20⁰ C incubator. After 5 days, the DO was measured again. A HACH LD0101 DO probe was used to measure the DO. Finally, the BOD₅ was calculated according to the following formula:

$$\text{BOD}_5 \text{ (mg/L)} = (\text{D}_1 - \text{D}_2)/\text{P} \dots\dots\dots(3.4)$$

Where,

D₁ = DO of diluted samples immediately after preparation (mg/L),

D₂ = DO of diluted samples after 5 day incubation at 20⁰ C (mg/L), and

P = Decimal volumetric fraction of sample used.

In case of the samples taken after 90 minutes, 3 mL and 5 mL of filtered sample were used to measure the BOD₅.

3.4.9 Biodegradable COD

A simple batch reactor was used to determine the readily biodegradable COD as illustrated in Figure 9. An Erlenmeyer flask of 1 L volume was used as a reactor. Air was supplied continuously by using a small tube at the bottom of the flask and a magnetic stir plate and stir bar were used to keep the contents of the reactor in suspension. The water loss due to evaporation was accounted for and replaced by distilled water. The experiment was operated at room temperature. The sides of the reactor and aeration tubing were cleaned regularly by using a bottle brush to ensure the suspension of biomass in the reactor.

Samples collected initially and after 90 minutes of application of ozone-hydrodynamic cavitation were assessed for soluble biodegradable COD. In both cases, 200 mL of filtered sample were taken from the reactor and then 2 mL of activated sludge from the pilot plant was added. Phosphate buffer was added to both reactors to maintain the pH around 7.0. Initial soluble COD was measured. Samples were taken from the reactor and soluble COD was measured until the soluble COD stabilized in the reactor.



Figure 9: Readily biodegradable COD

Chapter 4: Results and Discussion

4.1 Introduction

In this chapter experimental results are presented, compared and discussed for three pre-treatment i.e., cavitation, ozone and combination of ozone and cavitation. Applicability of the disintegrated sludge is also discussed.

4.2 Cavitation device

Before beginning the experimental program, the cavitation device i.e., 2 mm orifice was tested for the generation of cavities. It was not possible to directly observe cavitation during operation with sludge. However, the generation and collapse of cavities were visually observed downstream of the orifice, using tap water as a medium, during operation at pressures and flow rates that were comparable to those applied for sludge treatment. Moreover the cavitation number (C_v) was calculated from the equation 2.1. Cavitation generally occurs at $C_v < 1$ (Gogate and Pandit, 2000b). The cavitation numbers calculated for the inlet pressures of 515 Kpa and 275 Kpa were 0.25 and 0.50 respectively, indicating the strong likelihood that cavitation was occurring. For both calculations, atmospheric pressure was taken as recovered pressure.

4.3 Total and Volatile Suspended solids (TSS/VSS)

The concentration of suspended solids measured as both TSS and VSS were reduced by the three techniques as shown in Figures 10 and 11. A greater reduction of both TSS and VSS was found in the case of the combined application of ozone and cavitation, compared to the individual applications. TSS was reduced by 28% in the combined system, whereas only 19% by ozone and 6% by cavitation only. On the other hand VSS reduction was also much higher with the combined system compared to the individual application of ozone and cavitation (Figure 11). VSS was reduced by 31% in the combined system, whereas only 19% reduction was achieved with ozone and 4% with cavitation only.

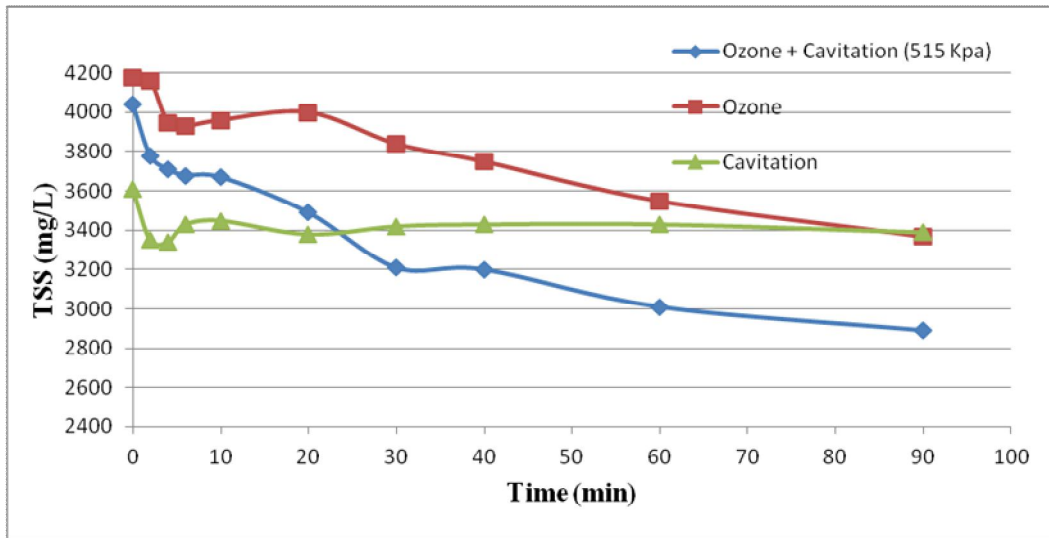


Figure 10: Reduction of TSS using different disintegration condition.

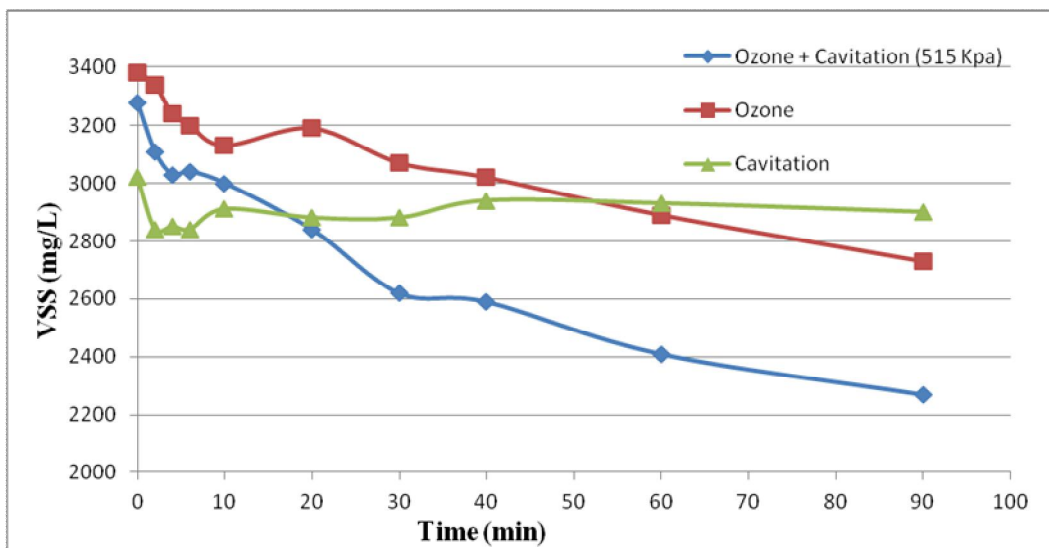


Figure 11: Reduction of VSS using different disintegration condition.

The effect of inlet pressure in the combined application of ozone and cavitation on suspended solids (TSS/VSS) reduction is shown in Figures 12 and 13. It was found that in the case of the lower pressure, a slightly lower fraction of suspended solids was reduced. At a pressure of 275 Kpa, TSS and VSS were reduced by approximately 23% and 22% respectively which was lower than the reduction of TSS and VSS at a pressure of 515 Kpa, although the amount of ozone applied was the same in both the cases.

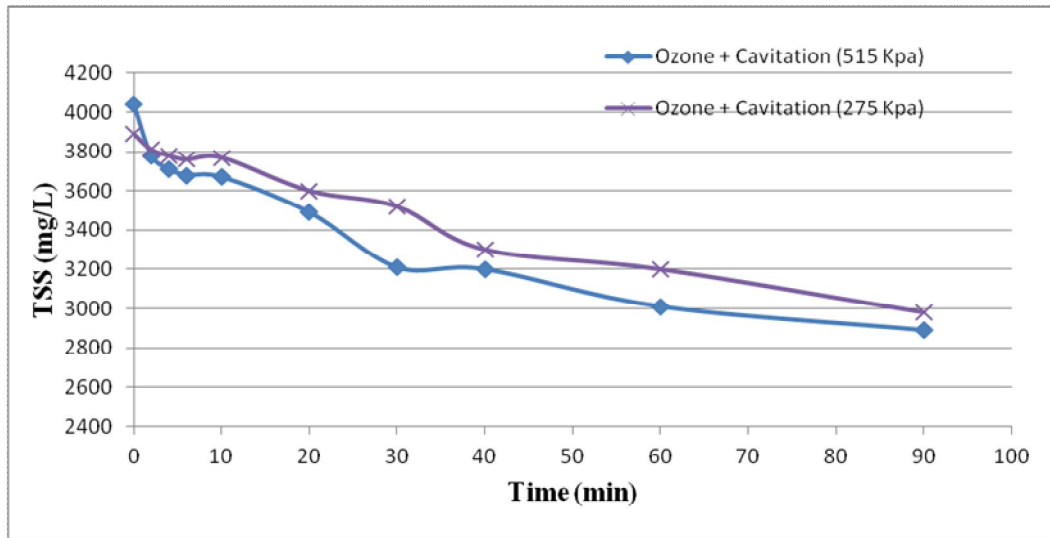


Figure 12: Reduction of TSS with different inlet pressures in combined ozone-cavitation treatment

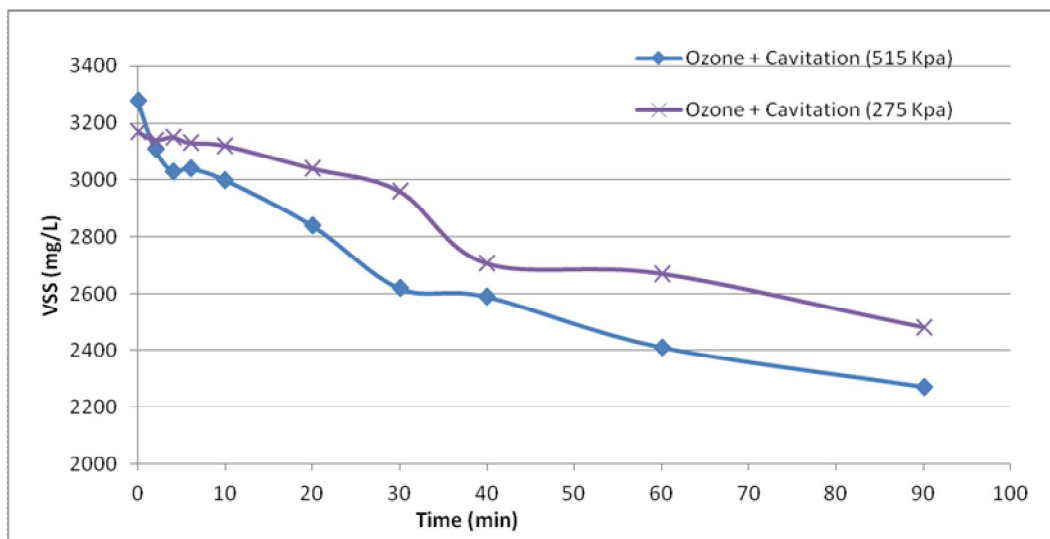


Figure 13: Reduction of VSS with different inlet pressures in combined ozone-cavitation treatment

From Figures 10-13 it was observed that the changes in the suspended solids continued for the entire 90 minute experiment. To estimate the maximum solids reduction achievable, the experiments were run for longer period of time. In a longer experimental run it was shown that the rate of reduction decreased with time. From Figures 14 and 15 it can be seen that the slope of the curve decreased with time. After 10 hours, TSS and VSS were reduced by 68% and 70% respectively.

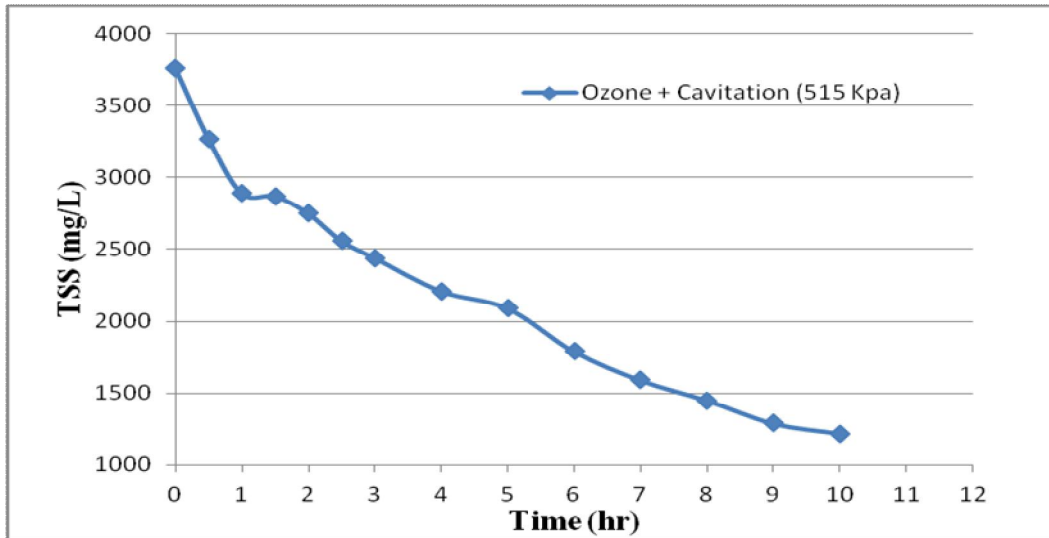


Figure 14: Reduction of TSS using combined application of ozone and cavitation

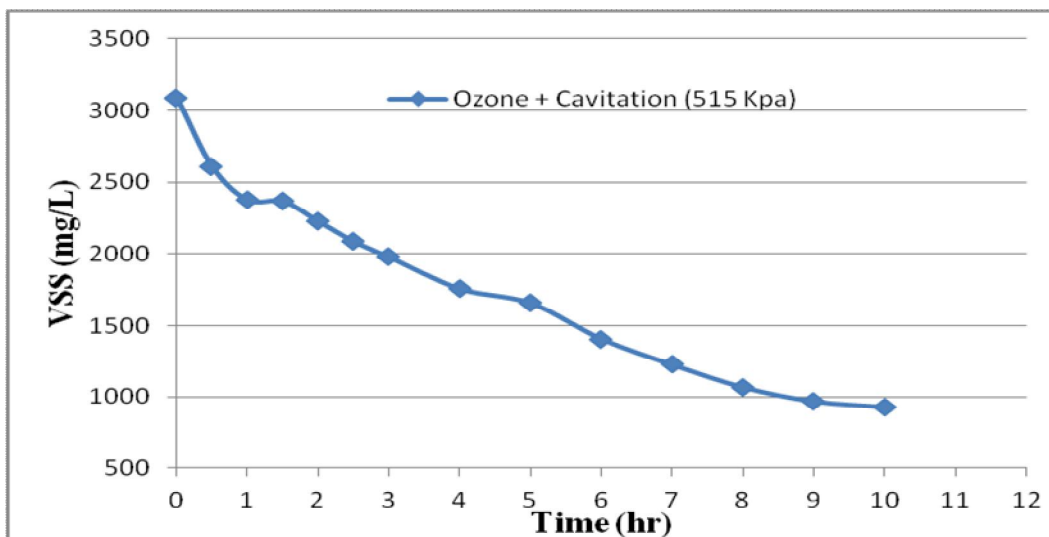


Figure 15: Reduction of VSS using combined application of ozone and cavitation

From the above discussion it can be concluded that the combined application of ozone and cavitation showed a marginally higher suspended solids (TSS/VSS) reduction at higher inlet pressure than the individual technologies and also that the rate of reduction decreased with time.

4.4 Soluble COD

Solubilisation of sludge was assessed in terms of the generation of soluble COD (SCOD). Figure 16 illustrates the SCOD concentration with time for the combined and separate applications of ozone and cavitation. The SCOD increased by approximately 1600 mg/L in the combined system, which was much higher than the individual effect of ozone or cavitation.

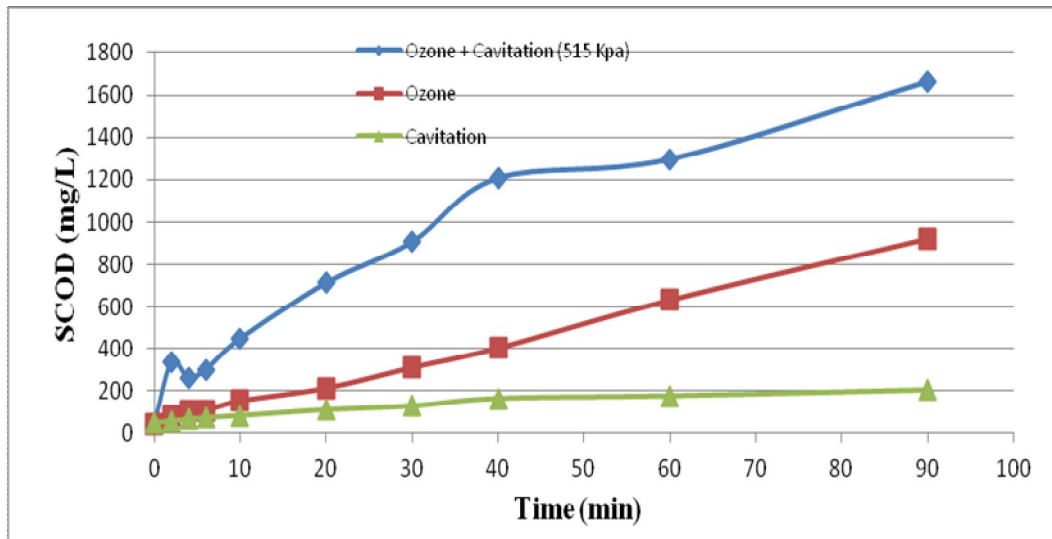


Figure 16: Concentration of SCOD using different disintegration conditions.

SCOD was also measured for the experiment with two different inlet pressures of 515 Kpa and 275 Kpa with the combined system. Figure 17 indicates that higher inlet pressure causes more sludge to solubilise although the difference is higher initially.

To determine the maximum possible solubilisation of sludge, the experiment was run for a longer period of time. Figure 18 illustrates that SCOD became almost stable at 2500 mg/L. In Table 7 it is indicated that the total COD of the sludge was approximately 5000 mg/L which means that after about 10 hours of treatment, 50% of the sludge was solubilised. Again from Figure 15 it was observed that the VSS was reduced by approximately 2000 mg/L. From these results it can be said that 1.25 mg COD/mg VSS was released which is in the range reported by other researchers (Contreras et al., 2002; Roels, 1983).

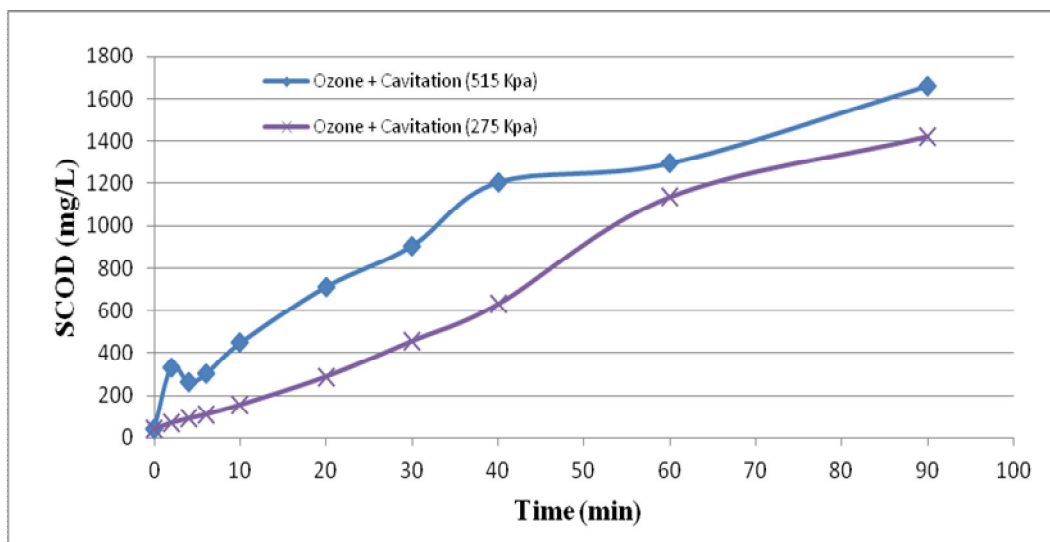


Figure 17: Concentration of SCOD with different inlet pressures in combined ozone-cavitation treatment.

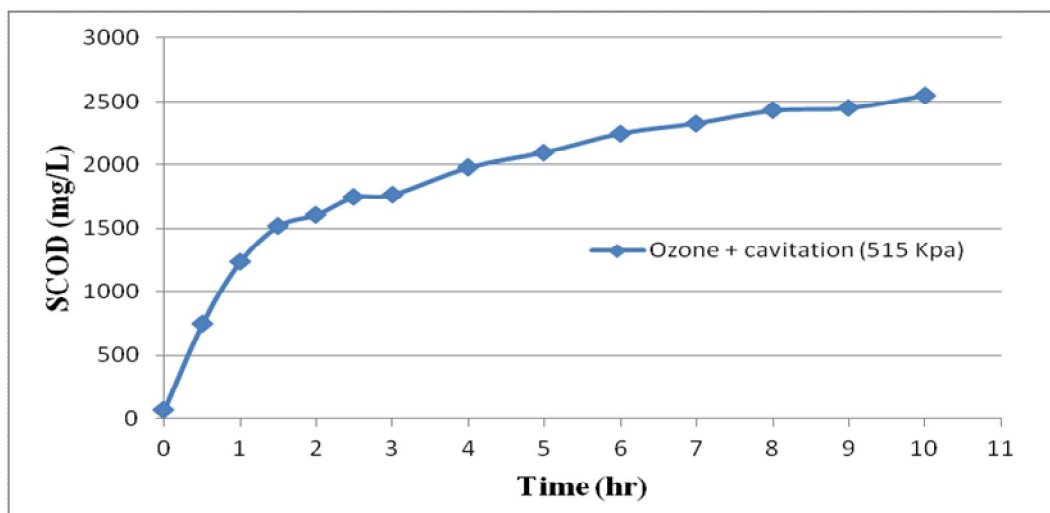


Figure 18: Concentration of SCOD using combined application of ozone and cavitation

Based on the concentration of SCOD obtained in the experiments it can be concluded that greater solubilisation of sludge was obtained in the combined application of ozone and cavitation at higher inlet pressure and also the rate of solubilisation decreases with time.

Table 7: Concentration of total COD and total phosphorus in the untreated sludge.

Parameter	Concentration (mg/L)
Total COD	5012 \pm 384
Total Phosphorus	152 \pm 3.70

4.5 Soluble total organic carbon (TOC)

The amount of organic matter released by sludge solubilisation was estimated by measuring soluble TOC. Figure 19 illustrates the amount of TOC released for the combined, as well as individual application of ozone and cavitation in the short term experiments. In the combined system, TOC increased by 50% the amount released by ozone alone. Only cavitation did not produce any significant release of soluble TOC compared to the other treatments.

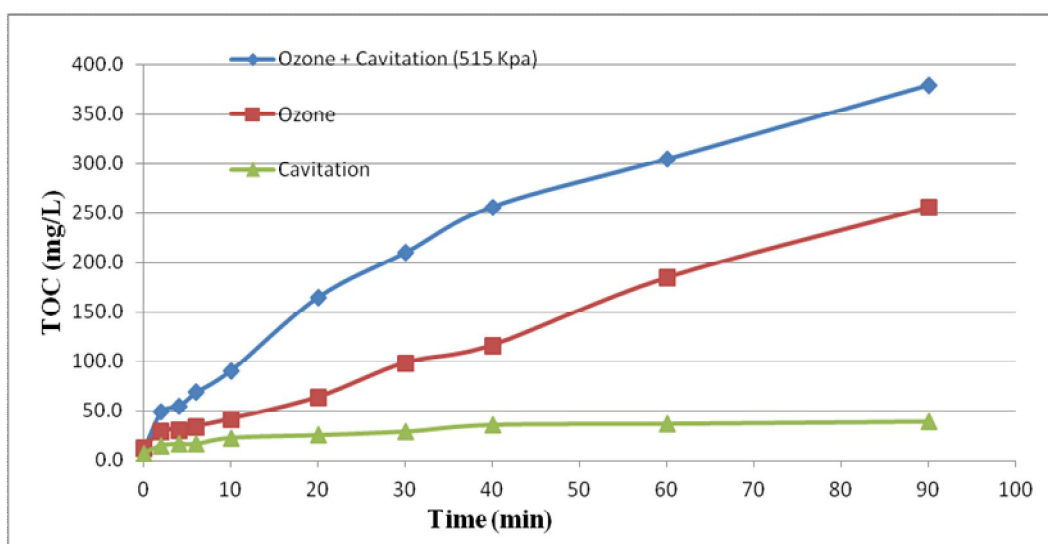


Figure 19: Release of soluble total organic carbon using different disintegration conditions

Figure 20 illustrates the effect of inlet pressure on organic matter release. It was observed that after 90 minutes of treatment, the TOC concentration was about 380 mg/L using an inlet pressure of 515 Kpa, whereas at an inlet pressure of 275 Kpa TOC concentration was 300 mg/L. Although ozone was injected at the same rate (3 Lpm) in both experiments, more organic matter was released at the higher inlet pressure.

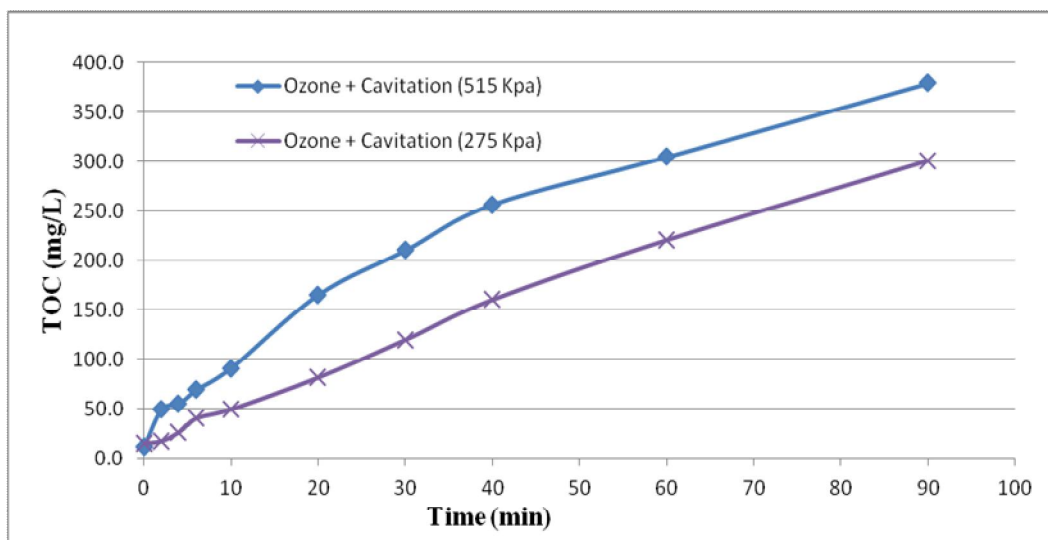


Figure 20: Release of soluble total organic carbon for different inlet pressures in combined application.

Figure 21 illustrates the TOC concentration during the long term experiment for combined application of ozone and cavitation. Although for the first couple of hours a sharp increase in TOC was observed, after that the concentration changed almost linearly with time. After 10 hours the soluble TOC was 918 mg/L.

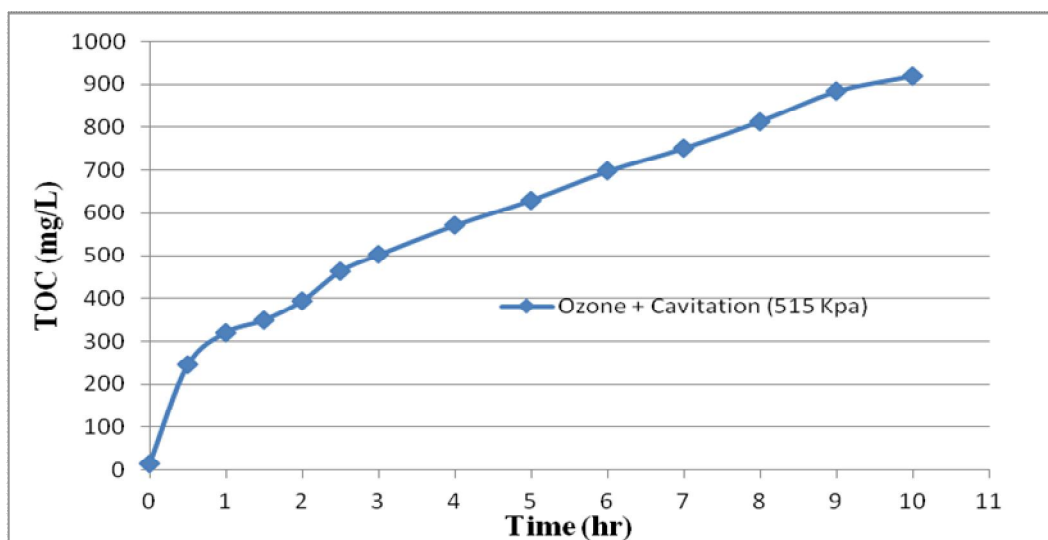


Figure 21: TOC concentration in combined long-term application of ozone and cavitation.

Among all the methods applied, the combined application of ozone and cavitation demonstrated the highest release of organic carbon at the higher inlet pressure due to a higher rate of solubilisation of the sludge. The concentration of TOC continued to increase with time, indicating the release of organic matter due to the cell disruption.

4.6 Volatile fatty acids

Volatile fatty acids (VFAs) concentrations were also measured for the three different disintegration techniques as the disintegrated sludge could be a source of VFAs for phosphorus-accumulating bacteria in the anaerobic zone of a biological nutrient process. From Figure 22 it was observed that with the combined application of ozone and cavitation, concentration of VFAs increased to 22 mg/L after 90 minutes of treatment. Ozone alone increased the concentration up to 14 mg/L and cavitation increased the concentration to about 5 mg/L. Overall the combined application did not indicate any substantial impacts on VFAs concentration

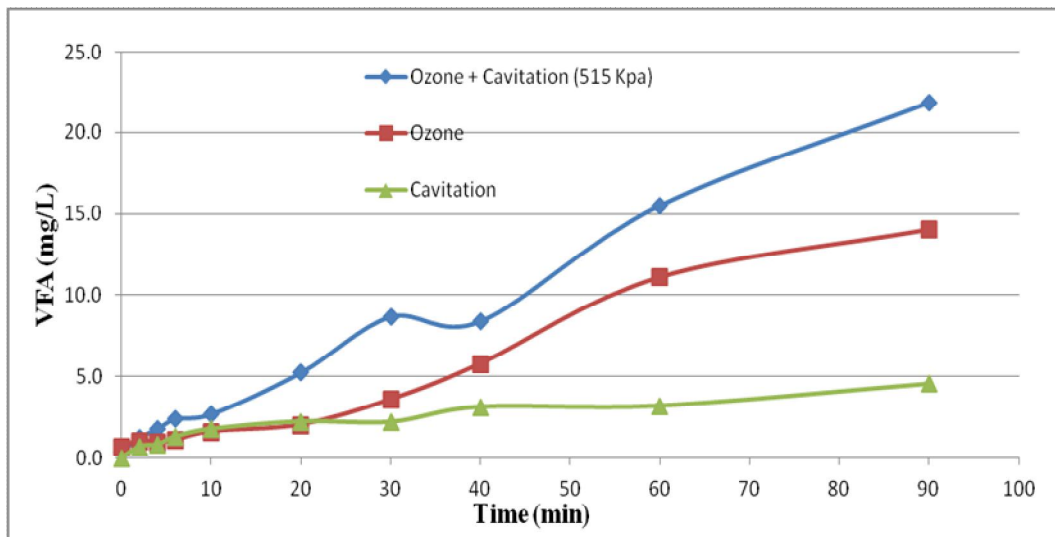


Figure 22: VFA release under different disintegration conditions.

The two different operating inlet pressures did not result in differences in VFAs concentration. From Figure 23 it can be observed that the same concentrations of VFAs were produced at the two inlet pressures of 515 Kpa and 275 Kpa. Figure 24 demonstrates the changes in VFA over a longer period of time for the combined application of ozone and cavitation. Although it follows a

similar pattern to that of TOC, the amount of VFA released was a small fraction of the solubilised TOC. After 10 hours the VFA concentration was 70 mg/L which was only 3% of soluble TOC.

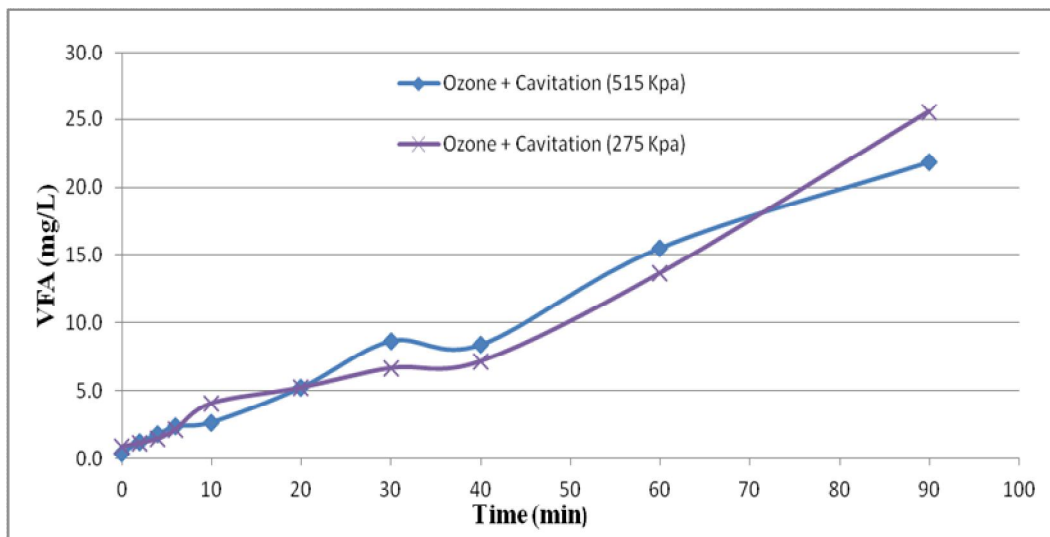


Figure 23: VFA release for different inlet pressures using combined treatment.

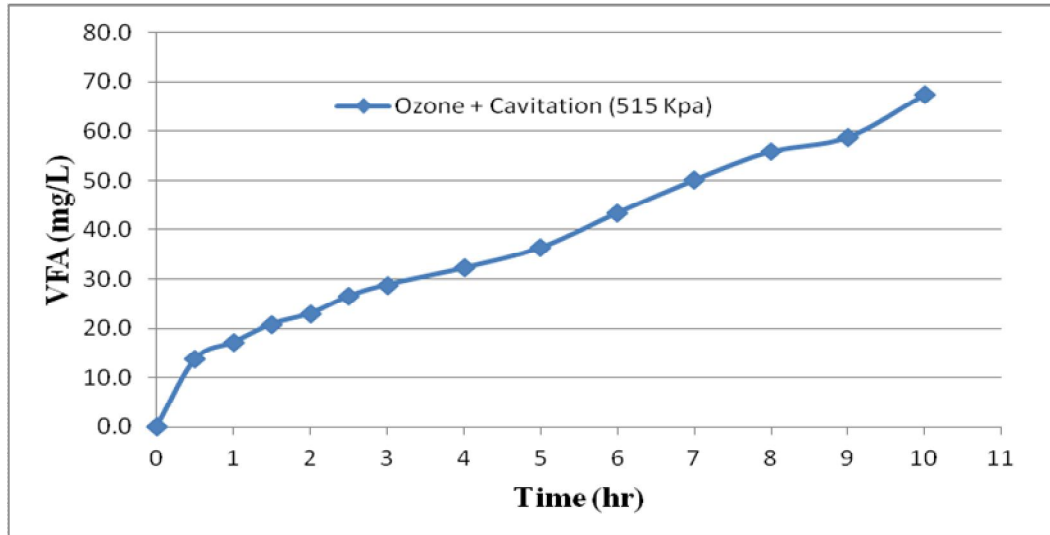


Figure 24: VFA release in combined application of ozone and cavitation.

From the above discussion it can be concluded that the combined application of ozone and cavitation does not have any substantial impact on VFAs production compared to the individual

treatment methods. Like the soluble TOC, the concentration of VFA continues to increase with time but it constitutes a very small fraction of the soluble TOC.

4.7 Ortho-phosphate-P

In the bio-p process, bacteria store phosphorus as polyphosphate in activated sludge and then are removed from the system as excess sludge. The disintegration of excess sludge will re-solubilise the phosphorus which can then be recovered in the form of struvite. More phosphate-P ($\text{PO}_4\text{-P}$) was released in the combined system compared to the other treatments. Figure 25 indicates the amount of phosphate released for the different disintegration techniques. With the combined treatment, about 30 mg/L $\text{PO}_4\text{-P}$ was released, which was higher than with the individual application of ozone alone. Cavitation itself did not produce a significant change in ortho-phosphate concentration. Figure 26 indicates the $\text{PO}_4\text{-P}$ concentrations for two different inlet pressures with the combined system, in which almost same amounts of phosphate were released for both the 515 Kpa and 275 Kpa inlet pressures.

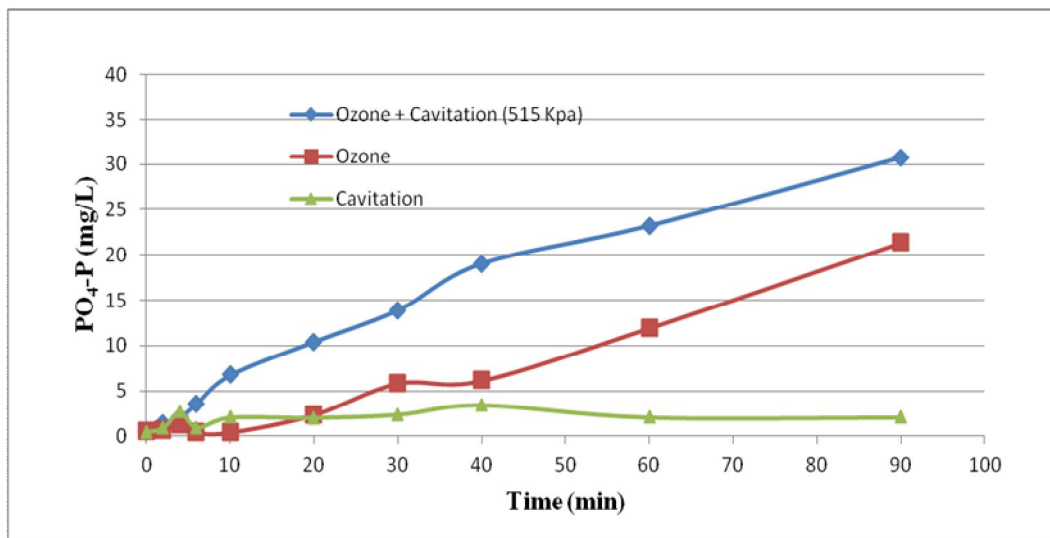


Figure 25: Release of phosphate-P under different disintegration conditions

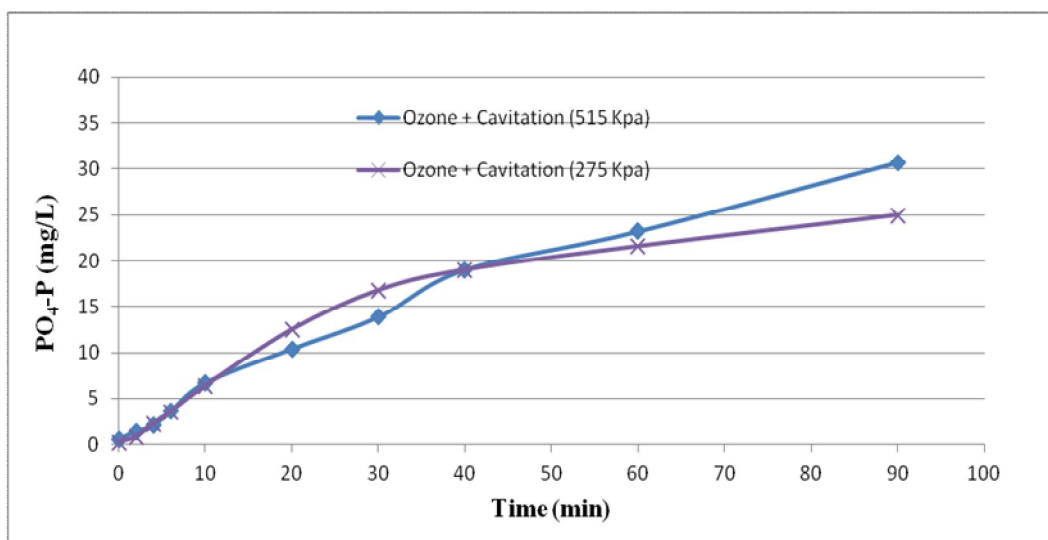


Figure 26: Release of phosphate-P for different inlet pressures in combined application.

To find out the maximum amount of phosphate that could be released with the combined technique, the experiment was run for longer period of time. From Figure 27 it can be observed that most of the $\text{PO}_4\text{-P}$ was released within first couple of hours. After 10 hours, the $\text{PO}_4\text{-P}$ concentration was 40 mg/L, of which only 9 mg/L were released during the last 8 hours. The total $\text{PO}_4\text{-P}$ concentration of sludge was 152 mg/L (Table 7) which means that approximately 26% of the total P was released to the solution.

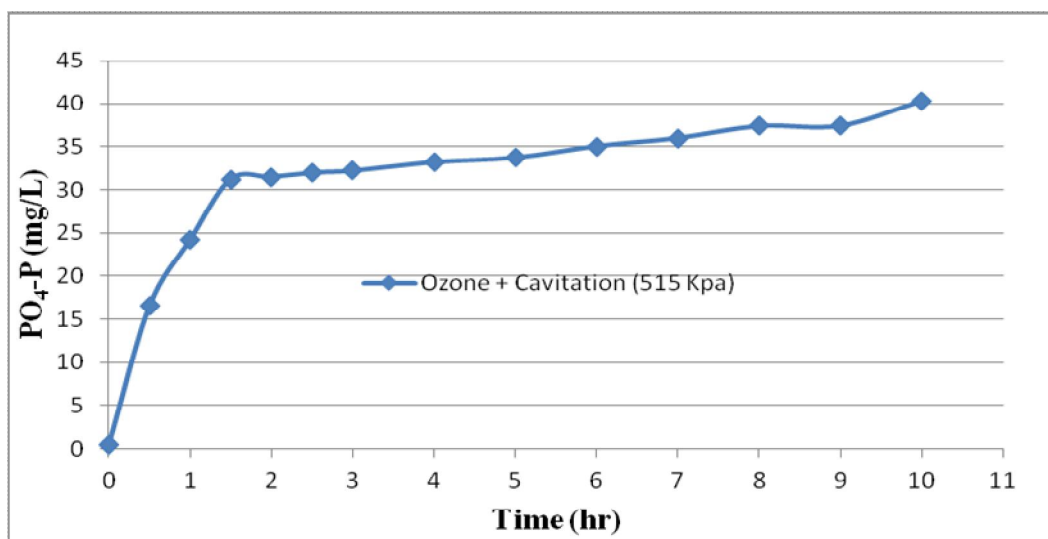


Figure 27: Release of phosphate-P with combined application of ozone and cavitation.

From the above discussion it can be concluded that the combined application of ozone and cavitation produced the greatest extent of phosphorus release from the sludge. A higher inlet pressure did not show any impact on phosphorus release. It was also observed that most of the maximum phosphorus was released initially. A similar pattern was reported by Saktaywin et al. (2005) who used ozone for disintegrating sludge. It was also found that approximately 26% of total phosphorus was released into the solution due to disintegration of sludge, indicating the solubilisation of extracellular exopolymers (EPS). Cloete and Oosthuizen (2001) reported that EPS alone contains 27% - 30% of total phosphorus.

4.8 Ammonium-nitrogen

For the formation of struvite, $\text{NH}_4\text{-N}$ is a necessary element. For the removal and recovery of nutrient (N, P) in the form of struvite, the required molar ratio of $\text{Mg}:\text{NH}_4:\text{PO}_4$ is 1:1:1 and the required mass ratio is 0.25:0.19:1. Disintegrated sludge can be used as a source of ammonium-nitrogen for struvite formation. The amounts of ammonium-nitrogen ($\text{NH}_4 - \text{N}$) released with the different disintegration techniques are presented in Figure 28. The concentrations of $\text{NH}_4 - \text{N}$ increased approximately 4 mg/L and 2.7 mg/L with the combined application of ozone and cavitation, and cavitation alone. When ozone alone was applied, no substantial change was observed. One of the reasons might be that ammonium can be oxidized to nitrate by ozone according to the following reaction (Singer and Zilli, 1974):



This suggests that the changes observed with the combined application were mostly due to the cavitation effect rather than to an ozone effect. Similarly from Figure 29, it was clear that at a pressure of 275 Kpa, the concentration of $\text{NH}_4 - \text{N}$ did not change much compared to the pressure of 515 Kpa.

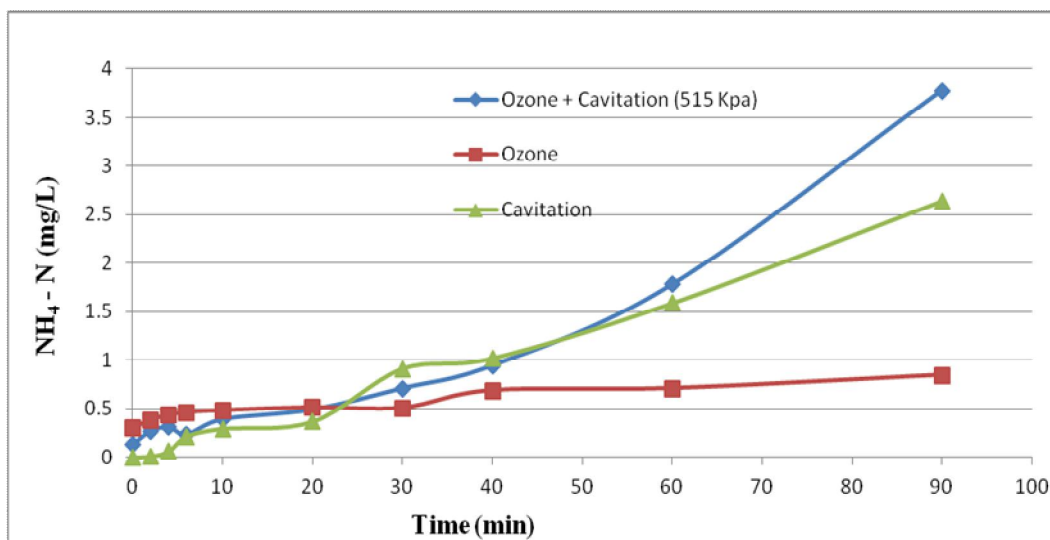


Figure 28: The effects of disintegration techniques on ammonium-nitrogen release.

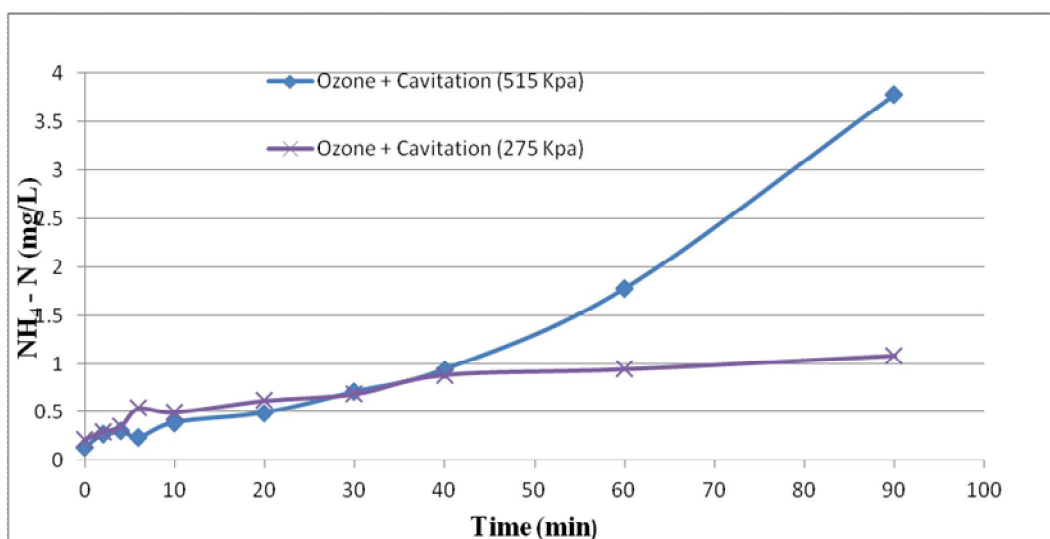


Figure 29: The effect of inlet pressure on ammonium-nitrogen release using the combined technique.

Figure 30 illustrates the changes in the concentration of $\text{NH}_4 - \text{N}$ over a longer period of time for combined application of ozone and cavitation. The concentration changes almost linearly with time. After 10 hours of treatment the $\text{NH}_4 - \text{N}$ concentration was about 12 mg/L.

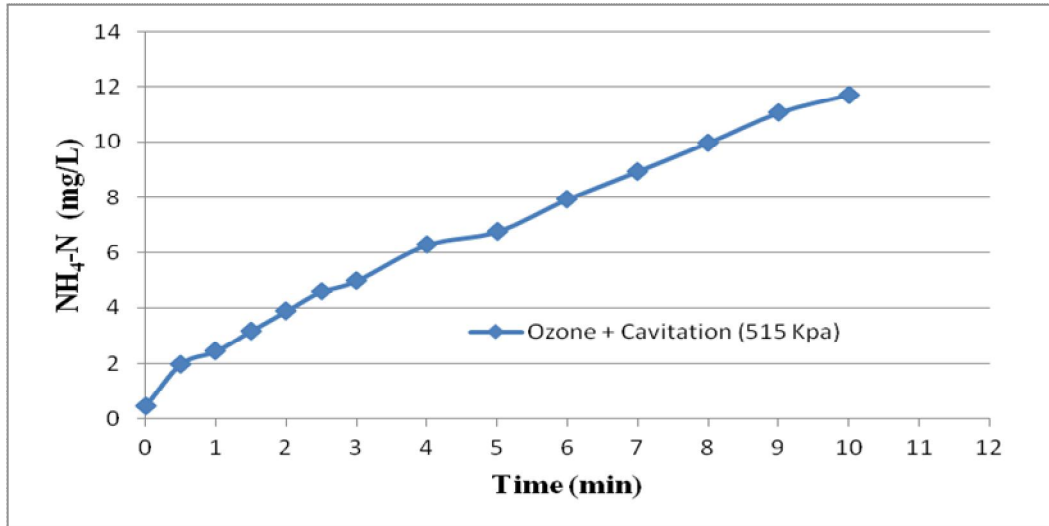
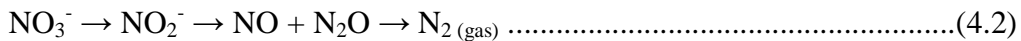


Figure 30: Release of ammonium-nitrogen with combined application of ozone and cavitation.

4.9 Nitrate + nitrite nitrogen

The concentrations of nitrate+nitrite-nitrogen (NO_x-N) for different disintegration techniques are presented in Figure 31. It was observed that with cavitation alone, the concentration of NO_x-N gradually decreased to zero with time. In the case of ozone and the combined application, NO_x-N concentration increased for a certain period of time and then stabilised. In the case of cavitation alone denitrification might have occurred in the tank which converts NO_x-N to N₂ according to following reaction. It also suggests the presence of active biomass in the system.



With ozonation alone and with the combined application, some NO_x-N might be produced according to equation 4.1. Figure 32 illustrates the effect of two different inlet pressures using the combined technique, on NO_x-N release. The concentration increased from 7 mg/L to 13 mg/L at 275 Kpa and to 10 mg/L at 515 Kpa. A slightly higher increase in concentration was found at low pressure.

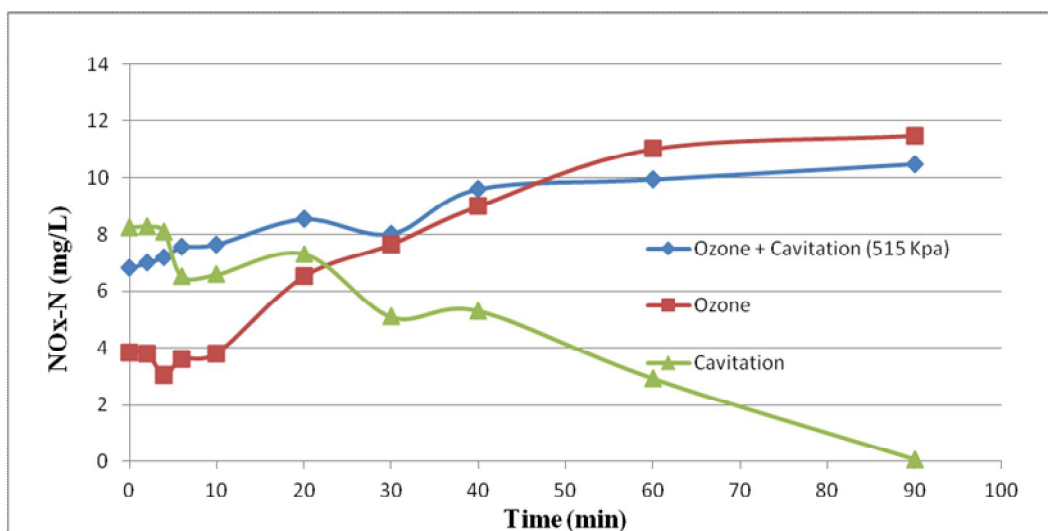


Figure 31: The effect of disintegration techniques on nitrate-nitrite nitrogen release.

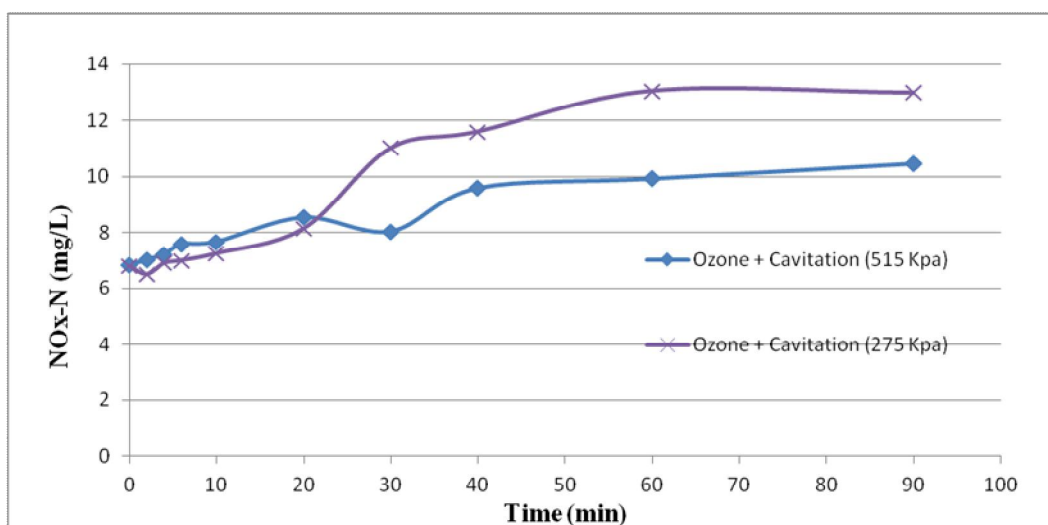


Figure 32: The effect of inlet pressure on nitrate-nitrite nitrogen release in combined technique.

Finally, the effect of long term application of combined ozone and cavitation techniques is presented in Figure 33. It was observed that concentration of NO_x-N increased from 5.5 mg/L to 11 mg/L within 1.5 hrs and after that the concentration increased very slowly up to 16 mg/L by 10 hrs. The reason might be the changes in pH. When ozone was applied the pH decreased from 6.9 to 4.0 in 10 hrs. At high pH ammonia is more reactive with respect to oxidation by ozone than at low pH (Singer and Zilli, 1974). So, as the pH decreased, the conversion of ammonia to nitrate decreased, which slowed down the increase of NO_x-N concentration. Moreover at lower

pH, organic species become more dominant with respect to oxidation by ozone than ammonia (Singer and Zilli, 1974). As the concentration of organic material increased with time, the oxidation of ammonia to NO_x-N is retarded by the organic species.

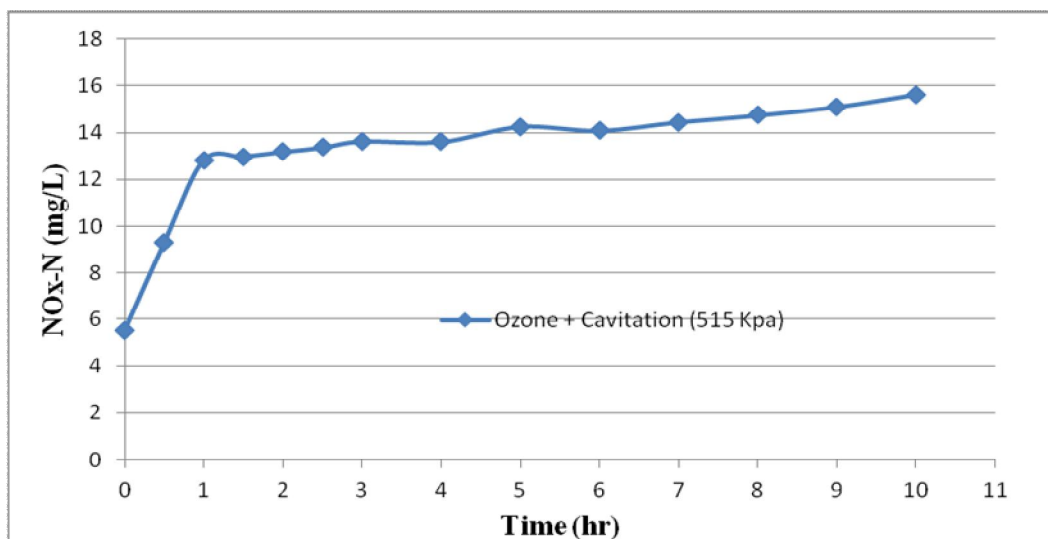


Figure 33: Nitrate+nitrite-nitrogen release with combined long term application of ozone and cavitation.

4.10 Biodegradable COD

It was observed that the soluble COD increased to approximately 1700 mg/L with the combined application of ozone and cavitation after 90 minutes. The portion of the soluble COD that was biodegradable was estimated by adding biomass to treated, as well as untreated, soluble samples (Sec 3.4.9). SCOD concentrations over time in the presence of biomass are shown in Figure 34 for both treated and untreated samples.

From the Figure 34 it can be observed that for untreated sample negligible changes occurred. But for the sample treated with ozone and cavitation, abrupt changes took place initially. The SCOD decreased from approximately 1700 mg/L to 425 mg/L in the first 3 days. After that, very little further change was observed. At the beginning, a large amount substrate was available for the small amount of biomass inoculum. So the biomass grew rapidly without decay. From this experiment it can be seen that almost 75% of the soluble COD was biodegradable and easily

consumed by the biomass. This indicates that the biodegradability of the sludge increases with the application of ozone and cavitation as the substrates comprising COD are biodegradable.

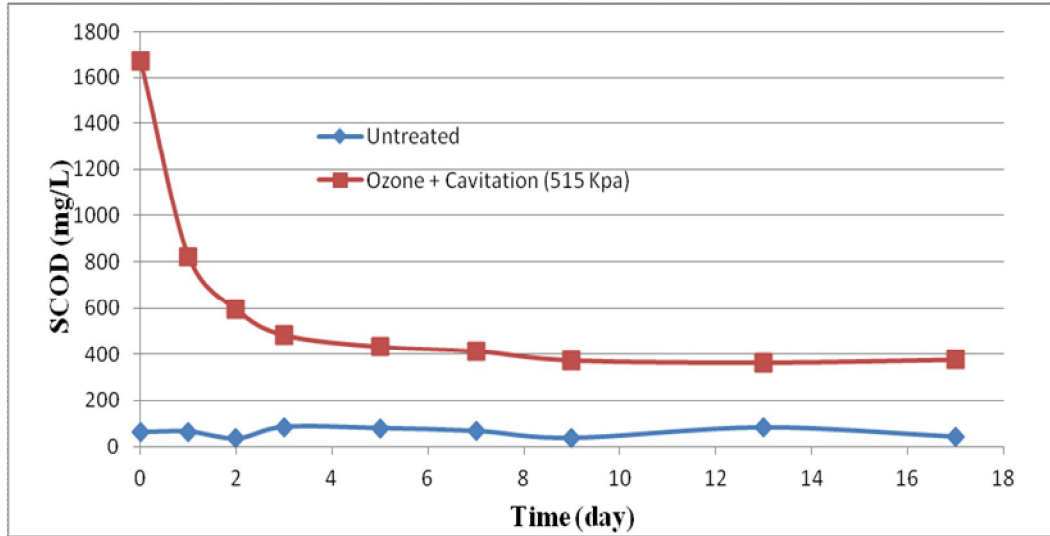


Figure 34: Changes of soluble COD over time.

4.11 Soluble BOD

The biodegradability of the sludge before and after treatment with ozone and also with combined ozone and cavitation for 90 minutes was measured. For the initial samples, 50 mL of filtered samples was used. 3 mL or 5 mL of filtered samples were used for the samples taken after 90 minutes. It was found that the soluble BOD ($SBOD_5$) of the untreated sludge was almost zero. From Figure 35 it can be observed that the $SBOD_5$ went up to 420 mg/L due to the combined application of ozone and cavitation which was significantly higher than the increase of $SBOD_5$ due to application of ozone alone which was 260 mg/L. As the change in SCOD was not significant due to the application of cavitation alone, it was assumed that the BOD of the filtrate due to the application of cavitation alone also would not be significant. Thus it can be concluded that the combined application of ozone and cavitation helps to release more organic material from inside the cell than does the individual application of ozone. In other words, combined application helps to convert refractory organic material present in the sludge to a more biodegradable form which will eventually help to minimize the sludge.

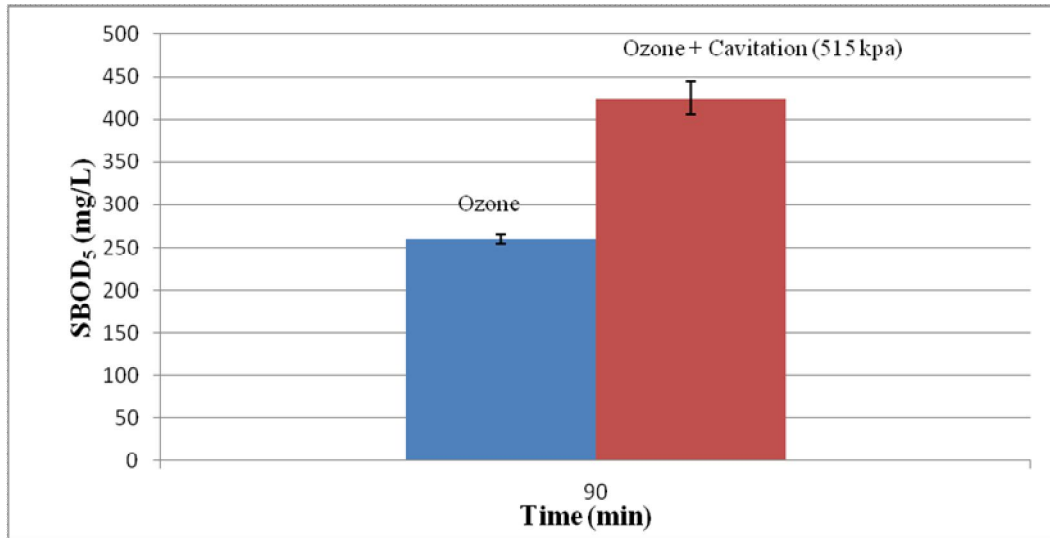


Figure 35: Soluble BOD₅ produced by different disintegration methods with 90 minutes of batch treatment (error bar presents the sampling error).

4.12 Temperature and pH

The changes in temperature and pH are illustrated in Figures 36 and 37 for different disintegration conditions. From Figure 36, a similar temperature (8⁰ C in 90 minutes) increase was observed for both the combined application of ozone and cavitation, and cavitation alone. This might be due to the collapse of cavities which causes the increase of temperature (Benito et al., 2005). On the other hand, no changes in temperature were observed with the application of ozone alone. This result also indicates that the pump itself did not have any impact on the temperature of the recirculated sludge.

Figure 37 indicates that the pH changed from 6.9 to 6.18 due to the combined application of ozone and cavitation during the 90 minute experiments. Similar changes were observed due to the application of ozone. This might be due to the formation of carboxylic acids from organic material and consumption of alkalinity by the oxidation of organic material (Bougrier et al., 2007). Cavitation alone did not result in any significant impact on pH.

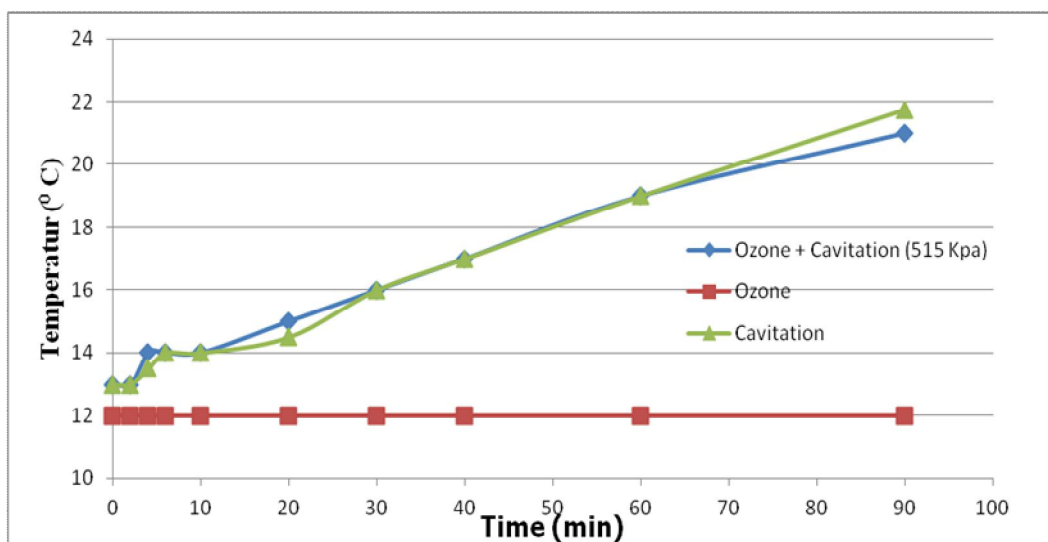


Figure 36: Changes in temperature for different disintegration conditions.

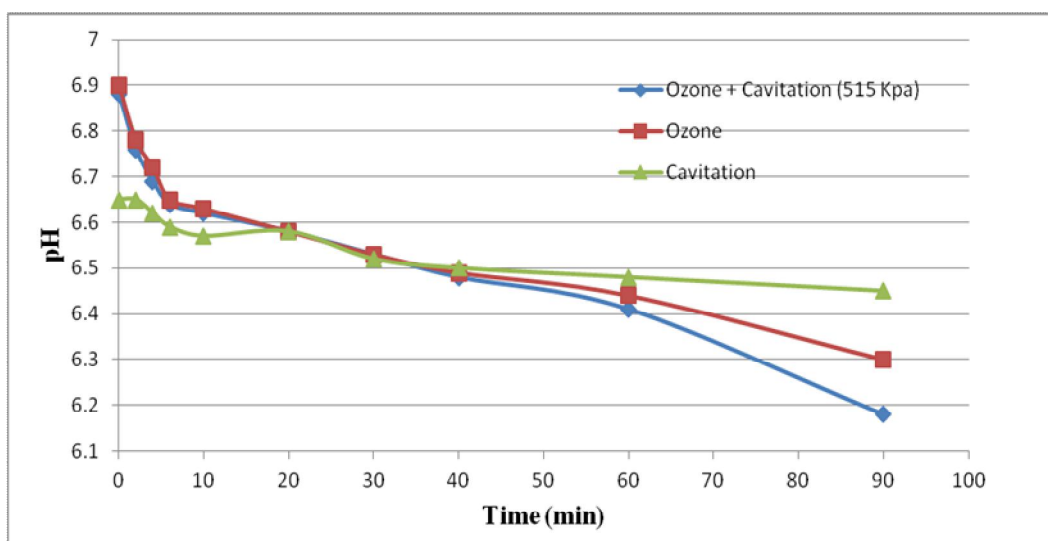


Figure 37: Changes in pH for different disintegration conditions.

4.13 Reproducibility-of the observations

The reproducibility of the experimental results was assessed in a qualitative manner by visually comparing the results from the short term and long term experiments involving the combined application of ozonation and cavitation. Figures 38 to 41 present the observed VSS reduction, % COD solubilization, mg TOC released/mg VSS and the % release of P to the solution for both the long term and short term experiments. The data in these figures were calculated according to

Equations 4.5-4.9. All the figures indicate that the results obtained for the first 1.5 hrs of the experiments, which were common for both the long term and short term experiments, are quite similar. This confirms that, at least for this phase of the experiments, the experimental results were reproducible.

$$\% \text{ VSS reduction} = (\text{Initial VSS} - \text{VSS at time } t) \times 100 / \text{Initial VSS} \dots \dots \dots (4.5)$$

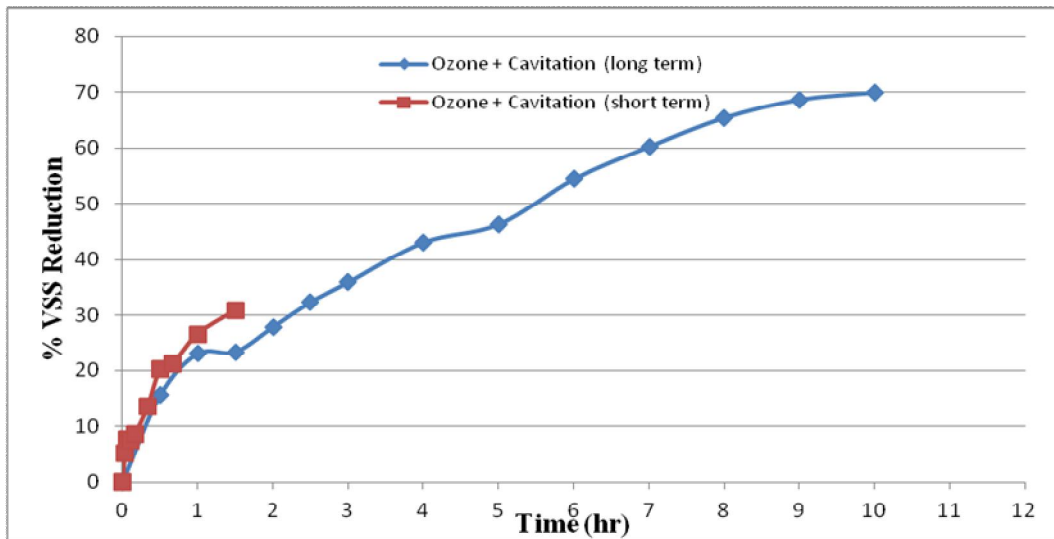


Figure 38: Reduction of VSS for combined application of ozone and cavitation

$$\% \text{ Solubilization} = \text{SCOD at time } t \times 100 / \text{Total COD} \dots \dots \dots (4.6)$$

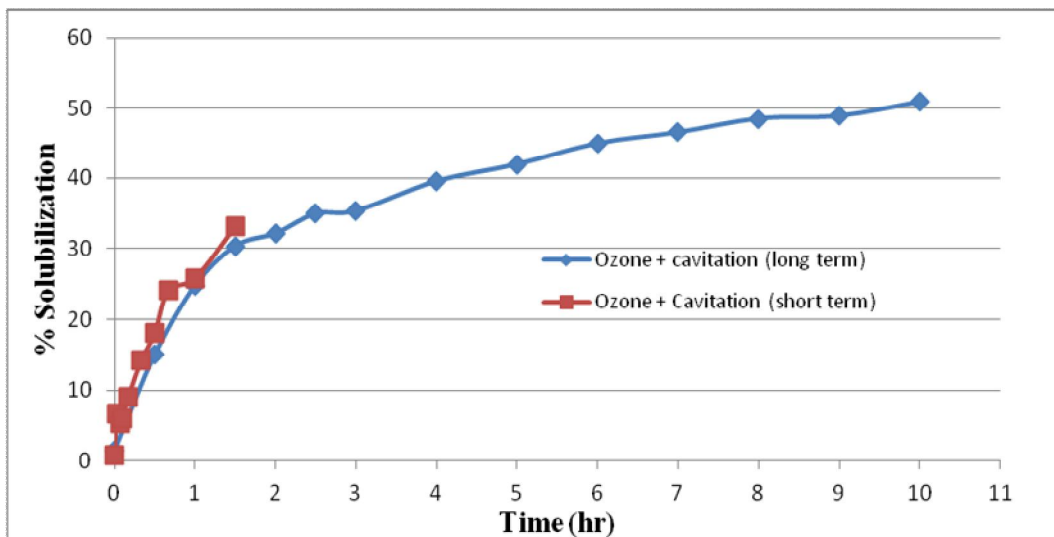


Figure 39: Changes in solubilization for combined application of ozone and cavitation

$$\text{mg TOC/mg VSS} = \text{Concentration of TOC at time } t \times 100 / \text{Initial VSS concentration} \dots \dots \dots (4.7)$$

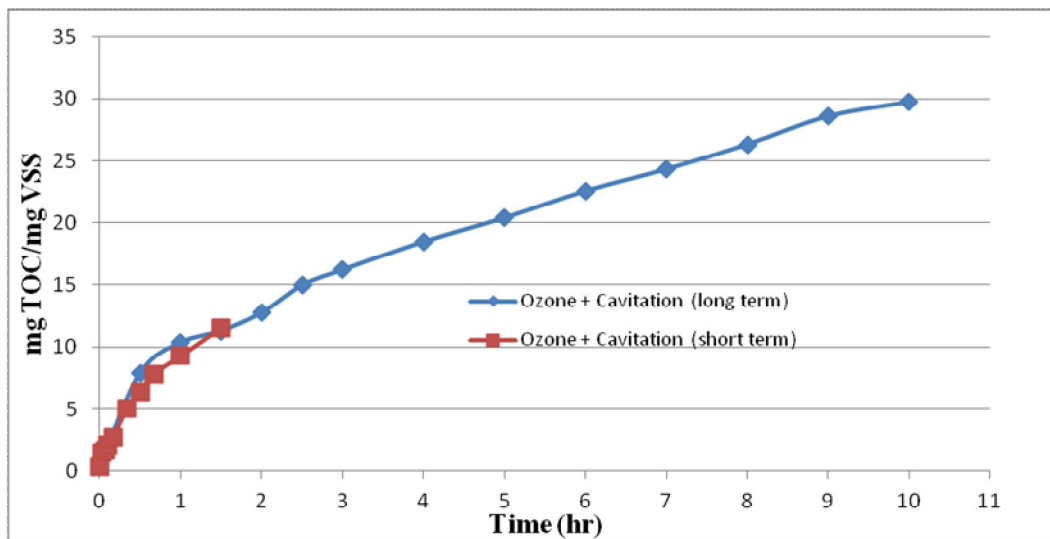


Figure 40: Release of mg TOC /mg of VSS for combined application of ozone and cavitation

$$\% \text{ of P release} = \text{Concentration of PO}_4\text{-P at time } t \times 100 / \text{Total P Concentration} \dots \dots \dots (4.8)$$

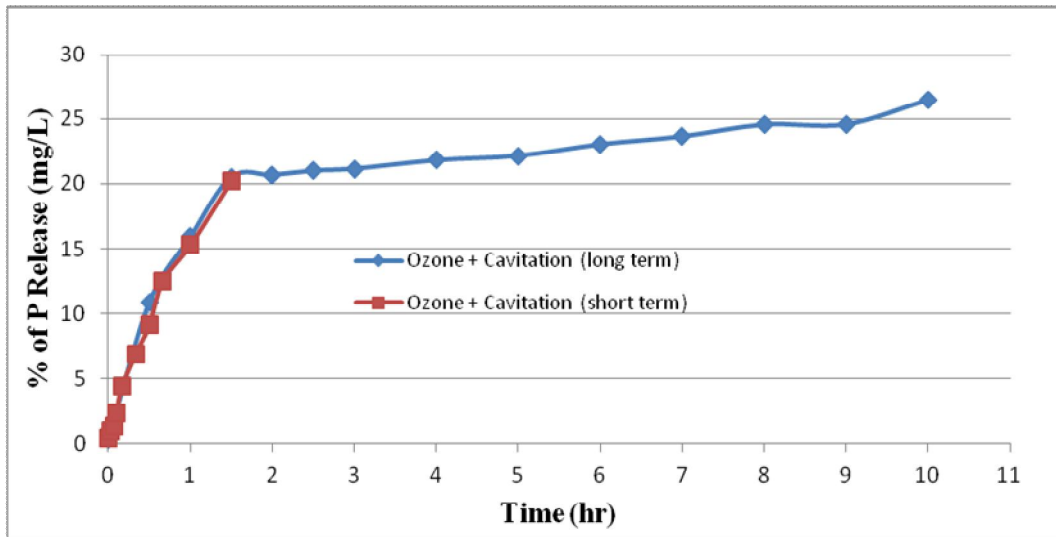


Figure 41: Release of P in the solution for combined application of ozone and cavitation

4.14 Discussion

All the experiments indicate that combined application of hydrodynamic cavitation and ozone resulted in better sludge disintegration than did the individual treatments. This may be due to the following reasons (Jyoti and Pandit, 2004).

- Cavitation causes the desegregation of flocs of microorganisms. Microorganisms present in the form of flocs may protect the inner microorganisms from contact with ozone. The cavitation breaks these flocs and exposes the inner microorganisms to ozone.
- Cavitation increases the penetration of ozone molecules to the microorganisms by accelerating mass transfer.
- Cavitation can also increase the permeability of the substances by breaking the chemical bonds between the molecular substances.
- The ozone decomposition and the activity of free radicals may be increased due to the cavitation process.

In activated sludge, bacterial cells form macroflocs with sizes ranging from 100 to 150 μm as presented in Figure 42. These macroflocs are composed of microflocs, of size ranging from 10-15 μm , which are mainly active cells entrapped in a matrix of exopolymer. Cavitation helps to break these flocs and to expose the inner particles to ozone, and this may increase the ozone activity against the sludge.

Cavitation has been shown to increase the aeration (K_{La}) efficiency which results in intensified interphase mass transfer. Similarly, with ozonation more effective utilization of ozone gas would be obtained (Dahl et al., 1976). Dahl et al. (1976) also mentioned that ozonation operates in three stages: an ozone demand phase, an inactivation phase and finally inactivation of composed microbial unit. Cavitation helps to eliminate the third phase.

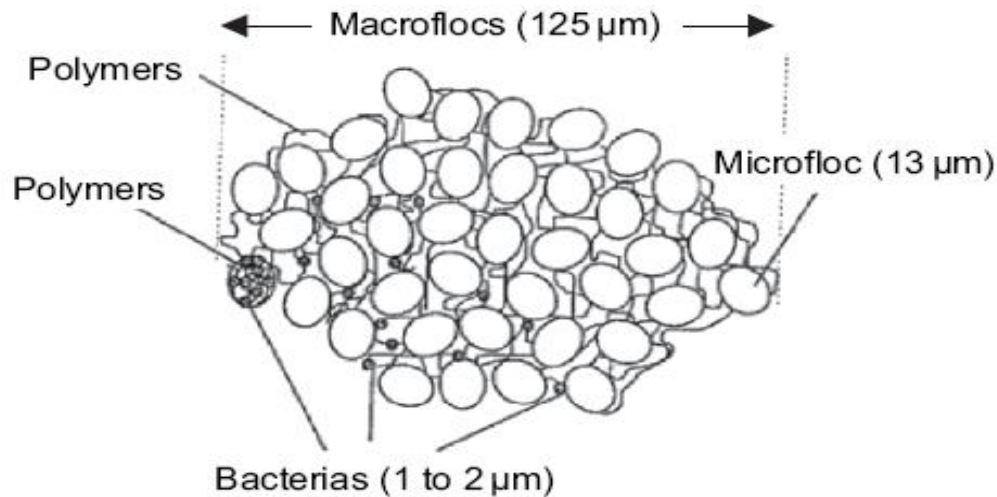


Figure 42: Schematic representation of activated sludge flocs (Jorand et al., 1995).

It can also be concluded from the results obtained in the experiments that cavitation itself is not sufficient to disintegrate the sludge within the present operating conditions. One of the reasons might be the relatively low inlet pressure applied. The pressure drop across the orifice plate increases with an increase of inlet pressure, and this increases the intensity of cluster collapse. Thus the cavitation effect increases due to the higher pressure generated with the collapse of the cavities (Kumar and Pandit, 1999). There is a minimum pressure requirement for cavitation inception which is known as the threshold value (Kumar and Pandit, 1999; Shirgaonkar and Pandit, 1998). Grubel and Machnicka (2010) used an inlet pressure of 1200 Kpa (12 bar) at a flow of approximately 8.50 Lpm to disintegrate sludge by using hydrodynamic cavitation conditions which were more intense than the conditions at 512 Kpa and 5 Lpm used in our experiment. So the increase in inlet pressure as well as flow could be effective here.

In our experiment we used a 2 mm single hole orifice. In model reactions using both rhodamine B and KI it has been observed that an orifice plate with a larger number of holes produces better results due to the high area of shear layer (Vichare et al., 2000; Sivakumar et al., 2001). So an multiple hole orifice, rather than single hole orifice might produce better results.

In the combined application of ozone and cavitation, slightly better sludge disintegration was obtained at higher inlet pressure. This is probably due to the fact that at lower pressure, the flow

was also lower. Thus, for the same time of treatment, sludge recirculation through the cavitation zone is more extensive for the higher inlet pressure according to the following equation:

$$\text{Number of passes} = \frac{\text{Flow rate through the pipe}}{\text{Volume of sludge}} \times \text{Total time of operation} \dots\dots\dots(4.3)$$

It was also observed that the disintegration of sludge increased with an increase of ozonation time which is directly related to the ozone dose. A similar finding was reported by Park et al. (2003) and Ahn et al. (2002). In the present study, the maximum dose applied in 90 minutes was 0.1 mg O₃/mg TSS. Ozone dose was calculated from the following equation:

$$\text{Ozone dose} = \frac{\text{Mass of ozone}}{\text{Mass of TSS}} = \frac{Q \times C_2 \times t}{V \times C_1} \dots\dots\dots(4.4)$$

Where,

Q = Flow rate of ozone injection (Lpm) C₁ = Concentration of TSS in sludge (mg/L)

V = Volume of sludge (L) C₂ = Concentration of ozone (mg/L)

t = Total time of ozone applied (minute)

Two main mechanisms were involved in the disintegration of sludge by ozonation i.e., disruption of cells present in the suspended solids and oxidation of soluble organic matter to CO₂. Cell disruption as well as oxidation of sludge increased with an increase of ozone dose (Park et al., 2003).

4.15 Application of disintegrated sludge

A typical set-up of the activated sludge biological nutrient removal process is presented in Figure 43. The process is composed of anaerobic, anoxic/denitrification, aerobic reactors to treat the wastewater by using biomass. Figure 43 illustrates the potential places for the application of

sludge disintegration with regards to the wastewater treatment and sludge management. Disintegrated sludge can be returned to both internal (D) and external (E) recirculation lines in the process together with sludge from the secondary settling tank to any of the anaerobic (A), anoxic (B) aerobic (C) reactors.

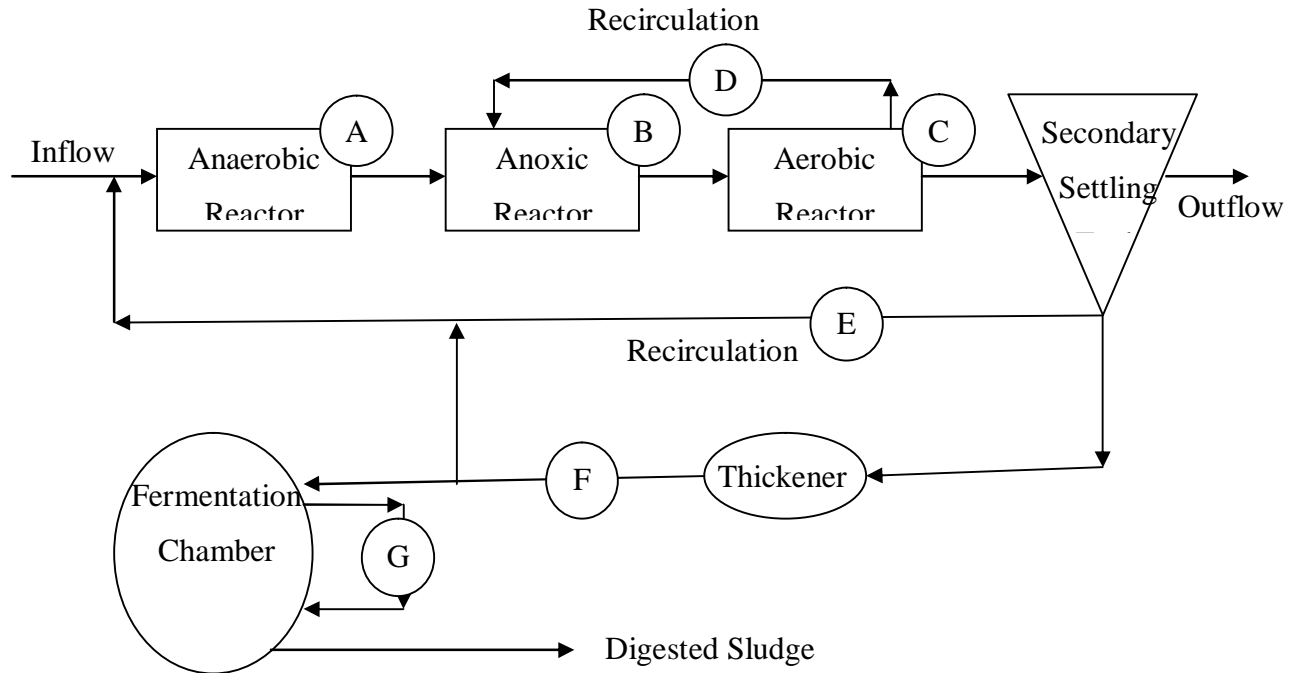


Figure 43: Potential places for adding sludge disintegration technology (Grubel and Machnicka, 2010).

In the anaerobic zone VFAs generated by fermentative bacteria, are taken up by phosphorus accumulating bacteria (PAO). The process efficiency depends on the speed of creation of VFAs in the anaerobic zone. In general, the consumption of VFAs by PAO is faster than the rate VFAs production in anaerobic zone. The return of disintegrated sludge to the anaerobic zone will increase the digestion activity of microorganisms and will also increase the VFAs concentration in the reactors. The present experiments indicated that the disintegration of sludge helps to release VFAs as well as organic substrate inside the cell. It also helps to increase the biodegradability of the sludge.

In the anoxic zone (B), disintegrated sludge can serve as a source of carbon which will assure nitrate removal through denitrification if there is a shortage of organic matter in the wastewater

flowing into the reactor. In the aerobic zone it will also help the phosphorus-accumulating bacteria to reproduce and easier collection of phosphorus and will guarantee their survival. Ahn et al. (2002) showed that the addition of disintegrated sludge to the anoxic reactor could provide an effective carbon source and it improved the nitrogen removal efficiency by 10% without reducing the effluent quality.

In the aerobic zone, non-settling, soluble and colloidal carbon compounds in wastewater are metabolized by heterotrophic microorganisms. The introduction of disintegrated sludge will provide additional organic substrate that may contribute to faster bacterial growth which will favor the development of feeding fauna. It has been reported that the addition of disintegrated sludge in the activated sludge chamber did not lead to the reappearance of filamentous bacteria (Grubel and Machnicka, 2010).

Disintegrated sludge can also be coupled to nutrient recovery, as struvite due to the release of phosphate and ammonia (Grubel and Machnicka, 2010, Nagara et al., 2008). The introduction of disintegrated sludge directly (G) or with thickened activated sludge (F) to a fermenter will improve the fermentation process. The direct addition of disintegrated sludge into the digestion chamber will help to increase the enzymatic activity of the fermentation process, which will increase the biogas production. The disintegration process helps to release the intra and extracellular enzymes by cell lysis and supplies the organic substrate to bacterial population in more digestible form (Grubel and Machnicka, 2010; Mechnica et al., 2008; Weemaes et al., 2000).

Chapter 5: Conclusions and Recommendations

5.1 Conclusions

The following conclusions were made based on the results obtained from the present study of the combined application of ozone-hydrodynamic cavitation for sludge disintegration.

- Combination of ozonation and cavitation has higher capacity for sludge disintegration than the individual technologies applied alone.
- Cavitation helps to improve the disintegration capacity of ozone.
- In combined application, slightly better disintegration was found at higher cavitation inlet pressure, although the production of VFA and the solubilisation of orthophosphate-P were almost the same at both pressures.
- Within the operating conditions applied, cavitation itself is not sufficient for the disintegration of sludge.
- A maximum of 50% of the sludge was solubilised after 10 hours treatment with the combined technologies. It was also found that 40 mg/L of PO₄-P were released to the solution after 10 hours due to the combined application of ozone and cavitation, which comprised 26% of the sludge total phosphorus. It was also observed that most of the phosphate was solubilised within the first 2 hours of treatment.
- Disintegration of sludge increased with an increase of the ozonation time.
- Disintegration helped to improve the biodegradability of the sludge.

5.2 Recommendations

- In our present study we have used an inlet pressure of 512 Kpa (75 psi) at a flow of 5 Lpm for cavitation which was low compared to the flow and pressure applied in other studies (Grubel and Machnicka, 2010). Research should be conducted at higher inlet pressure to find out the full potential of cavitation on sludge disintegration.
- In our present research we used a 2 mm single hole orifice to generate the cavities. Other researchers have shown that multiple hole orifices give better cavitation yield to

degrade KI and rhodamine B (Vichare et al., 2000; Sivakumar et al., 2001). Although cavitation can be induced with single or multiple hole orifices, there may be advantages in using a venturi for this purpose (Gogate and Kabadi, 2009). Further research might be useful to assess the effect of cavitation on sludge disintegration by using different sets of orifices or a venturi.

- In our present research we measured only the applied ozone concentration. No measurements were made of off-gas ozone concentration. To find out the actual ozone transfer efficiency it is necessary to find out the amount of ozone consumed by the sludge in a certain period of time. So in the next step of the research, off-gas ozone concentration should be considered to quantify the increase in the ozone transfer efficiency due to cavitation.
- In our present research we injected ozone after the cavitation. Changing the location of introduction of ozone will affect the downstream residence time which might also affect the disintegration capacity of the system. Further research is necessary to understand this design option.
- It was assumed in several previous studies that cavitation releases highly reactive free radicals, but none of the studies actually quantified the radical effects separately (Adewuyi, 2001; Pandit and Moholkar, 1996; Pestman et al., 1994; Shah et al., 1999; Suslick et al., 1990; Thompson and Doraiswamy, 1999). Further research is required to find out the radical effects of cavitation.
- Finally, combined application of ozone and hydrodynamic cavitation should be applied in a pilot scale wastewater treatment process and research is necessary to find out the behaviour of the process due to this application.

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Appendix A: COD calibration charts

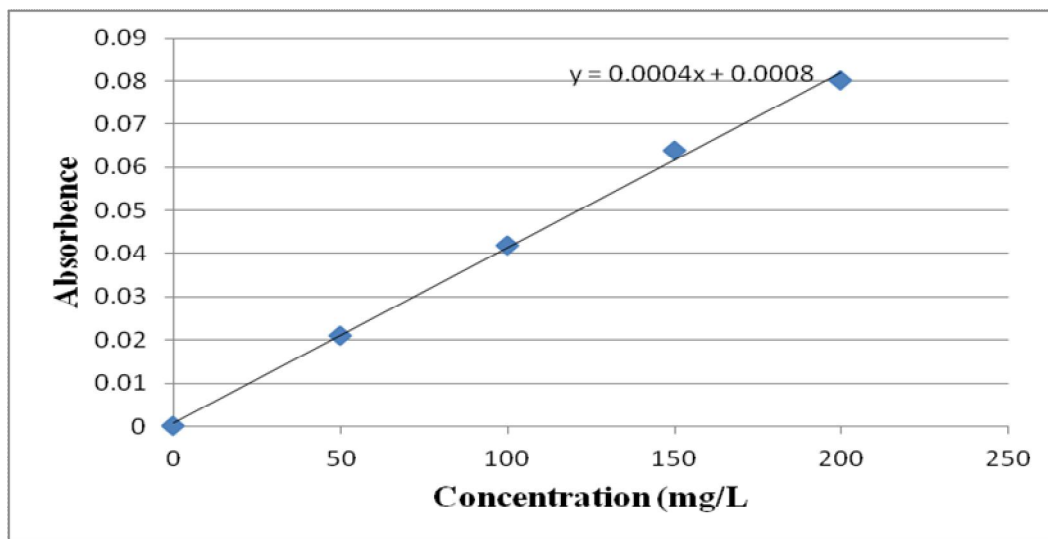


Figure 44: Calibration curve for low range COD determination (0-200 mg/L)

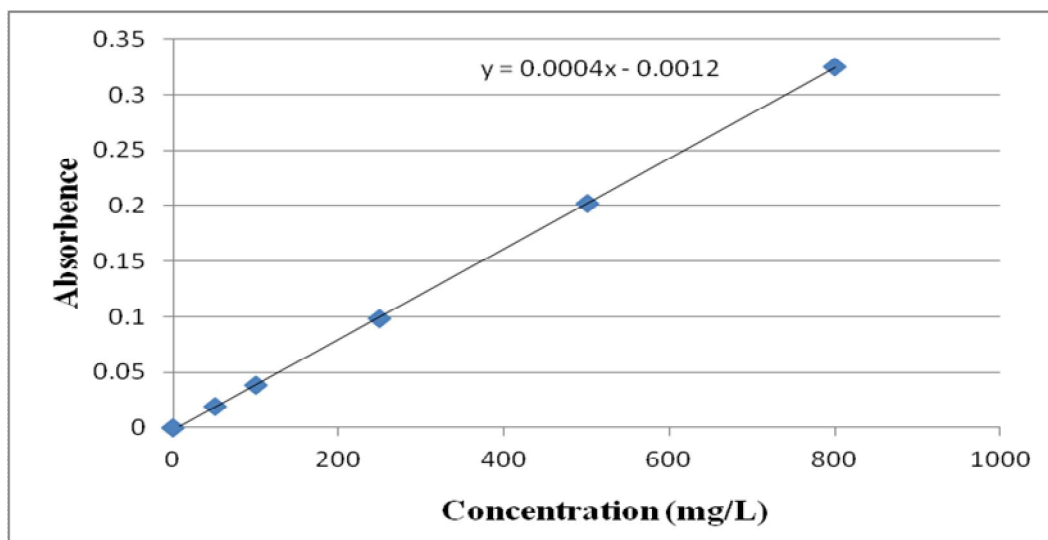


Figure 45: Calibration curve for high range COD determination (20-800 mg/L)

Appendix B: Average data of different parameters under different treating condition.

Table 8: Concentration of different parameters using combined application of ozone and cavitation at an inlet pressure of 515 Kpa

Time (min)	TSS (mg/L)	VSS (mg/L)	SCOD (mg/L)	VFA (mg/L)	NO _x -N (mg/L)	PO ₄ -P (mg/L)	NH ₄ ⁺ -N (mg/L)	TOC (mg/L)	BOD ₅ (mg/L)	Temperature (°C)	pH
0	4040	3280	43	0.40	6.82	0.60	0.13	11.50	0.00	13	6.88
2	3780	3110	333	1.26	7.02	1.43	0.27	48.87		13	6.76
4	3710	3030	263	1.79	7.22	2.06	0.31	54.80		14	6.69
6	3680	3040	301	2.41	7.58	3.60	0.24	68.76		14	6.64
10	3670	3000	448	2.70	7.67	6.72	0.39	90.86		14	6.62
20	3490	2840	713	5.25	8.55	10.42	0.49	165.05		15	6.58
30	3210	2620	906	8.68	8.05	13.90	0.71	210.07		16	6.53
40	3200	2590	1206	8.41	9.60	19.05	0.95	256.41		17	6.48
60	3010	2410	1296	15.53	9.94	23.23	1.78	304.62		19	6.41
90	2890	2270	1661	21.85	10.47	30.75	3.78	378.92	420.00	21	6.18

Table 9: Concentration of different parameters using combined application of ozone and cavitation at an inlet pressure of 275 Kpa

Time (min)	TSS (mg/L)	VSS (mg/L)	SCOD (mg/L)	VFA (mg/L)	NO _x -N (mg/L)	PO ₄ -P (mg/L)	NH ₄ ⁺ -N (mg/L)	TOC (mg/L)	Temperature (°C)	pH
0	3890	3170	40.00	0.9	6.8	0.25	0.22	14.81	16	7.13
2	3810	3140	70.00	1.2	6.5	0.8	0.3	17.00	16	7.13
4	3780	3150	90.00	1.5	6.9	2.2	0.35	26.00	16	7.02
6	3760	3130	110.00	2.2	7	3.5	0.54	40.00	16	6.98
10	3770	3120	155.50	4.1	7.25	6.33	0.5	49.23	16	6.9
20	3600	3040	288.00	5.3	8.14	12.47	0.62	81.30	17	6.74
30	3520	2960	456.00	6.7	11.005	16.77	0.69	119.46	17	6.67
40	3300	2706	630.00	7.2	11.6	19	0.89	160.00	17.5	6.68
60	3200	2670	1136.00	13.7	13.06	21.58	0.95	220.43	18	6.68
90	2980	2480	1422.00	25.6	12.99	24.98	1.09	300.72	18.5	6.51

Table 10: Concentration of different parameters using ozone at an injection flow of 3 Lpm

Time (min)	TSS (mg/L)	VSS (mg/L)	SCOD (mg/L)	VFA (mg/L)	NO _x -N (mg/L)	PO ₄ -P (mg/L)	NH ₄ ⁺ -N (mg/L)	TOC (mg/L)	BOD ₅ (mg/L)	Temperature (° C)	pH
0	4180	3380	43.00	0.7	3.86	0.51	0.30	13.00	0.00	12	6.9
2	4160	3340	83.00	1.0	3.82	0.66	0.38	29.35		12	6.78
4	3950	3240	103.00	1.0	3.05	1.31	0.43	30.91		12	6.72
6	3930	3200	108.00	1.1	3.62	0.39	0.46	34.20		12	6.65
10	3960	3130	153.00	1.6	3.81	0.42	0.48	41.82		12	6.63
20	4000	3190	213.00	2.0	6.52	2.37	0.51	64.07		12	6.58
30	3840	3070	310.50	3.6	7.67	5.82	0.51	98.47		12	6.53
40	3750	3020	403.00	5.8	9.00	6.12	0.69	116.48		12	6.49
60	3550	2890	633.00	11.1	11.01	11.93	0.71	184.37		12	6.44
90	3370	2730	923.00	14.0	11.48	21.34	0.85	255.48	260.00	12	6.3

Table 11: Concentration of different parameters using cavitation at an inlet pressure of 515 Kpa

Time (min)	TSS (mg/L)	VSS (mg/L)	COD (mg/L)	VFA (mg/L)	NO _x -N (mg/L)	PO ₄ -P (mg/L)	NH ₄ ⁺ -N (mg/L)	TOC (mg/L)	Temperature (° C)	pH
0	3610	3020	48.00	0.0	8.27	0.47	0	7.6	13	6.65
2	3350	2840	58.00	0.7	8.28	0.89	0	15.0	13	6.65
4	3340	2850	65.50	0.8	8.11	2.69	0.06	16.6	13.5	6.62
6	3430	2840	73.00	1.3	6.53	0.95	0.22	16.6	14	6.59
10	3450	2910	83.00	1.8	6.59	2.06	0.29	22.7	14	6.57
20	3380	2880	110.50	2.2	7.33	2.04	0.37	25.5	14.5	6.58
30	3420	2880	128.00	2.2	5.09	2.38	0.91	29.1	16	6.52
40	3430	2940	163.00	3.1	5.29	3.43	1.02	35.9	17	6.50
60	3430	2930	175.50	3.2	2.93	2.06	1.59	37.0	19	6.48
90	3390	2900	203.00	4.6	0.07	2.05	2.64	39.2	21.75	6.45

Table 12: Concentration of different parameters using combined long term application of ozone and cavitation at an inlet pressure of 515 Kpa

Time (min)	TSS (mg/L)	VSS (mg/L)	COD (mg/L)	VFA (mg/L)	NO _x -N (mg/L)	PO ₄ -P (mg/L)	NH ₄ ⁺ -N (mg/L)	TOC (mg/L)	Temperature (°C)	pH
0	3760	3090	71	0.2	5.50	0.50	0.47	14.78	18	6.55
0.5	3270	2610	751	13.8	9.30	16.52	1.98	244.17	22	6.1
1	2890	2380	1241	17.3	12.82	24.20	2.44	320.02	25	5.5
1.5	2870	2370	1522	21.0	12.98	31.22	3.17	348.77	28	5.19
2	2750	2230	1612	23.1	13.18	31.45	3.87	393.72	30.5	4.71
2.5	2560	2090	1752	26.6	13.36	31.95	4.58	462.12	31	4.46
3	2440	1980	1772	28.9	13.62	32.18	4.99	500.55	33	4.4
4	2210	1760	1982	32.3	13.60	33.18	6.29	570.27	32	4.26
5	2090	1660	2102	36.46	14.25	33.71	6.78	629.70	35.5	4.19
6	1790	1410	2252	43.51	14.08	35.04	7.94	696.73	37	4.09
7	1590	1230	2332	50.15	14.44	35.97	8.94	750.74	37	4
8	1450	1070	2432	55.93	14.73	37.36	9.97	812.88	38.5	3.92
9	1290	970	2452	58.88	15.10	37.39	11.07	882.60	38.5	3.92
10	1220	930	2552	67.5	15.63	40.26	11.73	918.67	39	3.9