Application of Hydrodynamic Cavitation in Environmental Engineering

Janusz Ozonek

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APPLICATION OF HYDRODYNAMIC CAVITATION IN ENVIRONMENTAL ENGINEERING

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About the author

Janusz Ozonek, a graduate of Silesian Technical University in Gliwice was specializing in the scope of chemical engineering in the fields close to the problems of environmental protection. After the studies he worked in the following research institutes: Inorganic Chemistry Research Institute in Gliwice and Organic Industry Institute in Warsaw. For the next 8 years he worked in the industry in the Company of Chemical Reagents in Lublin.

He has been connected with Lublin University of Technology since 1980. In this University he started an intensive research on the ozone synthesis process and improvement of the phenomenological description for this process in the plasma-chemical reactor. The research constituted the basis for the doctoral dissertation, defended at the Chemical Department of the Silesian Technical University in Gliwice. The development of the model of temperature distribution in the ozonizer depending on the hydrodynamic parameters and power supply was also an important achievement resulting from the conducted research.

Most of the works of Janusz Ozonek are interdisciplinary. The chemical ozone synthesis process itself, along with running the processes in the environment of low-temperature plasma require an approach from the side of physical elementary processes and is purposeful for the environmental engineering.

Janusz Ozonek is an author or co-author of 5 books, over 40 papers published in technical magazines and over 80 papers presented on the scientific and technical symposiums and conferences both national and international. The subject of the papers is focusing on environmental protection and is mainly connected with the issue of reducing the energy consumption in the process of ozone synthesis and its usage in eco-technologies.

He is a member of the International Ozone Association, a member of the Committee of Low-Temperature Plasma Chemistry of the Lublin department of the Polish Academy of Sciences, a member-correspondent of Lublin Science Society and a member of Polish Chemical Society.

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List of symbols

A	m^2	area
c_p	$\mathrm{J \cdot kg^{-1} \cdot K^{-1}}$	specific heat
d	m	diameter
f	Hz	frequency
g	$\mathrm{m \cdot s^{-2}}$	acceleration due to gravity
K	–	cavitation number
L	m	characteristic dimension
$\dot{m}$	$\mathrm{kg \cdot s^{-1}}$	mass flow
M	$\mathrm{kg \cdot mol^{-1}}$	molar mass
p	$\mathrm{N \cdot m^{2}}$	pressure
P	W	power
p_g	$\mathrm{N \cdot m^{-2}}$	static pressure of gas in the bubble
p_n	$\mathrm{N \cdot m^{-2}}$	vapour pressure of the liquid
R	m	radius of cavitation bubble
R_0	m	initial cavitation bubble radius
S	$\mathrm{J \cdot K^{-1}}$	entropy
t	°C	temperature
t	s	time
T	K	temperature
U	W	internal energy
$\dot{V}$	$\mathrm{m^3 \cdot s^{-1}}$	liquid flow rate
w	$\mathrm{m \cdot s^{-1}}$	fluid velocity
x	–	distance coordinate
z	–	polytrophic exponent

GREEK CHARACTERS

α	$\mathrm{m^{-1}}$	ratio of the perimeter of a hole to the hole area
β	–	dimensionless number, ratio of the sum of the hole area(s) of the orifice plate to the pipe area
μ	$\mathrm{kg \cdot m^{-1} \cdot s^{-1}}$	dynamic viscosity
ρ	$\mathrm{kg \cdot m^{-3}}$	liquid density
ω	$\mathrm{m \cdot s^{-1}}$	ultrasonic wave velocity
α	$\mathrm{m^{-1}}$	ratio of the perimeter of a hole to the hole area
ν	$\mathrm{m^2 \cdot s^{-1}}$	kinematic viscosity
η	$\mathrm{Pa \cdot s}$	dynamic viscosity

SUBSCRIPTS

o	– initial
w	– water
k	– final
l	– liquid
max	– maximum value
min	– minimum value
g	– gas
el	– electric
AOPs	Advanced Oxidation Processes
EDCs	Endocrine Disrupting Compounds
EPA	Environmental Protection Agency
GC-MS	Gas Chromatography Mass Spectrometry
HC	Hydrodynamic Cavitation
m/z	Mass/charge (electron) ratio
MS	Mass Spectrometry
PAH	Polycyclic Aromatic Hydrocarbons
US	Ultrasound

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Introduction

With the development of civilization and industry an increasing number of new and complex chemical compounds are being produced which, together with sewage, municipal and industrial wastes find their way into the natural environment. These substances do not remain inert to living organisms, including humans, and unfortunately in most cases leave permanent traces in nature.

Cavitation is a phenomenon, widespread in many areas of technology. This phenomenon accompanies liquid flow through channels with variable geometries. In the environmental protection technologies the effects of cavitation have become very useful in assisting chemical processes, especially in technologies related to the degradation of substances particularly harmful to humans and his immediate surroundings.

Traditional treatment methods do not always produce the expected results. There exists a certain group of organic non-biodegradable pollutants, having toxic, mutagenic, or carcinogenic properties. An important requirement is that the flow containing the hazardous compounds be treated in the cheapest possible but safe manner. Therefore, there is also the need to use modern treatment techniques, which undoubtedly include Advanced Oxidation Processes (AOP), based on reactions involving hydroxyl ($^{\bullet}OH$) radicals. These methods are currently being intensively investigated with the aim of applying them to the removal of certain compounds from wastewater. The removal of these compounds using conventional oxidation methods increases the cost of the process, due to increased oxidant consumption. However, using advanced oxidation processes, it is possible to obtain a greater degree of pollutant degradation.

Research results from the past few years, into the application of advanced oxidation processes in environmental engineering technologies, show that cavitation is a promising technique in this field, due to the accompanying sonochemical processes.

It should be noted that the processes involving hydrodynamic cavitation may complement other methods such as ozonation, oxidation using hydrogen peroxide (H_2O_2), or techniques based on UV radiation or ultrasound, which in total leads to a greater effectiveness in pollution reduction, whilst at the same time reducing costs and energy consumption.

In the subject literature there are many studies related to acoustic cavitation and the use of associated processes in water and effluent treatment technologies. Despite knowing about hydrodynamic cavitation for many years, its use to eliminate pollutants in contaminated water and effluent, particularly industrial, has not been fully researched.

Until recently, attention has been focused mainly on the negative effects of cavitation and its influence on the durability of equipment (e.g. cavitational erosion). However, as research carried out in recent years has shown, physical and chemical processes accompanying cavitation can be used in new technologies to treat water, sewage and to decompose low biodegradable compounds.

Contemporary research into cavitation is concentrated mainly into three areas. The first concerns the development of a model describing the phenomenon, which reflects the imploding bubble dynamics, both in terms of a single bubble as well as the entire population. Existing classical models initiated by Rayleigh in 1917 require a number of simplifications and omit many factors which significantly impact the physicochemical processes that occur during cavitation. The second research area focuses on the negative impact of hydrodynamic cavitation in liquids and depends on reducing its negative effects on a vessel's propulsion system, or on pump rotors. The third area of research is the search for the utilisation of cavitation's positive effects, in as wide an area as possible. Examples include the speeding up of the sonochemical reactions inside the cavitation bubbles, sonoluminescence, coagulation and dispersion, and many others. It is this group of problems which is being analysed in this book.

The use of hydrodynamic cavitation allows, among other things, to increase the amount of effluent saturation (solutions) with oxidising gases such as ozone or oxygen, and it also allows to intensify the oxidation processes occurring on the phase boundary surfaces by significantly increasing the surface area. During the processes which accompany the disappearance of cavitation (implosion), there is an intensive exchange of substances in the cavitation regions (bubbles, caverns) which support the chemical processes, including oxidation.

The problem of utilising hydrodynamic cavitation in technical solutions, to increase the decomposition effectiveness of low biodegradable chemical compounds, is not only valid, but constitutes an increasing call for man to work on the protection of his natural environment. It is also the author's area of academic interest, and this book presents a theoretical analysis, along with experimental work in this field, developed on the basis of literature, research reports and personal experience.

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CHAPTER 1

Characteristics of the cavitation phenomenon

1.1 THE ESSENCE OF CAVITATION

The name cavitation as used in physics and technology originates from the Latin word *cavitas* (a hollow space or cavity). The first correct analysis of this phenomenon was presented by Reynolds in 1894. Cavitation describes a particular phenomenon which occurs inside a liquid when subjected to changes in the pressure field over time and distance. These changes depend on the liquid rarefying to a sufficiently low critical pressure, causing the formation of voids, filled with vapour from the liquid, as well as dissolved gases in the liquid. Then upon violent compression these voids, filled with vapour and gas, implode.

Cavitation is not observed in gases, which is due to the lack of surface tension, as well as other characteristics of the gaseous state. Liquids, however, even under an isothermal fall in pressure to saturated vapour pressure, turn into the gaseous state, in which the phenomenon is discrete within the liquid and the vapour is released in the form of spherical bubbles throughout the volume of the liquid.

Thus, bubbles (also termed cavitation cavities) form in the cavitation liquid, filled with the liquid's vapour as well as any dissolved gases in the liquid. In the region of higher pressure, above a critical value, the bubbles implode violently which causes in the imploding microregion of the collapse, a dramatic increase in pressure. Hence, cavitation affects the condition of the material over its surface since regions are formed, not only filled with the liquid but also with vapour and gases dissolved in the liquid. If the pressure of the liquid is less than the saturated vapour pressure, the bubbles increase in volume, which causes larger regions of cavitation liquid formation.

There are many different causes of cavitation (Figure 1.1). However, they most commonly appear in the following processes when applied to liquids, namely:

1. In hydrodynamic processes—cavitation occurs in a flowing liquid during a fall in the static pressure, caused by flow conditions or external influences. It is commonly produced in constricted or curved channels and also as a result of motion of bodies in a liquid such as a ship's propeller. Thus, this type of cavitation appears as a result of a local constriction to the flow path of the liquid or the detachment of the stream from the surface of streamlined bodies.
2. In processes involving ultrasound, cavitation in such cases is induced by the pulsations within the liquid due the dispersion of acoustic waves created by impact, vibrations of the surfaces enclosing the liquid or the vibration of submerged objects within the liquid. The separation of the liquid molecules and the formation of the cavitation bubbles occur during the rarefaction

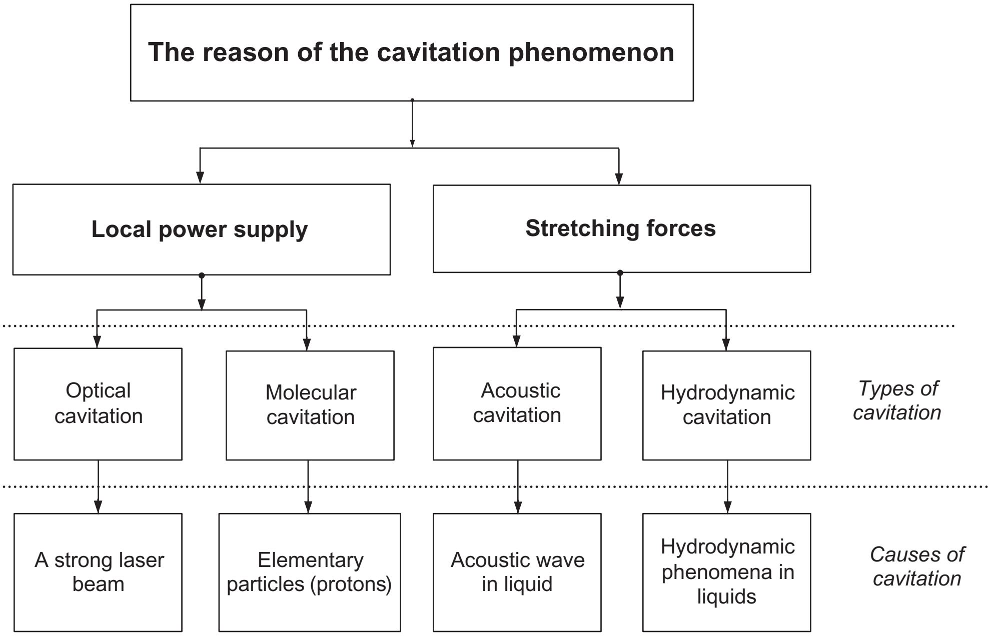

Figure 1.1. The main causes of cavitation in liquids.

half-cycle, and their disappearance during the compression half-cycle of the cavitation medium.

3. In processes which supply significant energy to small volumes within the liquid e.g. by a laser beam or a stream of heavy elementary particles such as protons. Both methods cause a local increase in the internal energy of the liquid, up to a point, at which the liquid undergoes a phase change into the gaseous state thereby releasing the dissolved gases. The effect is to create bubbles of vapour and gases similar to the ones produced in hydrodynamic cavitation.

In the case of hydrodynamic and acoustic cavitation, cavitation bubbles appear inside the liquid as a result of the local pulling apart of the medium under the influence of great expansive forces, which are produced as a result of a sudden drop in local pressure, which can occur in hydrodynamic processes, as well as in high intensity ultrasonic fields (20 kHz to 1 MHz).

Optical and molecular cavitation is a consequence of local dissipation of energy, whose source can be for example a strong laser beam causing electrostriction of the environment and the creation of local pressures (Śliwiński, 2001, Elpiner, 1968). This method of cavitation generation enables precisely controlling the cavitation parameters such as the size of the bubbles and their location within the liquid. Due to the high operating costs, both optical cavitation, as well as molecular cavitation have not found wide scale practical applications, and are only the subject of laboratory research (Margulis, 2004, Piotrowska, 1968, Hoffman, 1996).

In this book the author has concentrated mainly on the phenomenon of hydrodynamic cavitation produced in a liquid flowing through geometric volumes favourable to the appearance of this phenomenon. Hence, the rest of this book relates mainly to this subject.

1.2 TYPES OF CAVITATION—FORMS OF CAVITATION CLOUDS

We can identify the various types of cavitation depending on where the cavitation cloud occurs and the initial conditions. With reference to scientific literature in Poland and worldwide, it is possible to identify several characteristic forms of cavitation. The difficulty in developing a single method of classification is caused by a diversity of conditions when performing the analysis. Franc and Michel (2004) identify eight characteristic types namely:

1. Travelling Bubble Cavitation appears as bubbles moving along a solid body which become visible in the vicinity of a low pressure point.
2. Cavitation bubbles in the shear layer develop when a submerged liquid jet is introduced into a container containing water and on a sharp edge of a boundary layer separation.
3. Sheet cavitation also described as attached bubble cavitation. For axisymmetric bodies the term 'ring cavitation' is used. The bubbles are formed on the surface of the solid body and subsequently are then detached by the flow.
4. Sheet cavitation is also known as laminar cavitation in its advanced stage. This type of cavitation appears as a cavity filled with a homogenous mixture of vapour and gas with a glossy surface.
5. Localised attached cavitation, also described as localised sheet cavitation is associated with the local roughness of the surface and appears as attached cavities.
6. Localised bubble cavitation occurs as a continuous stream of bubbles forming in specific places on the surface of a solid body. This form is also associated with the pitted nature of the surface.
7. Hub vortex cavitation occurs in the cores of vortices spiralling away from the flow around the obstacle.
8. Tip vortex cavitation, appears in the core of vortices flowing from the load bearing surface.

In turn Arzumanov differentiates only two basic forms of cavitation depending on the shape of the cavitation cloud (Bagieński, 1998):

1. Surface cavitation – develops on the surface of streamlined bodies and remains attached to their surfaces
2. Detached cavitation – carried along with the liquid flow.

Surface cavitation occurs on well streamlined surface elements forming points of resistance. It is created e.g. from cavitation nuclei present on boundary surfaces restricting flow and develops on the element's surface. It can be found in pipelines, Venturi restrictions etc. This cavitation which can take on many different forms is dependent on the geometry of the conduit and the flow parameters. It can be in the form of bubbles, sheet (laminar) or attached sheet cavitation.

Detached vortex cavitation appears along the axis of the steam, in vortices behind the "weak" streamlined elements forming places of resistance. It also develops from nucleation (cavitation nuclei) found in crevices, on boundary surfaces restricting flow, and also in the wake itself. It also appears in the wake flowing with significant speed from orifices or zone linking streams from various directions. Detached vortex cavitation, in places of resistance, appears in the form of a vortex. In places of different types of resistance both forms of cavitation may appear.

According to the Polish Standard (PN-86/H-04426) the following forms of cavitation are differentiated:

1. Vaporous Cavitation – cavitation dependent on the sudden evaporation of the liquid from the bubbles' surface following a fall in pressure to that below the critical value, frequently close to the liquid's vapour pressure at a given temperature. It is characterised by the fact that the bubbles are vapour-filled and grow very quickly.
2. Gaseous cavitation – cavitation induced in a supersaturated liquid with the diffusion of dissolved gases. It is dependent on the diffusion of the gas into the gas- and vapour-filled bubbles already present in the liquid. It is characterised by the fact that the bubbles grow and collapse more slowly than during vaporous cavitation and are filled primarily with gases, diffusing from the liquid.
3. Flow cavitation (hydrodynamic) – cavitation formed in the flowing liquid during a fall in the static pressure caused by flow conditions or external factors. It is frequently found in constricted flow channels, in places of kinematic path curvature and deviations from the plane of the streamlined body.
4. Vibratory cavitation (acoustic) – cavitation induced by pressure pulsations within the liquid, caused most frequently by the dispersion of acoustic waves created by impact, vibrations of the surfaces enclosing the liquid or the vibration of bodies submerged within the liquid. The separation of the liquid molecules

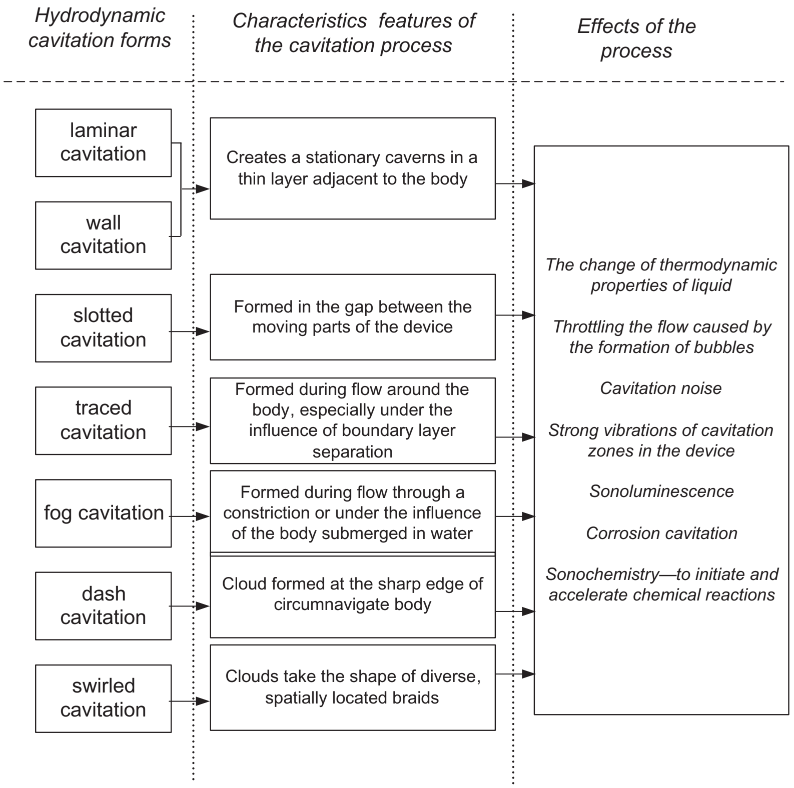

Figure 1.2. Classification of the main forms of cavitation according to their characteristics or behaviour of the cavitation medium and their interactions on the container walls.

and the formation of the cavitation bubbles occur during the rarefaction half-cycle whilst their collapse occurs during the compression half-cycle.

Due to characteristic features of the cavitation zone such as location and physical conditions, it possible to classify the types of cavitation depicted in Figure 1.2.

1.3 FACTORS FAVOURING THE FORMATION OF CAVITATION

Cavitation is caused by a number of factors which encompass not only the physical properties of the liquid, described by the appropriate physical properties (Brennen, 1995, Wójs, 2004, Cai et al., 2009), the thermal state of the liquid, but also the gaseous impurities dissolved in the liquid or other liquid impurities (Gogate, 2008, Margulis, 1995) and also impurities in the form of submerged bodies.

The cavitation nuclei, appearing in the form of gaseous, vapour microbubbles or particulates are essential to the formation of cavitation, the result of a reduction in the capability of the liquid to transfer tensile stress.

In pure liquids, deprived of any impurities, the liquid-gas phase transition as a result of liquid expansion is almost impossible, since large tensile stresses (negative pressures) in the order of hundreds of megapascals are necessary (Wójs, 2004). However, in reality, in nature and technology we have liquids containing large numbers of cavitation nuclei.

Possible potential cavitation nuclei can be found in large numbers in the liquid in the form of primary additives and pollutants. The division of additives and pollutants in natural waters is shown in Figure 1.3.

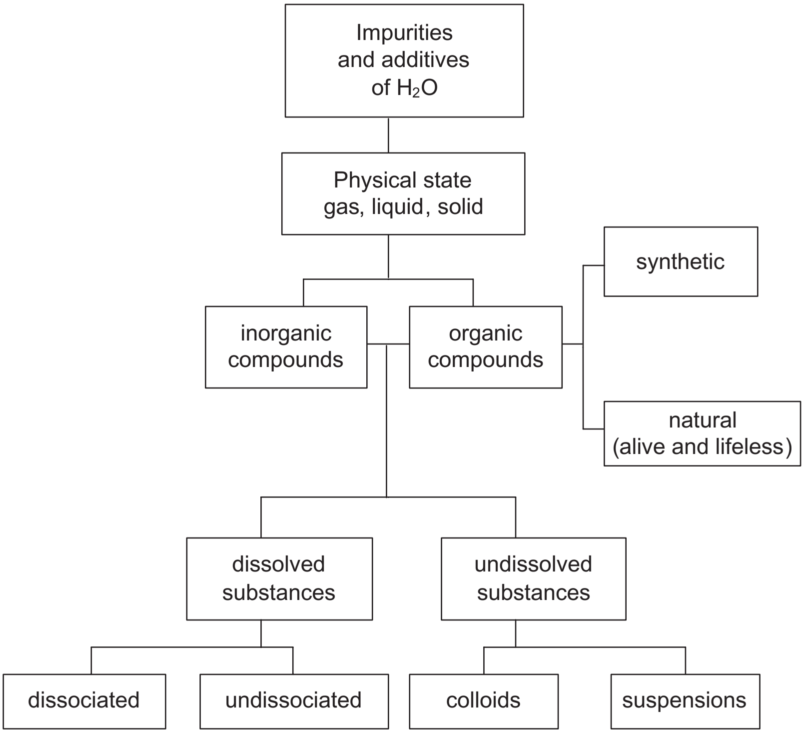

Figure 1.3. Division of pollutants and additives in natural waters.

Additional impurities may appear in the waters used in practice depending on the technological processes. Water, previously purified by distillation may also be used.

1.4 PHYSICOCHEMICAL EFFECTS OF THE CAVITATION PROCESS

Over the past couple of years intense research has been carried out into the possibility of utilising the cavitation phenomenon in many fields related to environmental protection. Cavitation drives many important physicochemical effects which can be utilised to degrade and/or oxidise pollutants found in water and sewage. Cavitation bubbles produced by pressure pulsations fulfil the function of "microreactors" which within a very short period of time reach extreme temperatures and pressures and produce hydroxyl radicals, one of the most powerful oxidants and excellent initiators of chain reactions.

The effects of cavitation can be broadly split into mechanical effects and physicochemical, related to the changes taking place within the cavitation bubble from the moment of its creation to its implosion (Figure 1.4).

The best known indication of cavitation is cavitation noise produced over a frequency range from 100 Hz to 100 kHz, the result of bubble implosions. Cavitation favours energy dissipation leading to a temperature rise in the vicinity of the collapsing bubbles and cavities. The implosions also produce a series of other physicochemical and mechanical effects (Figure 1.5). The formation of the cavitation bubbles and their implosions is characterised by very high energy densities in the order of 10^{18} kW/m^3. The formation and disappearance of cavities can occur over millions of locations in the reactor producing local conditions of high temperatures and pressures in close proximity to where physicochemical processes are taking place.

During the implosion of the cavitation bubbles a primary shockwave is produced with a pressure amplitude of around 240 MPa and a molecular speed of up to 1700 m/s. Local to the collapsing bubble, secondary waves are also produced with speeds of around 1800 m/s and pressures of up to 70 GPa (Wójs, 2004).

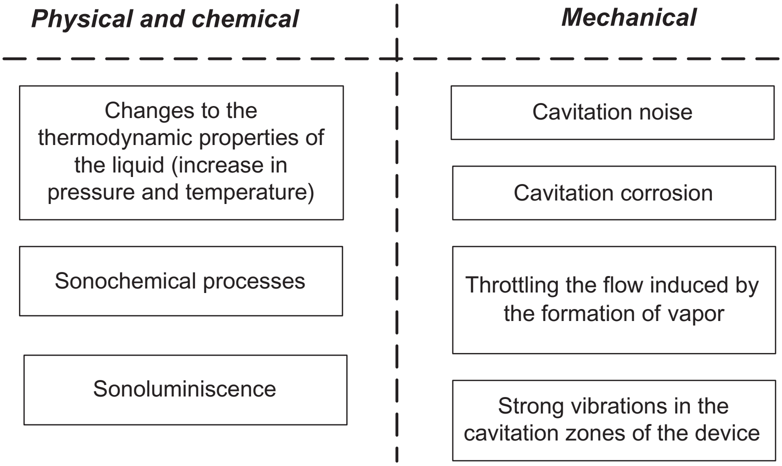

Figure 1.4. Useful cavitation effects in environmental engineering technologies.

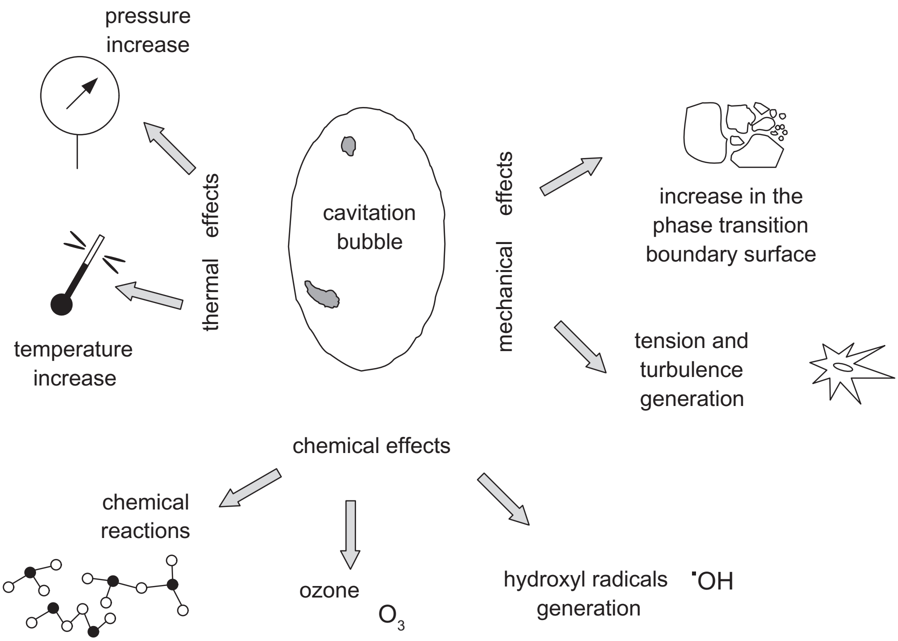

Figure 1.5. Physicochemical effects produced during the cavitation process.

These intensive shockwaves lead to a dramatic increase in temperature (greater than 1000 K) at the centre of the bubble and a significant increase in the phase transition boundary surface, which leads to changes in the chemical composition, speeds up the chemical reactions and mass transfer.

1.5 SUMMARY

From the beginning, when interest in cavitation began, this phenomenon was treated as destructive and undesirable. All research and analysis into the causes of, and the process itself were undertaken with the aim of preventing cavitation or limiting its destructive effects on hydrodynamic installations, devices and hydrodynamic equipment. Currently, the above mentioned issues have not lost any of their “negative” importance, the scope being cavitation arising spontaneously under the influence of phenomena and factors set out in section 1.1.

In the light of current research into cavitation, it has been ascertained that there might be positive properties, desirable in other technological fields, such as the possibility of significantly reducing flow resistance of submerged bodies in liquids, and consequently the possibility of a decisive increase in their speed. Another example is the possibility of utilising cavitation in certain chemical technologies as well as in processes related to the protection of the natural environment. In these cases, it is about cavitation being specifically caused by one of the methods set out in Figure 1.1. Thus, we need to examine the phenomenon of hydrodynamic cavitation and its consequences in relation to technological fields as either negative or positive.

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CHAPTER 2

The physical basics of hydrodynamic cavitation

2.1 TYPES OF CAVITATION LIQUIDS. BASIC CLASSIFICATION

Hydrodynamic cavitation occurs and spreads in a jet of water flowing through a channel whose geometry causes the appropriate static pressure variations in the flow (Brennen, 1995, Bagieński, 1998, Gogate et al., 2000). During the process of such cavitation three characteristic, consecutive stages can be distinguished:

- The Cavitation Inception Stage—the formation of cavitation bubbles on a macro-scale with dimensions in microns. Under practical conditions, the basis for bubble formation is the existence of cavitation nuclei in water—gas-filled or vapour-filled micro-bubbles or alternatively solid micro-particles
- Bubble Growth—the growth of bubbles or other enclosed volumes called cavities, the expansion of these volumes is the consequence of the loss of equilibrium between the internal and external forces at the phase transition boundary layer between the liquid and gaseous phases
- The Dissolution Stage—the collapse of cavitation regions, being of an implosive nature, due to a rapid increase in external forces acting on them

From a physical point of view, three characteristic types (forms) of cavitation can be distinguished in water:

1. Vaporous cavitation
2. Gas-vapour cavitation
3. Gaseous cavitation

Vaporous cavitation relates to a homogenous material, which during cavitation undergoes a series of phase transition changes from liquid to vapour and from vapour to liquid. For this type, the cavitation zones are filled with wet saturated vapour—remaining in contact with the liquid from which they originated.

The very fast growth in bubble volume is caused by the rapid increase in the internal partial vapour pressure of the bubble, which effectively blocks the diffusion of gases dissolved in water into the bubble.

Gas-vapour cavitation occurs when the bubbles are filled as a result of evaporation from the liquid and the diffusion of gases through the phase transition boundary layer.

Water undergoes phase transition changes: liquid—wet saturated vapour—liquid. However gases released from an aqueous solution diffuse into expanding cavitation regions due to differences in the partial pressures outside the cavitation bubbles. The dynamic rate for this process in this form differs from the rate for the vapour form, which extends the gas diffusion time and produces comparable amounts of vapour and gas within the bubbles.

Gaseous cavitation within the water environment occurs and develops under conditions favourable for the concentrated release of gas from solution and its diffusion into the cavitation regions. It is characterised by bubbles growing and collapsing more slowly than during vapour cavitation and which are primarily filled with gases released from the given liquid.

2.2 PHASE TRANSITION CHARACTERISTICS OF WATER

Water, as a triatomic chemical compound, consists of molecules having covalent bonds which form a triangular structure (Figure 2.1).

In nature, water can be most commonly found as $^{1}H_2{}^{16}O$ and is a molecular dipole which leads to many anomalies e.g. its greatest density occurs at 3.98°C; an increase in pressure leads to the lowering of its freezing point; during freezing the volume of ice increases by about 10%. This has a significant influence on the behaviour of water in its various energy states, and also on its physical properties, in particular thermal.

Water's physical properties which influence cavitation and are useful in the analysis of this phenomenon belong to the majority of molecules. These are: liquid and vapour density, coefficients of dynamic and kinematic viscosity of the liquid and vapour, specific heat capacity of the liquid and vapour, latent heat of vaporisation, diffusion coefficient and heat conduction of the liquid and vapour; all are dependent on the temperature.

As is well known, water can exist—depending on the temperature and pressure conditions—in three states namely: solid, liquid and gaseous. The states are treated as single systems (collections of the substance) in physical and chemical terms, which are met for distilled water.

For the analysis of the cavitation phenomenon, including hydrodynamic, the liquid and gaseous (vapour) states are significant as well as the transition between them.

In the gaseous state the vapour can exist in three characteristic states:

- Wet saturated vapour, remaining in contact (equilibrium) with the liquid from which it originates; the volume of such a state is bounded by the saturated liquid (sometimes superheated) and the state of dry saturated vapour (sometimes supercooled), such states are essential for cavitation.
- Dry saturated vapour, after all the liquid has evaporated from which it originates
- Superheated vapour

The physical properties of water are defined by density, viscosity, surface tension, heat of vaporisation etc. The relationship between water density and temperature is shown in Figure 2.2 whilst that for water viscosity and temperature is shown in Figure 2.3. The viscosity of water clearly drops with a rise in

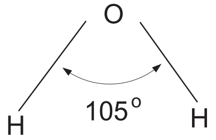

Figure 2.1. The structure of a water molecule.

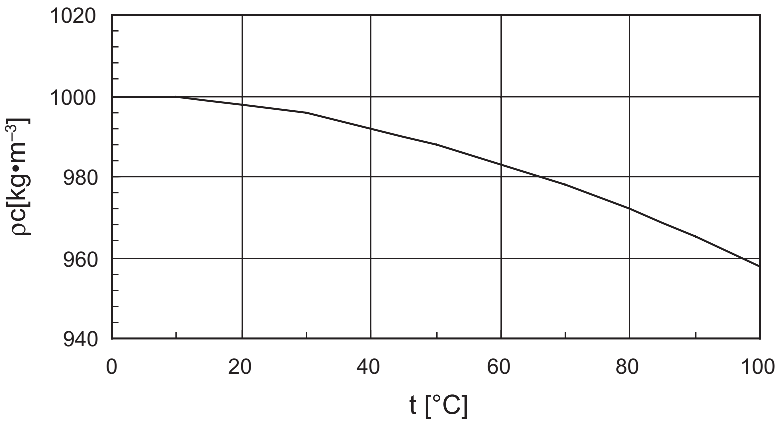

Figure 2.2. The effect of temperature on density for water.

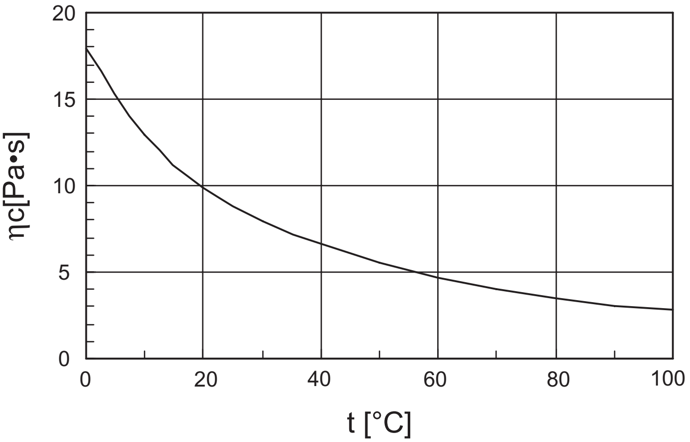

Figure 2.3. The effect of temperature on viscosity for water.

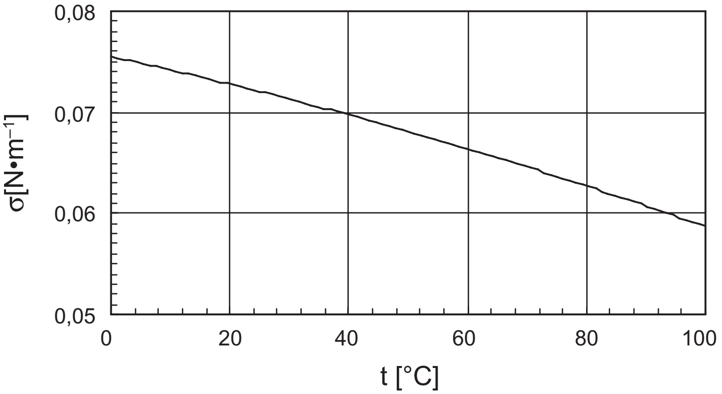

Figure 2.4. The effect of temperature on the surface tension for water.

temperature especially when close to the ambient temperature, on average a few per cent per degree kelvin. Similarly, with a rise in temperature the surface tension drops (Figure 2.4). The relationship between the saturated vapour pressure and temperature is shown in Figure 2.5.

Cavitation, as mentioned previously, depends on the formation, in the flowing liquid, of spherical bubbles or cavities filled with wet vapour and dissolved gases (Bagieński, 1998, Wójs, 2004). This creates a particularly complex case for the flow in the medium with the simultaneous existence of two states: liquid and gaseous.

The formation of the bubbles in the liquid can occur in two ways; either by raising the temperature to above the equilibrium condition for the phase transition under isobaric conditions (boiling) or through the lowering of the pressure to below the same equilibrium condition under isothermal conditions. We then have to deal with cavitation.

Figures 2.6 and 2.7 are charts which show the states in *p-v* and *T-s* coordinates for one kilogram of water with the area in which cavitation can appear shown.

An assumption made during the analysis of this work is that in the region of thermodynamic equilibrium any transitional changes, including state, are treated as being in equilibrium, even though successive states may be different with appropriate parameters. Phase equilibrium is one of the equilibrium cases. Transitional changes occurring during cavitation in water are phase changes of the first type with visible changes to the structure of the substance and volume, which has significant thermodynamic consequences.

The number of independent intensive variables from all the parameters which characterise water in successive stages of cavitation can be written applying Gibb's Phase rule:

$$\varphi - s - f + 2 \tag{2.1}$$

where:

φ – the number of independent intensive variables in the system (number of degrees of freedom), whose values can be arbitrarily defined with-

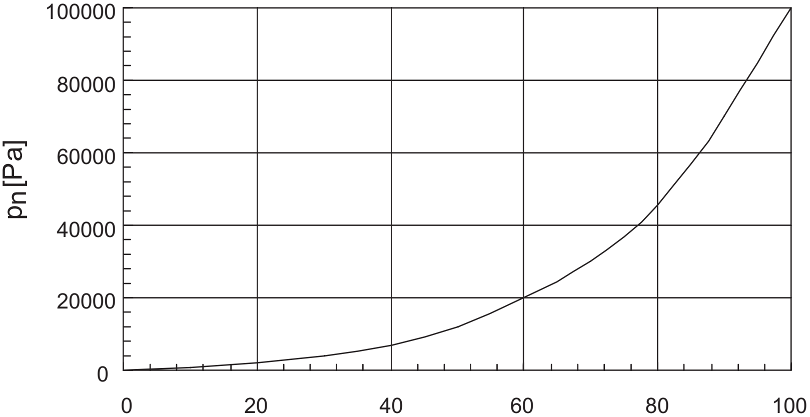

Figure 2.5. The effect of temperature on the saturated vapour pressure for water.

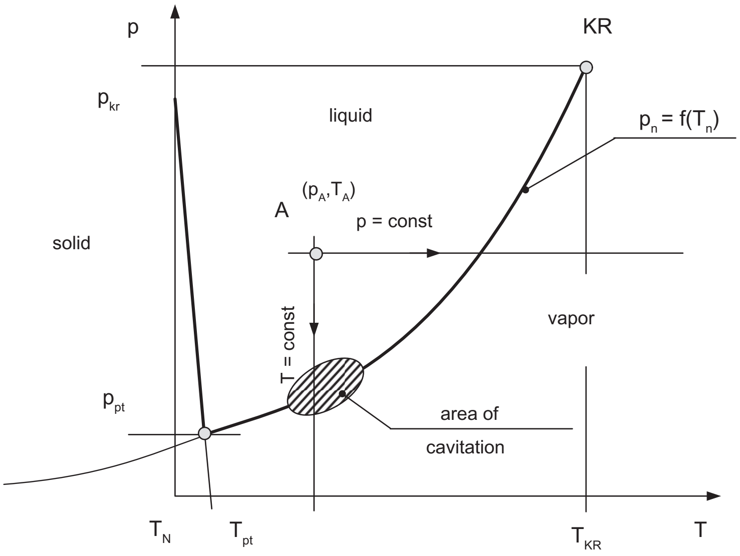

Figure 2.6. The phase diagram for water. The triple point parameters—p_{pt}, T_{pt}, critical parameters p_{kr}, T_{kr} · $T_N = 273.15$ K.

out influencing the number of components and phases constituting the system configuration.

s – the number of chemical components
f – the number of phases in the system

2.3 THE SOLUBILITY OF SELECTED GASES IN WATER

The causes of the appearance in water of dissolved gases or gas bubbles are fairly natural, since water is almost always in contact with air. Gases that easily dissolve in water, which is in contact with atmospheric air, are CO_2, O_2, and H_2S whilst it is more difficult for N_2. The solubility of gases in water is significantly dependent on their partial pressure above the still mirrored water. It rises as these pressures rise and falls as the water temperature rises. Bearing in mind practical applications, Figures 2.8 and 2.9 show the relationship between solubility and temperature for carbon dioxide, oxygen and nitrogen in water.

The dissolved gas exists in the liquid in the form of individual molecules, however groups of molecules can, under certain conditions, form gas bubbles. This process is made easier, the greater the degree of saturation of the gas in the liquid, and moreover, can also be helped through rarefaction in the liquid, forced through pressure pulsations, turbulence or phenomena causing fluctuations on the molecular level.

Liquids have the capability of dissolving gases up to saturation, which is dependent on temperature and pressure. Upon exceeding saturation they are released from the liquid in the form of gaseous bubbles. In the saturated solution, and in certain unsaturated conditions, some of the gas appears as undissolved in the form of microscopic bubbles of dimensions in the range 0.1–10 μm, which

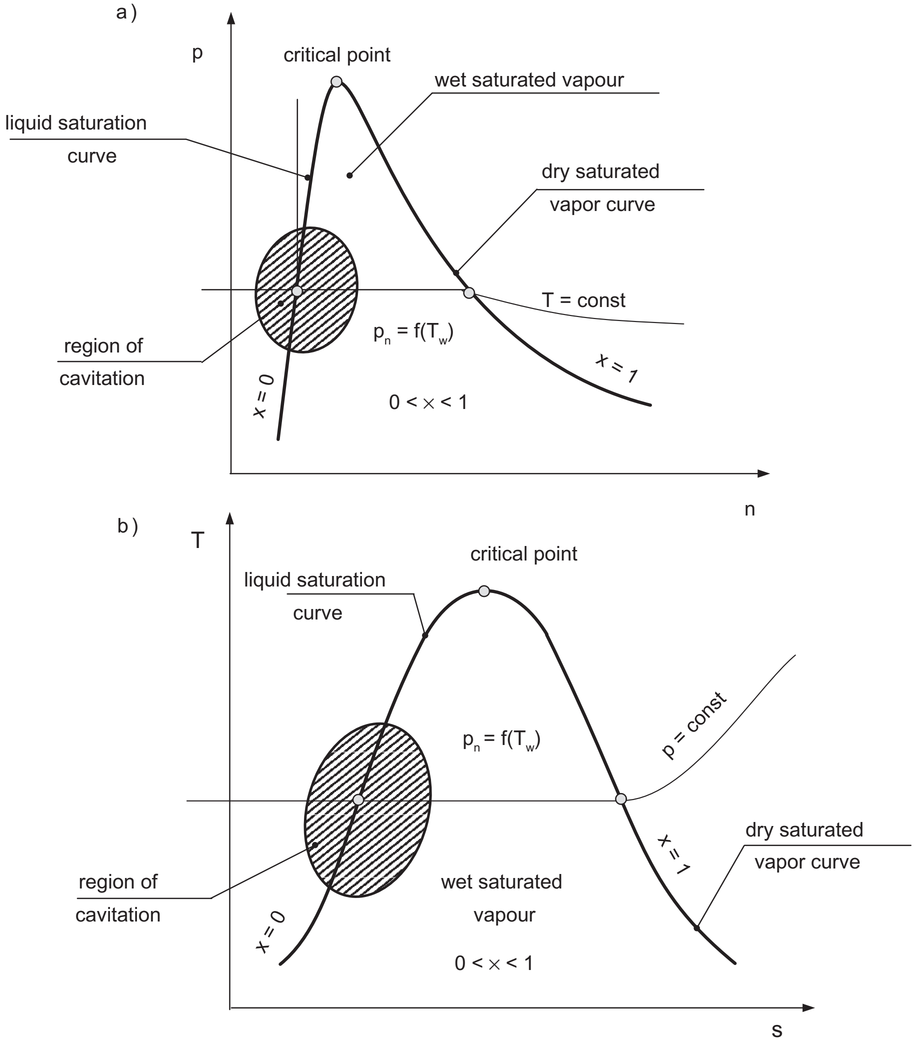

Figure 2.7. Charts for water a) in *p*-*v* coordinates, b) in *T*-*s* coordinates.

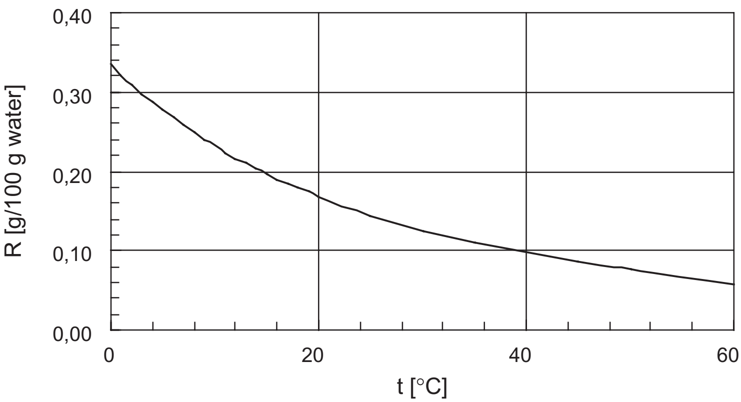

Figure 2.8. The effect of temperature on the solubility of carbon dioxide in water.

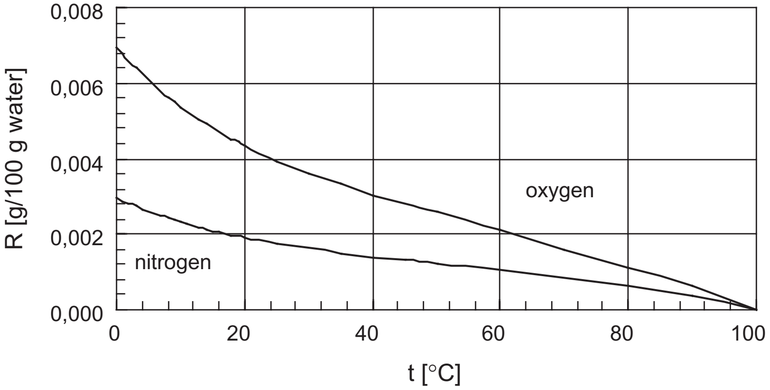

Figure 2.9. The effect of temperature on the solubility of oxygen and nitrogen in water.

can become cavitation nuclei. The amount of gas dissolved in the liquid obeys the Henry-Dalton law which states that the solubility of each part of a mixture of gases is directly proportional to the partial pressure of that given gas above the solution. The solubility of gases in water increases with the rise in pressure. However, it decreases with a rise in temperature.

2.4 THE THERMODYNAMIC MODEL OF HYDRODYNAMIC CAVITATION

Due to the diversity of factors which influence the emergence, the process and intensity of the cavitation process it is necessary to take into account the main factors which influence this process.

The thermodynamic model takes into account the phenomena, which accompany the individual stages of cavitation i.e. the inception, growth and collapse of gaseous, vapour-gas and vapour bubbles. During the cavitation process the surface tension plays a significant role in a particular state of the liquid namely the bubble's surface.

2.4.1 *The thermodynamic model for the liquid-vapour transformation at the phase transition interface*

Substances in a liquid state remaining in direct contact with gas molecules or vapour exhibit the capability to form on the phase transition interface (from the liquid's point of view) characteristic surface layers of a few molecules thickness which are closely associated with the liquid molecules (Figure 2.10).

The surface layer, of negligible thickness in comparison to the remaining liquid dimensions has the following characteristics, namely:

1. The internal energy of the liquid molecules in the surface layer is greater than the internal energy of the molecules deep within the liquid (Franc et al., 2004). This energy difference is the result of work done in transporting the molecules

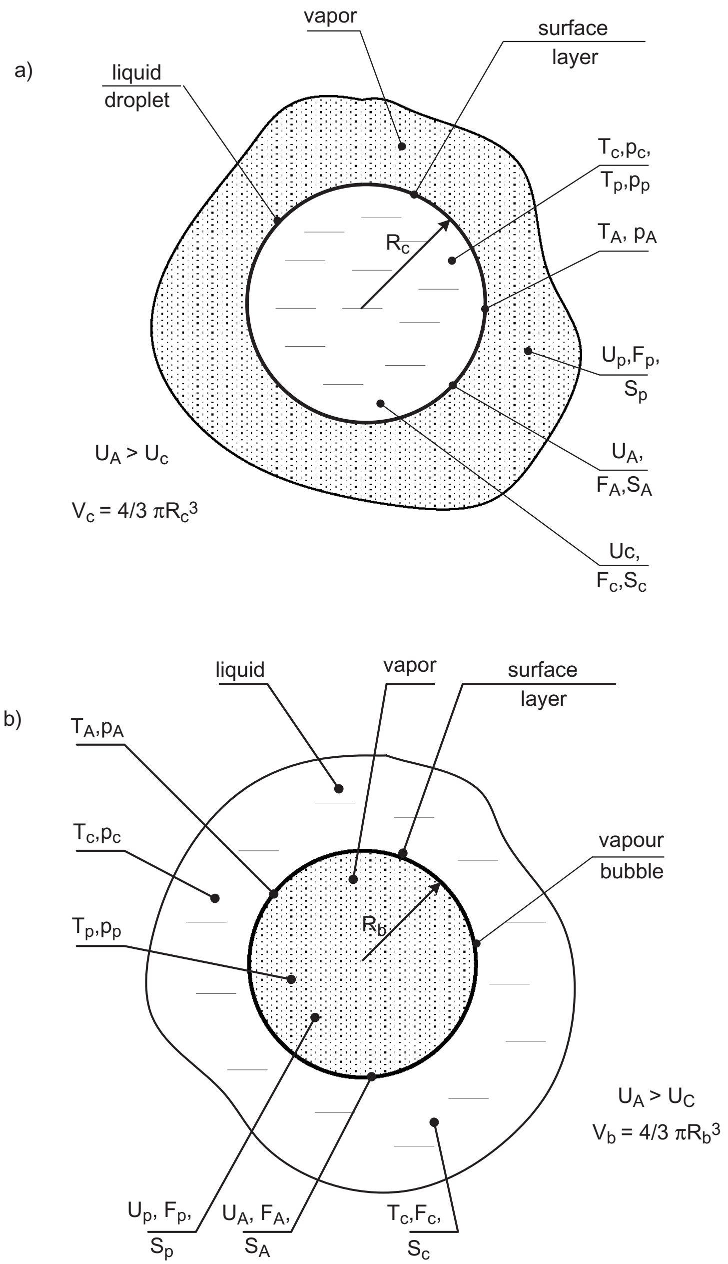

Figure 2.10. The change in thermal properties at the liquid to gas phase transition, a) on the surface of the droplet, b) on the surface of the bubble.

from within the liquid to the surface layer (work done against random forces acting on the molecules in the surface layer directed into the liquid).

2. The surface layer experiences an internal pressure from the whole volume of the liquid. In the case of water at a temperature of 373 K and at one atmosphere pressure acting upon it from the outside, the calculated internal pressure is in the order of $5.8 \cdot 10^8$ Pa (Brennen, 1995).

The surface tension depends on the type of liquid and temperature; a rise in temperature causes a fall in the surface tension which means easier evaporation.

Surface tension is given by the formula:

$$\sigma = \frac{dE_A}{dA}\,[\mathrm{J/m^2}] \tag{2.2}$$

where:

dE_A – the free surface energy
dA – the unit area of the surface layer

Extensive thermodynamic parameters (summarised in Table 2.1) can be assigned to the surface layer which is of negligible thickness i.e. on the surface.

From the first and second laws of thermodynamics we obtain the relationship for the surface entropy:

$$dS_A = \frac{dU_A - \sigma U_A}{T} = \frac{dU_A + dL_A}{T} \tag{2.3}$$

where:

σU_A – the work required to form a surface layer from the liquid molecules called the surface.

Taking into account Maxwell's equation we get (Franc et al., 2004):

$$s_A = \left(\frac{\partial S}{\partial A}\right)_T = -\frac{d\sigma}{dT} \tag{2.4}$$

After taking into account that for a surface $s_A > 0$, this always gives $\frac{d\sigma}{dT} < 0$
From the first law of thermodynamics

$$dU_A = TdS_A + \sigma dA \tag{2.5}$$

After appropriate manipulation the resultant equation describes the unit internal surface energy:

$$u_A = \left(\frac{\partial U_A}{\partial T}\right)_T = \sigma - T\frac{d\sigma}{dT} \tag{2.6}$$

Table 2.1. Thermodynamic functions relating to the surface of the liquid gas phase transition.

Item	Thermodynamic function	Formula	Equation
1.	Internal surface energy	$V_A = u \cdot A$	(2.3)
2.	Surface energy	$S_A = s_A \cdot A$	(2.4)
3.	Free energy	$F_A = U_A – T \cdot S_A$	(2.5)
4.	Thermodynamic potential. Free enthalpy	$G_A = U_A – G \cdot A – T \cdot S_A$	(2.6)

From the definition of surface heat and the second law of thermodynamics we obtain the relationship for the specific heat capacity of the surface:

$$c_A = -T \frac{d^2\sigma}{dT^2} \tag{2.7}$$

where:

c_A – Specific heat capacity per unit area [kJ · m^{-2} · K^{-1}]

From equations 2.5, 2.8 and 2.10 we obtain the relationship which describes the free surface energy:

$$F_A = \sigma_A \tag{2.8}$$

And for the unit free energy:

$$f_A = \sigma \tag{2.9}$$

2.4.2 *The cavitation bubble dynamics model*

Detailed knowledge on the topic of cavitation bubble dynamics has a key meaning for research into the processes present during cavitation. The cavitation process is very complicated and many attempts have been made to theoretically explain the mechanism of its creation. The basic problem is the issue of the non-linear forced oscillation response of the bubbles, which they are subjected to during the cavitation process (Brennen, 1995, Franc et al., 2004, Bagieński, 1998).

Cavitation forms and develops in a flowing liquid through zones, in which the pressure of the liquid falls below a critical value, normally close to the saturated vapour pressure at a given temperature for the liquid. The value for this pressure is dependent not only on the type of liquid, but also on the amount of pollutants such as micro-particles or macro-particles, and micro-bubbles containing incompletely dissolved gases. Figure 2.11 illustrates the hypothetical growth and collapse of cavitation bubbles.

Cavitation is a dynamic process, dependent on continuous changes over time to the volume and geometry of the bubbles and cavities. The timescale for this is in the order of milliseconds. After moving through the cavitating liquid into regions exceeding the critical pressure, the bubbles and cavities undergo sudden implosions in time periods significantly smaller than milliseconds, thus creating a local rise in pressure in different zones of the region. Locally, the pressures in the liquid can reach values of hundreds, and even thousands of megapascals. Characteristic effects which accompany the cavitation bubble implosions are hydrodynamic, mechanical, acoustic, chemical, thermal and even electrostatic.

Firstly, we need to consider and take into account the factors which cause hydrodynamic cavitation bearing in mind parameter changes, such as the input pressure and the positioning of the cavitation driver relative to the orifice opening. It is important to assign boundary values to the main parameters which

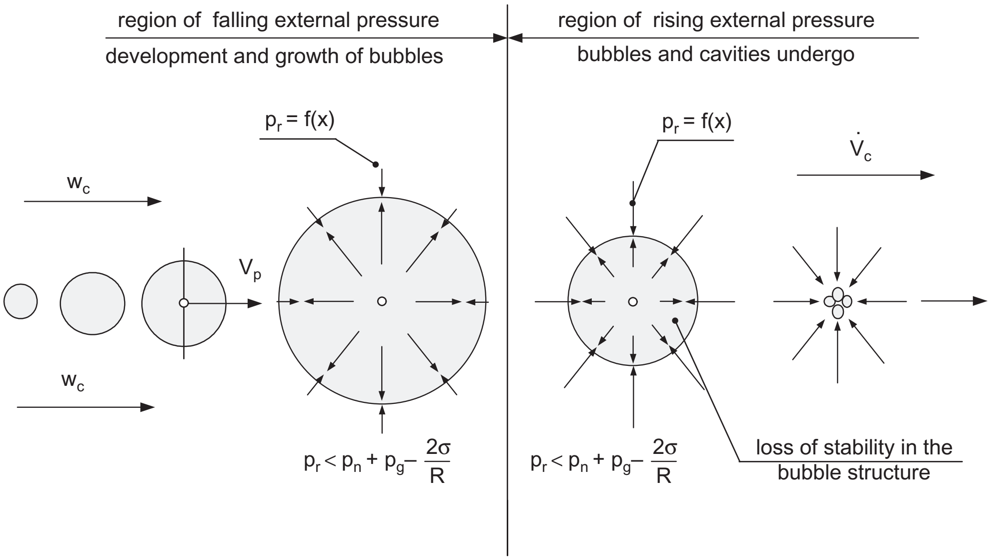

Figure 2.11. Diagram showing the development and collapse of cavitation bubbles in a liquid flowing through regions of variable pressure.

determine cavity inception, such as cavitation bubble size, their concentration in the flowing liquid and the static pressure on the outside of the bubble at the moment of its implosion. Familiarity with the range of values for these parameters enables the inception of hydrodynamic cavitation in a controlled manner, under conditions most favourable from the technological point of view for the degradation of chemical bonds (Brennen, 1995, Wójs, 2004, Moholkar et al., 2001, Gogate, 2000).

In theoretical considerations we frequently make use of the bubble dynamics model described by the Rayleigh-Plesset equation (Brennen, 1995, Franc et al., 2004). It is accepted that the bubbles' surface moves through a viscous Newtonian liquid whilst inside the bubbles the changes are polytropic of exponent z where $1 \leq z \leq k$. The bubbles have a spherical geometry (Figure 2.12) whilst the pressure on the surface of the bubble in the spherical r, φ, Θ notation is a function only of radius.

Thus the basic equation, taking into account the liquid viscosity, is as follows:

$$
\begin{aligned}
&R\frac{d^2R}{dt^2} + \frac{3}{2}\left(\frac{dR}{dt}\right)^2 \\
&= \frac{1}{\rho}\left(p_{g0} + \frac{2\sigma}{R_0} - p_n\right)\left(\frac{R_0}{R}\right)^{3z} + p_n - \frac{2\sigma}{R} - \frac{4\eta}{R}\frac{dR}{dt} - p_{c0} - p_\infty(t)
\end{aligned}
\tag{2.10}
$$

For cavitation occurring in viscous fluids e.g. Newtonian, the pressures on the bubble surface (phase interface) can be written as a function of the rate of change of the external pressure. In regions of falling external pressure the bubbles change their geometries relatively slowly and then the above-mentioned

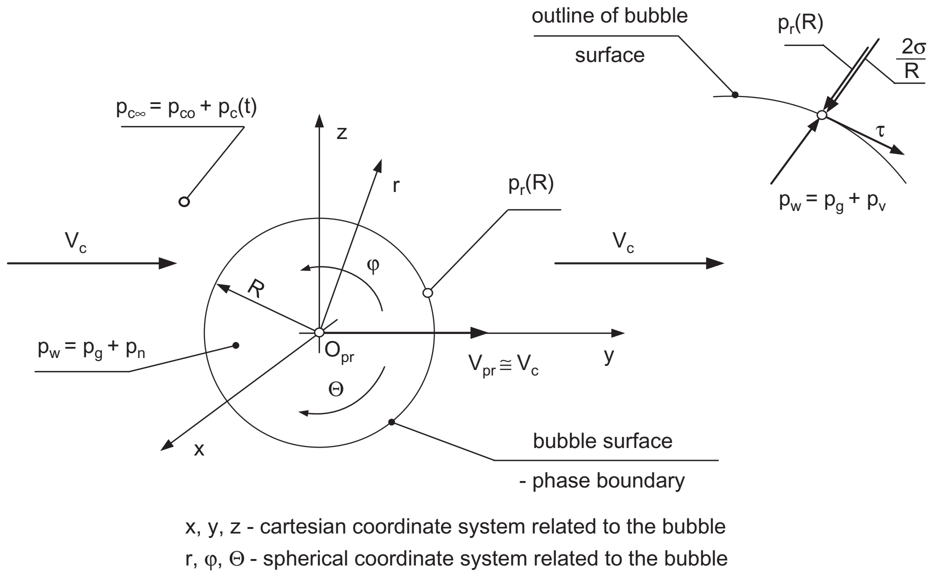

Figure 2.12. The geometry of a cavitation bubble moving with the liquid showing the various types of pressure.

polytropic change can be approximated by the isotherm (z = 1), which yields the following equation:

$$p(R) = \left(p_0 + \frac{2\sigma}{R_0} - p_n\right)\left(\frac{R_0}{R}\right)^3 + p_n - \frac{2\sigma}{R} - \frac{4\eta}{R}\frac{dR}{dt} \tag{2.11}$$

In regions of rising external pressure, particularly prior to imploding, the changes to the bubble geometry (collapse) occur more violently which justifies accepting as a first approximation the adiabatic transformation ($z = k = 4/3$). Then equation 2.11 becomes:

$$p(R) = \left(p_0 + \frac{2\sigma}{R_0} - p_n\right)\left(\frac{R_0}{R}\right)^4 + p_n - \frac{2\sigma}{R} - \frac{4\eta}{R}\frac{dR}{dt} \tag{2.12}$$

It must be stressed that during the bubble's lifetime the internal pressure is practically radius independent, it is equal to the summation of the partial pressures:

$$p_w = p_g(R) + p_n(T) \tag{2.13}$$

where:

$$p_g = \left(p_0 + \frac{2\sigma}{R_0} - p_n\right)\left(\frac{R_0}{R}\right)^{3z} \quad \text{and} \quad p_{g0} = p_0 + \frac{2\sigma}{R_0} - p_n \tag{2.14}$$

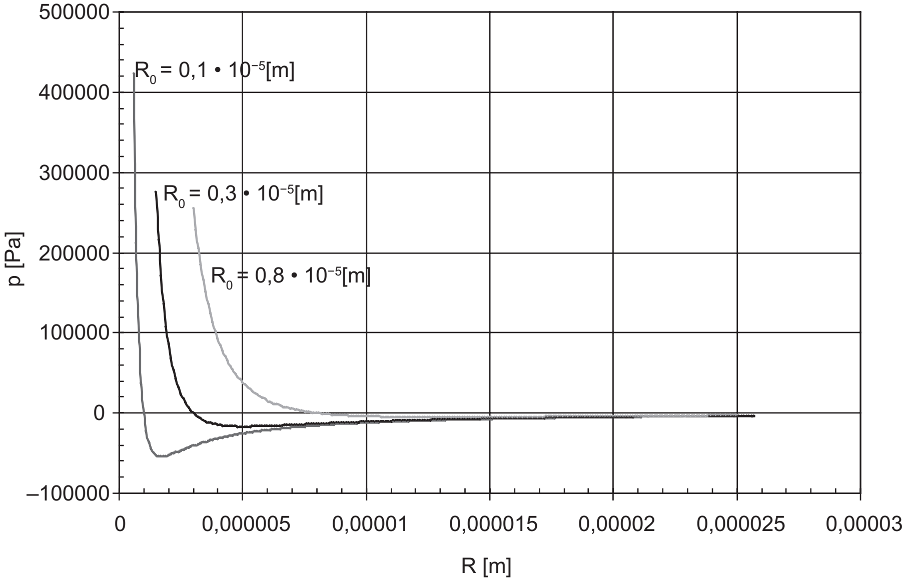

Figure 2.13. The dependency of equilibrium pressure in water on the initial and selected bubble radius for a starting pressure $p_0 = 1 \cdot 10^{-5}$ bar, $\sigma = 7.35 \cdot 10^{-2}$ N · m^{-1}.

In the case of water, using equation 2.11, and the following boundary conditions: $p_0 = 10^{-5}$ Pa, $R_0 = 10^{-6}$ m, $\dot{R}_o = 0$, $\rho = 1000$ kg · m^{-3}, $\sigma = 0.0735$ N · m^{-1}, $p_n = 1230$ Pa, $\mu = 1.33 \cdot 10^{-7}$ Pa · s and $1.33 \cdot 10^{-6}$ Pa · s, Figure 2.13 shows the pressure changes plotted against the radius with the initial bubble radius R_0 in the range 1–8 μm.

From calculations and analysis of equation 2.12 it appears that for a given initial radius value R_0, equation 2.15 has its minimum in a state of equilibrium, at a critical liquid pressure of p_{kr} and radius R_{kr}. For a given value of pressure there are two values for the radius: the smaller value to the left of the inflection, where the bubble is in a static equilibrium (its size remains constant) and a larger value lying to the right of the inflection where the bubble tries to increase its radius.

During equilibrium the pressure inside the bubble must be greater than the pressure in the surrounding liquid by a value equal to $2\sigma/R_0$. For a bubble of radius 1 mm this is 0.1 MPa (Wójs, 2004). In smaller bubbles this surplus must be appropriately greater. In reality this requirement is not fulfilled and what is observed is the existence and growth of gas bubbles.

Equation 2.14 can be solved using numerical methods with given initial and boundary conditions. An example of the calculations (Wójs, 2004) for $R_0 = 10^{-6}$ m, $\rho = 1000$ kg · m^{-3}, $\eta = 1.33 \cdot 10^{-7}$ Pa · s and $\eta = 1.33 \cdot 10^{-6}$ Pa · s is shown in Figures 2.14 and 2.15.

The cavitation bubble dynamics model worked out by Rayleigh and improved by Plesset is the basis for modelling the motion of cavitation bubbles (Brennen, 1995, Franc et al., 2004). The theoretical bubble dynamics models, on which its form and oscillations are based are being continuously improved taking into account experimental data (Gagate, 2000, Wolfram et al., 2003, Arrojo et al., 2008, Lucia et al., 2009, Qin et al., 2007).

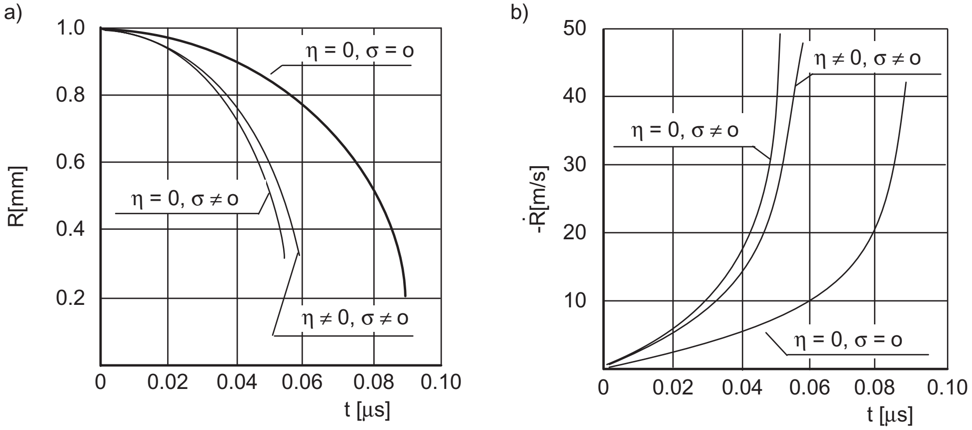

Figure 2.14. The influence of viscosity and surface tension on: a) bubble radius b) bubble surface speed (Wójs, 2004).

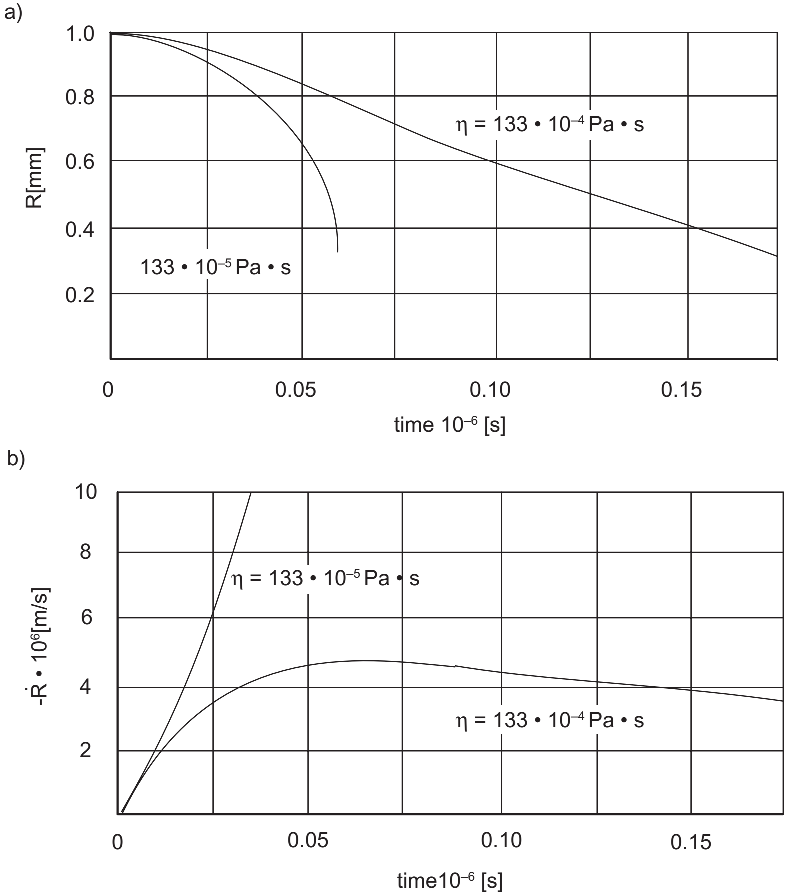

Figure 2.15. Changes in an imploding vapour bubble over time for: a) bubble radius, b) bubble wall velocity (Wójs, 2004).

2.4.3 *Static equilibrium in a gas bubble*

Under cavitation conditions there is a possibility of undissolved gas remaining in the form of spherical micro-bubbles filled with gas or vapour, surrounded by a "protective" organic layer (Bagieński, 1998). The function of this layer is to absorb and compensate the tensile stresses, which prevent the "barrier" from breaking and the gas dissolving in the water. The spherical bubble is in a state of equilibrium, if the forces directed radially in onto the surface are balanced. They develop as a result of water pressure and surface tension (Figure 2.16).

The dynamic mechanical equilibrium of the bubble is not steady state, since the inward radial surface tension increases as the bubble size decreases. If the bubble size is smaller than some critical value it will disappear due to a rise in the surface tension. If the bubble size is greater than the critical value, the surface tension decreases and the bubble will grow to a macroscopic size until such a time as when the external temperature and water pressure and the internal vapour pressure do not change.

The growth of the cavitation bubble can be the result of:

- relatively slow diffusion of gas from the water into the bubble—known as gas cavitation
- the loss of steady state equilibrium and the rapid increase in the volume of the vapour-filled bubble—known as vapour cavitation.

Assuming steady state conditions it is possible to analyse the bubble's static equilibrium conditions. The static equilibrium equation for the bubble can be written as:

$$p = p_n + p_g - \frac{2\sigma}{R} \tag{2.15}$$

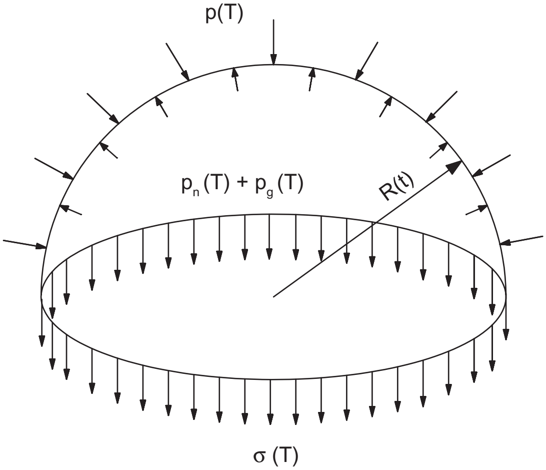

Figure 2.16. Static forces acting on a spherical bubble: $p_n(T) + p_g(T)$ – the sum of the saturated water vapour pressure and the pressure of the gas in the bubble, $p(T)$ – water pressure on the bubble's surface varying over time, $\sigma(T)$ – surface tension, $R(T)$ – bubble radius varying over time.

The pressure p_v and the surface tension are dependent on the temperature, e.g. for water at $T = 293$ K (20°C), $p_n = 2350$ Pa, $\sigma = 7.35 \cdot 10^{-2}$ N $\cdot$ m^{-2}. Frequently, in the case of vapour cavitation, (when $p_g = 0$) the static equilibrium condition takes on the form:

$$p = p_n - \frac{2\sigma}{R} \tag{2.16}$$

When $p < p_n - 2\sigma/R$, the vapour bubble grows and when $p > p_v - 2\sigma/R$, the vapour bubble shrinks.

It is commonly accepted that the pressure changes of the gas in the bubble occur in accordance with the laws of thermodynamics. The acceptance of such an assumption is correct, since the heat related with the collapse of the bubble is quickly absorbed by the water, as is the case when the speed of travel of the bubble is small and as a result of the large heat capacity of the water and the small mass of the gas. The relationship between the gas pressure and the bubble's radius in accordance with the Boyle-Mariotte Law can be written as:

$$p_g \cdot R^3 = p_{g0} \cdot R_0^3 \tag{2.17}$$

For the isothermal transformation the critical value for the bubble's radius is determined by the formula:

$$R_{kr} = \sqrt{3} \cdot R_0 \sqrt{\frac{R_0 \cdot p_{g0}}{2\sigma}} \tag{2.18}$$

The critical value for the vapour-filled bubble's radius is equal to the value of the radius corresponding to the static equilibrium, and can be represented as:

$$R_{kr} = \frac{2\sigma}{p_n - p} \tag{2.19}$$

For the isothermal transformation the critical value for the pressure is determined from the formula (*Brennen*, 1995):

$$p_{kr} = p_n - \frac{4\sigma}{3\sqrt{3}R_0} \sqrt{\frac{2\sigma}{R_0\left(p_0 - p_n + \dfrac{2\sigma}{R}\right)}} \tag{2.20}$$

2.5 CAVITATION BUBBLE OSCILLATIONS AND IMPLOSIONS

As mentioned previously, the cavitation phenomenon is tied in with cavitation nuclei and their growth, followed by cyclic implosions, disappearance and repeated explosive growth. The mechanism of this phenomenon is slightly different in the various forms of cavitation. The driving energy for the cavitation process is the variable pressure field, generated by the flow conditions, vibrations of the static body immersed in the liquid or the energy beam delivered to the liquid in the form of acoustic waves or laser light.

Figure 2.17 illustrates the mechanism for the cavitation arising during flow through a constriction.

When the liquid flows through the venturi, the cavitation nucleus, in the form of a bubble ranging in size between 10^{-9} to 10^{-4} m in the concentrator, grows as a result of the pressure falling. Gases dissolved in the liquid diffuse into the bubble. When the liquid pressure in the constriction reaches a critical value, less than or equal to p_v the bubble rapidly increases in volume due to evaporation from the bubble's surface. When the vapour-gas bubble moves into a region of rising pressure in the diffuser section, condensation takes place with an implosive reduction in the size of the bubble. Liquid flows into the "empty space" at a rate of several hundred metres per second, causing compression of the remaining gases locally. The strongly compressed gas up to pressures of several hundred megapascals undergoes expansion, which causes an explosive rise in the number of bubbles. During the explosion, effectively due to the liquid's inertia, the pressure drops and repeated evaporation occurs on the surface of the growing bubble. This is repeated manifold, even several hundred times, causing the movement of the cavitation zone beyond the constriction.

Figure 2.18 illustrates the mechanism for the inception and disappearance of the cavitation bubbles during flow around a body. Likewise, as in the case of flow through a constriction, the process of creation and disappearance of bubbles is related to the pressure changes during flow in an aerodynamic profile (Wójs, 2004).

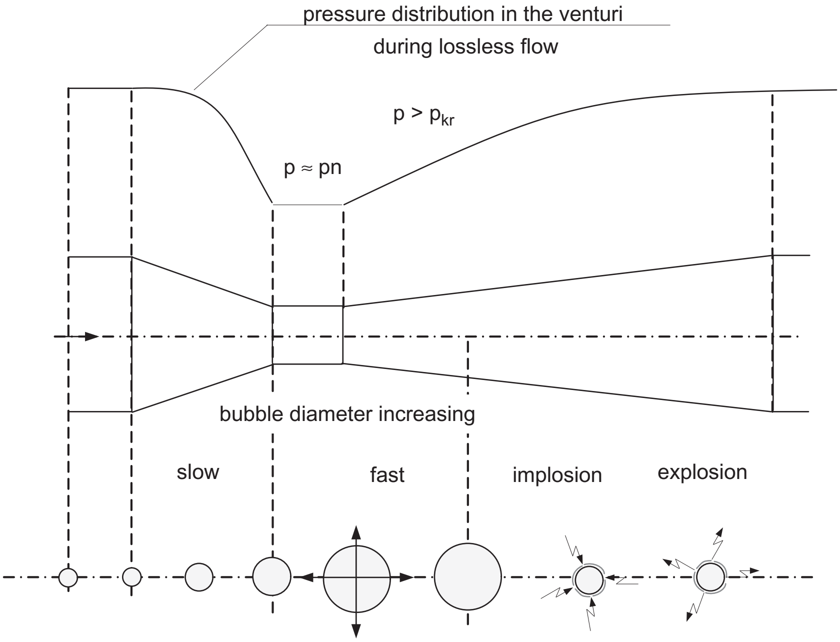

Figure 2.17. The formation and collapse of vapour-gas bubbles in the venturi.

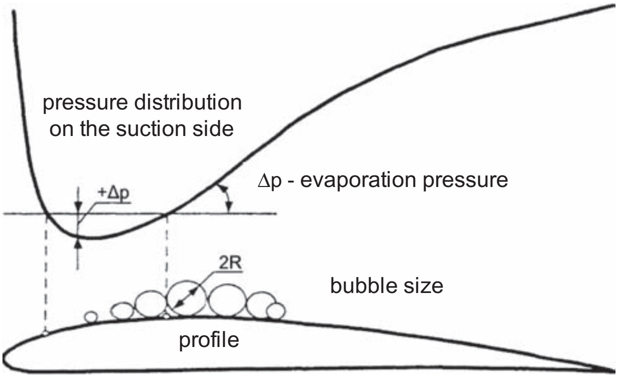

Figure 2.18. The formation and collapse of cavitation bubbles in a flow around a profile (Wójs, 2004).

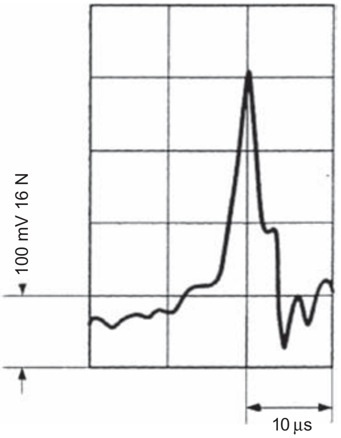

Figure 2.19. A typical trace of a single cavitation pulse (Wójs, 2004).

The disappearance of vapour-gas bubbles in a real liquid has a very complicated character. It has significant meaning as a result of its consequences, especially cavitational erosion. As a result, this problem was the subject of both theoretical and experimental research carried out by many authors (Lucia et al., 2009, Qin et al., 2007, Franc et al., 2004). The time taken for the vapour-gas bubble to disappear is very short. Figure 2.19 shows a typical trace for a single cycle consisting of the growth and decay for a bubble.

From the trace in Figure 2.19 it appears that the time for the formation and collapse of the bubble is around 10 μs during which the implosion is of a shorter duration than the bubble inception. However, the maximum pressure pulse inside the bubble lasts about 1 μs.

In the presented models of bubble dynamics it is assumed that its shape is spherical during the complete creation and collapse cycle. In reality however, due to a variety of factors such as variable external pressure, the effects of other bubbles, the influence of walls etc., the bubble's shape during oscillation undergoes severe deformation. Bubbles formed by a single pulse have different shapes. The

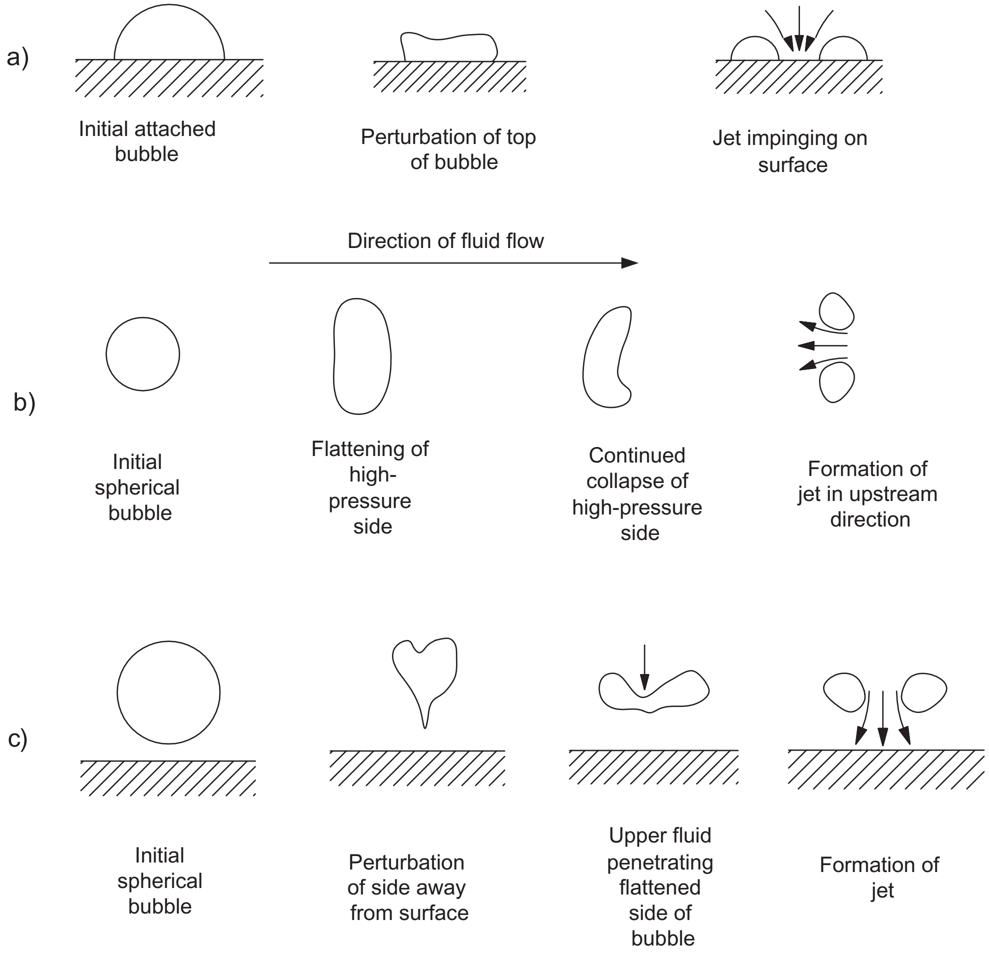

Figure 2.20. Jet collapse models for: (a) a hemispherical bubble attached to a wall (b) a bubble moving into a pressure gradient. (c) a bubble collapsing near a wall.

evidence is provided in the photographs taken by many researchers including (Wolfram et al., 2003, Franc et al., 2004). The greatest deformation occurs for bubbles collapsing near boundaries which restrict flow. A boundary restricting the flow of liquid into an empty region causes an asymmetrical collapse of the bubble and the liquid flows only from the opposite side. A cumulative micro-jet forms in the liquid, directed towards the boundary with a velocity of more than 100 m/s. The asymmetric bubble explosion causes a pressure pulse directed towards the boundary. The effect creates cavitation erosion and vibrations in the cavitation setup. Figure 2.20 illustrates the proximity effect of a boundary on the shape of the collapsing cavitation bubbles.

2.6 CAVITATION NUMBER

In analysing the cavitation phenomenon a parameter or a criterion number should be specified, allowing for a quantitative flow assessment in two aspects:

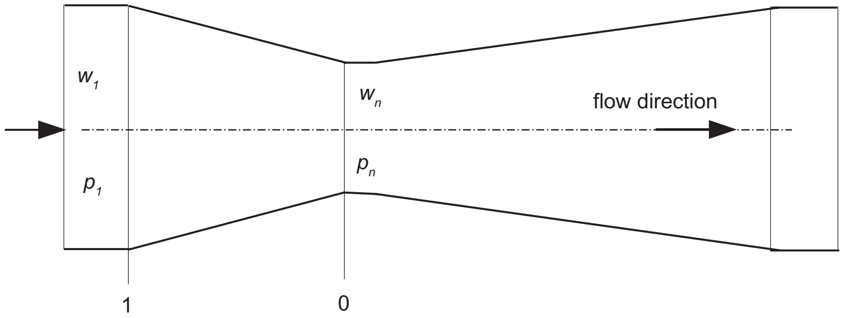

Figure 2.21. Flow through a constriction.

- a parameter, which assumes a unique value for each set of dynamically similar cavitation conditions
- a parameter describing the flow conditions without cavitation and also conditions for the creation, collapse or at the various stages of cavitation development.

Consider the flow of a liquid through a venturi as depicted in Figure 2.21 and assume that in the smallest cross sectional area the pressure is p_w, and the flow is w_k. The Bernoulli equation for the one dimensional steady flow of the ideal liquid for the cross sections at 1 and 0 is:

$$\frac{p_1}{\rho}+\frac{w_1^2}{2}=\frac{p_n}{\rho}+\frac{w_n^2}{2} \tag{2.21}$$

where:
p – static pressure in non-turbulent flow
ρ – density of the liquid
W – velocity of the non-turbulent liquid

Rearranging:

$$w_n^2-w_1^2=\frac{2(p_1-p_n)}{\rho} \tag{2.22}$$

or

$$\frac{w_n^2}{w_1^2}-1=\frac{(p_1-p_n)}{\frac{\rho\cdot w_1^2}{2}} \tag{2.23}$$

If we assume that cavitation occurred at 0 that is, the normal tension in the element becomes zero, then p_n is the saturated vapour pressure at a given temperature. The right hand side of equation 2.23 has the form of Euler's number and is known as the Cavitation number K.

$$K=\frac{(p_1-p_n)}{\frac{\rho\cdot w_1^2}{2}} \tag{2.24}$$

The left hand side of equation 2.27 is known as the dispersion factor (Bagieński, 1998).

$$Z = \frac{w_k^2}{w_1^2} - 1 \qquad (2.25)$$

A physical meaning to the cavitation number can be assigned as follows: in equation 2.24, pressure appears in the numerator which determines when cavitation will disappear whilst dynamic pressure appears in the denominator. A pressure change at a boundary or on the surface of a body, around which the liquid flows, is in the main part dependent on the change in the flow rate. Therefore, the dynamic pressure can be regarded as defining the size of the pressure drop, resulting in cavities forming and growing.

Determining the hydrodynamic cavitation intensity plays an important role in the design of technical solutions. The basis for assessing the intensity of the cavitation process is the Rayleigh-Plasset equation.

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Application of Hydrodynamic Cavitation in Environmental Engineering – Ozonek

CHAPTER 3

Sonochemical processes in support of oxidation processes

3.1 ADVANCED OXIDATION PROCESSES

In recent years intensive research has been conducted into finding effective methods for removing toxic pollution occurring in water and sewage, both in minute quantities as well as in relatively high concentrations.

Conventional methods of sewage treatment are not always effective, particularly in the case of disposing of substances which are not easily biodegradable such as chlorinated organic compounds, aliphatic and aromatic hydrocarbons, phenols and their derivatives, organic dyes, surface-active substances and pesticides. These compounds as well as their partially oxidised derivatives, even in low concentrations in the cleansed sewage, can negatively influence the colour, taste, smell of water and pose a danger to living organisms.

Conventional methods such as coagulation or activated carbon adsorption are usually associated with the transfer of pollution from one stage to another and they do not completely eliminate the pollution. Advanced oxidation processes (AOPs) can be an alternative to other oxidation methods (Figure 3.1). They were first defined by Glaze (Glaze et al., 1987) as processes during which highly reactive $^{\bullet}OH$ radicals are generated, being one of the most powerful oxidising agents which react very quickly with most organic compounds. With the help of the hydroxyl $^{\bullet}OH$ radicals, organic compounds dissolved in water or sewage are oxidized into simple more biodegradable compounds.

The effectiveness of removing pollution from water and sewage using advanced oxidation processes depends mainly on:

- the type and concentration of organic compounds susceptible to oxidation as well as organic and mineral compounds which stimulate or inhibit the formation of $^{\bullet}OH$ radicals, i.e. Fe^{2+} and Cu^{2+} ions, chlorides, carbonates, bicarbonates as well as organic compounds such as tert-butanol, isopropanol, pH value, water and sewage turbidity,
- the type and dose of reagents, the concentration ratio of oxidants to oxidized compounds, the reaction time, and also the wavelength and intensity of UV radiation,
- the location of the advanced oxidation process in the technological system of sewage and water treatment.

In each of these methods, due to the number of reactions e.g. initiation, propagation and termination, hydroxyl radicals are created amongst others, but with a lower oxidising potential. In the presence of organic compounds the $^{\bullet}OH$ radicals react with them to form organic radicals ($R^{\bullet}$, $ROO^{\bullet}$) which, being

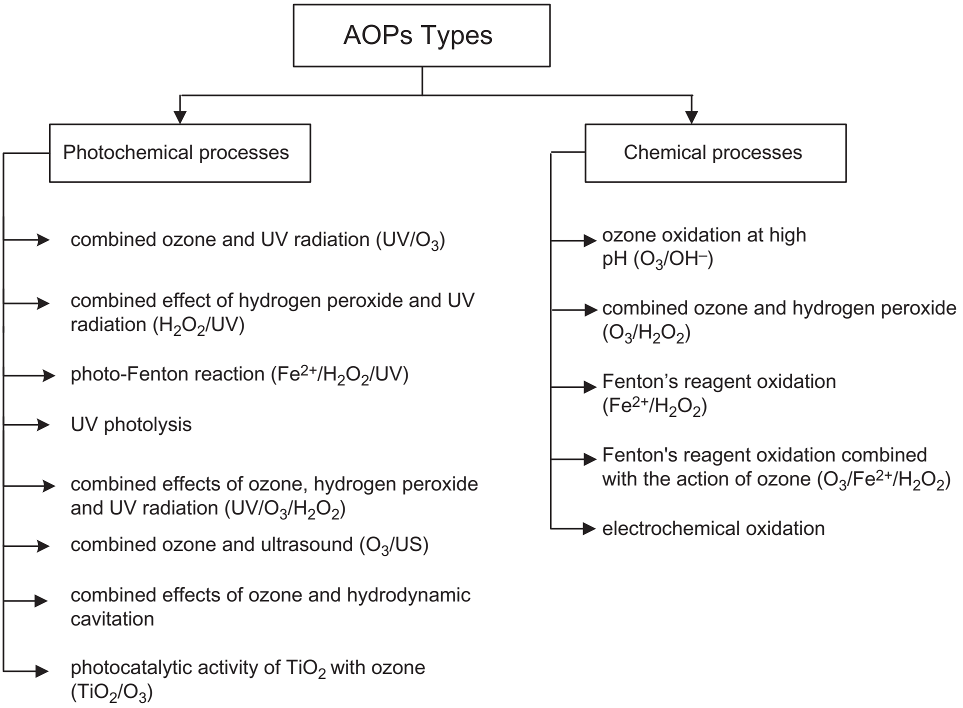

Figure 3.1. General classification of the advanced oxidation processes.

transitional products of the oxidation process, initiate further oxidation and degradation chain reactions, leading to carbon dioxide, water and inorganic compounds in the final stage (Nawrocki et al., 2000, Munter, 2001, Ledakowicz et al., 2002, Poyatos et al., 2010).

In recent years increasing attention has been devoted to exploiting the phenomenon of both ultrasonic and hydrodynamic cavitation in advanced oxidation processes, for example in water treatment, sewage treatment processes (Gogate, 2002, Gogate et al., 2005, Litter, 2005, Poyatos et al., 2010) as well as in sludge treatment (Pilli et al., 2011, Bień et al., 1995, Naumczyk et al., 2006).

The effects resulting from the use of cavitation technology relate to both pathogen destruction, the decomposition of organic compounds of low biodegradability, as also the enhancement of interactions between immiscible liquids and accelerating chemical reactions (Esplugas et al., 2002, Gandhi et al., 1999, Andreozi et al., 1999, Jyoti et al., 2004, Gogate, 2002, Gogate et al., 2005).

3.2 THE MECHANISM AND KINETICS OF REACTIONS INVOLVING HYDROXYL RADICALS

In advanced oxidation processes various oxidising agents are used whose common feature is the creation of hydroxyl radicals $^{\bullet}OH$ during the reactions. They are extraordinarily reactive, having the highest redox potential (2.81 V) amongst the known oxidising agents in water (Table 3.1).

One of the characteristics of the hydroxyl radical is its very fast reaction times with many organic compounds, the reaction rate constants are very high,

Table 3.1. Oxidising potentials of selected oxidising agents.

Species	Redox reaction	Standard potential [V]
Xenon acid (VIII)	$H_4XeO_6 + 2H^+ + 2e^- \leftrightarrow XeO_3 + 3H_2O$	3.00
Fluorine	$F_2 + 2e^- \leftrightarrow 2F^-$	2.87
Hydroxyl radical	$^{\bullet}OH + H^+ + e^- \leftrightarrow H_2O$	2.81
Atomic oxygen	$O + 2H^+ \leftrightarrow H_2O$	2.42
Ozone	$O_3 + 2H^+ \leftrightarrow O_2 + H_2O$	2.07
Hydrogen peroxide	$H_2O_2 + 2H^+ + 2e^- \leftrightarrow 2H_2O_2$	1.77
Permanganate (VII)	$MnO_4^- + 4H^+ + 3e^- \leftrightarrow MnO_2 + 2H_2O$	1.68–1.70
Hydroperoxyl radical	$HO_2^{\bullet} + H^+ + e^- \leftrightarrow H_2O_2$	1.44–1.70
Chlorine monoxide (IV)	$ClO_2 + e^- \leftrightarrow ClO_2^-$	1.07–1.57
Iodine acid (I)	$HIO + H^+ + 2e^- \leftrightarrow I^- + H_2O$	1.45
Chlorine	$Cl_2 + 2e^- \leftrightarrow 2Cl^-$	1.36
Oxygen	$O_2 + 4H^+ + 4e^- \leftrightarrow 2H_2O$	1.26

in the order of 10^8–10^{10} $dm^3mol^{-1}s^{-1}$ (at 25°C), which at the radical concentration of 10^{-10} $moldm^{-3}$ amounts to a value of 0.01 s^{-1} for the pseudo first-order reaction rate constant with respect to the oxidised constituent (Esplugas, 2002). Besides, the $^{\bullet}OH$ radical characterises itself with a stronger oxidation impact in an acidic environment as well as sensitivity to the presence of radical acceptors, so called scavengers, in the water environment, such as carbonates and bicarbonates and also humus matter found in water (Biń, 2002).

One of the characteristics of the hydroxyl radical is its very fast reaction times with many organic compounds, the reaction rate constants are very high, in the order of 10^8–$10^{10} dm^3 \cdot mol^{-1}s^1$ (at 25°C), which at the radical concentration of 10^{-10} $mol \cdot dm^{-3}$ amounts to a value of 0.01 s^{-1} for the pseudo first-order reaction rate constant with respect to the oxidised constituent (Esplugas, 2002). Besides, the $^{\bullet}OH$ radical characterises itself with a stronger oxidation impact in an acidic environment as well as sensitivity to the presence of radical acceptors, so called scavengers, in the water environment, such as carbonates and bicarbonates and also humus matter found in water (Biń, 2002).

Reactions involving the hydroxyl radicals display an atypical selectivity in reactions regarding organic compounds, where reaction rates are extremely high in the order of 10^8–10^{11} $mol^{-1}s^{-1}$ (at 25°C). Table 3.2 shows the reaction rate for ozone and the hydroxyl radicals.

A number of reaction mechanisms involving hydroxyl radicals can be identified:

- reaction involving the removal of the hydrogen atom

$$^{\bullet}OH + RH \rightarrow R^{\bullet} + H_2O \qquad \text{(R 3.1)}$$

- reaction involving the addition of the oxygen molecule

$$R^{\bullet} + O_2 \rightarrow ROO^{\bullet} \qquad \text{(R 3.2)}$$

- reaction involving electron transfer

$$^{\bullet}OH + RH \rightarrow RH^{\bullet+} + HO^- \qquad \text{(R 3.3)}$$

- electrophilic addition to a π-bond:

$$^{\bullet}OH + {>}C = C{<} \rightarrow {>}C(OH)C^{\bullet}{<} \qquad \text{(R 3.4)}$$

Table 3.2. Reaction rate constants ($mol^{-1}s^{-1}$) for selected organic compounds with ozone and hydroxyl radicals (Litter, 2005).

Compound	Ozone (O_3)	Hydroxyl radical ($^{\bullet}OH$)
Chlorinated alkenes	10^3–10^4	10^9–10^{11}
Phenols	10^3	10^9–10^{10}
Aromatics	1–10^2	10^8–10^{10}
Ketones	1	10^9–10^{10}
Alcohols	10^{-2}–1	10^8–10^9
Alkanes	10^{-2}	10^6–10^9

The speed and the effectiveness of the oxidation and degradation, relating to the creation and reactivity of the intermediate radicals, depends to a significant degree on the oxygen concentration and also on the energy required for the breaking of the appropriate chemical bonds.

In addition to the oxidation processes initiated by the $^{\bullet}OH$ radicals, other reactions also take place in water which remove them, thus slowing down these processes. These $^{\bullet}OH$ radical acceptors are mainly bicarbonate and carbonate ions

In spite of a variety of advanced oxidation techniques, identical or similar radical reactions are common in water. Some of them underpin the chain reactions which create the hydroxyl radicals, some lead to a reaction with the primary oxidising compounds creating carriers in the kinetic chain.

In advanced oxidation processes we have to deal with synergism, which means that the effect of simultaneously applying different AOPs has a greater effect than the sum of the effects of the individual processes applied alone. Synergism deals with, not only the degree of degradation of pollution, but also the mineralising rate of pollutants in sewage or the reduction in their toxicity.

In advanced oxidation processes, from the process point of view, the important factors are the reaction rate and its productivity. Introducing an additional oxidising agent, fundamentally changes the type of reaction, from molecular to free radical, thanks to which, the effects of faster oxidation reactions are observed (Perkowski et al., 2005).

3.3 CAVITATION CHARACTERISTICS WITH THE PARTICIPATION OF ULTRASOUND

Ultrasounds are elastic waves with a frequency higher than those which can be heard by a human being. The frequency range relating to ultrasound is from 20 kHz to 1 GHz. The upper limit is determined by the technical capabilities of creating ultrasound. The ultrasonic vibrations propagate in elastic environments such as: gases, liquids and solids. Due to their different structure, the speed of propagation for each of these environments is different. However, the nature of ultrasound in each of the above mentioned environments is identical.

The basis of ultrasonic propagation in elastic environments is wave motion. The essence of this process is the assumption that the disturbance caused in the environment moves from particle to particle with a specific speed. Each particle therefore undergoes a vibration around its equilibrium centre, transferring the energy to its neighbour occupying a different position in space.

The basic parameters used to describe the ultrasonic waves include the wavelength and its frequency. The wavelength depends on the environment through which the wave propagates. The basic equation relating frequency to wavelength is as follows:

$$\lambda = \frac{\omega}{f} \; [m] \tag{3.1}$$

where:

ω – The speed of propagation of the ultrasonic wave in an environment (ms^{-1})
f – The frequency of vibration of the ultrasonic wave (Hz)

The longest wavelengths correspond to waves propagating in solid bodies, whilst the shortest in gases. For the upper limit in the ultrasonic frequency range (1 GHz), the wavelength varies from $5.0 \cdot 10^{-6}$ m for solid bodies, through $1.5 \cdot 10^{-6}$ m for liquids to $3.4 \cdot 10^{-7}$ m for gases.

The acoustic field can be characterised by the amount of energy, which describes the transfer of energy by the waves. The amount of energy transferred by the acoustic wave in one second, over a surface at right angles to the direction of wave propagation, is called the sound intensity or acoustic intensity:

$$I = \frac{N}{A} \left[Wm^{-2}\right] \tag{3.2}$$

where:

N – The power transferred by the ultrasonic wave (W)
A – The surface area over which the wave propagates (m^{-2})

The wave intensity (I), as a magnitude characteristic of the ultrasonic field and related to the speed of propagation of the wave in a given medium and its density, can be given by the following equation:

$$I = \frac{\rho w}{2} F^2 \omega^2 \left[Wm^{-2}\right] \tag{3.3}$$

where:

ρ – The density of the medium (kgm^{-3})
w – The speed of propagation of the ultrasonic wave in a given medium (ms^{-1})
F – The amplitude of the ultrasonic wave (m)
ω – $2\pi f$

The action of the ultrasonic wave on the medium is primarily dependent on the energy, which the interaction brings with itself. For this reason two types of interactions are differentiated: passive and active. In the passive case the ultrasonic wave has a small amount of energy and amplitude. However, in the active case the ultrasonic wave usually has a high intensity and amplitude. The active interaction of the ultrasonic wave creates large local forces, which consequently lead to processes normally causing irreversible macroscopic changes to the medium. The action may cause new processes to be created, as well as influencing the current processes in the medium already under the influence of ultrasound.

The mechanism for the active interaction of ultrasound is normally divided into primary and secondary. Primary mechanisms are those which describe the basic amplitude of the acoustic field, amongst which the most important are: the periodic acoustic pressure, radiation pressure, cavitation, that is processes responsible for the forces which create the secondary mechanisms. Figure 3.2 illustrates the phenomena which accompany the passage of an ultrasonic wave through a medium. Secondary phenomena of a physicochemical nature are:

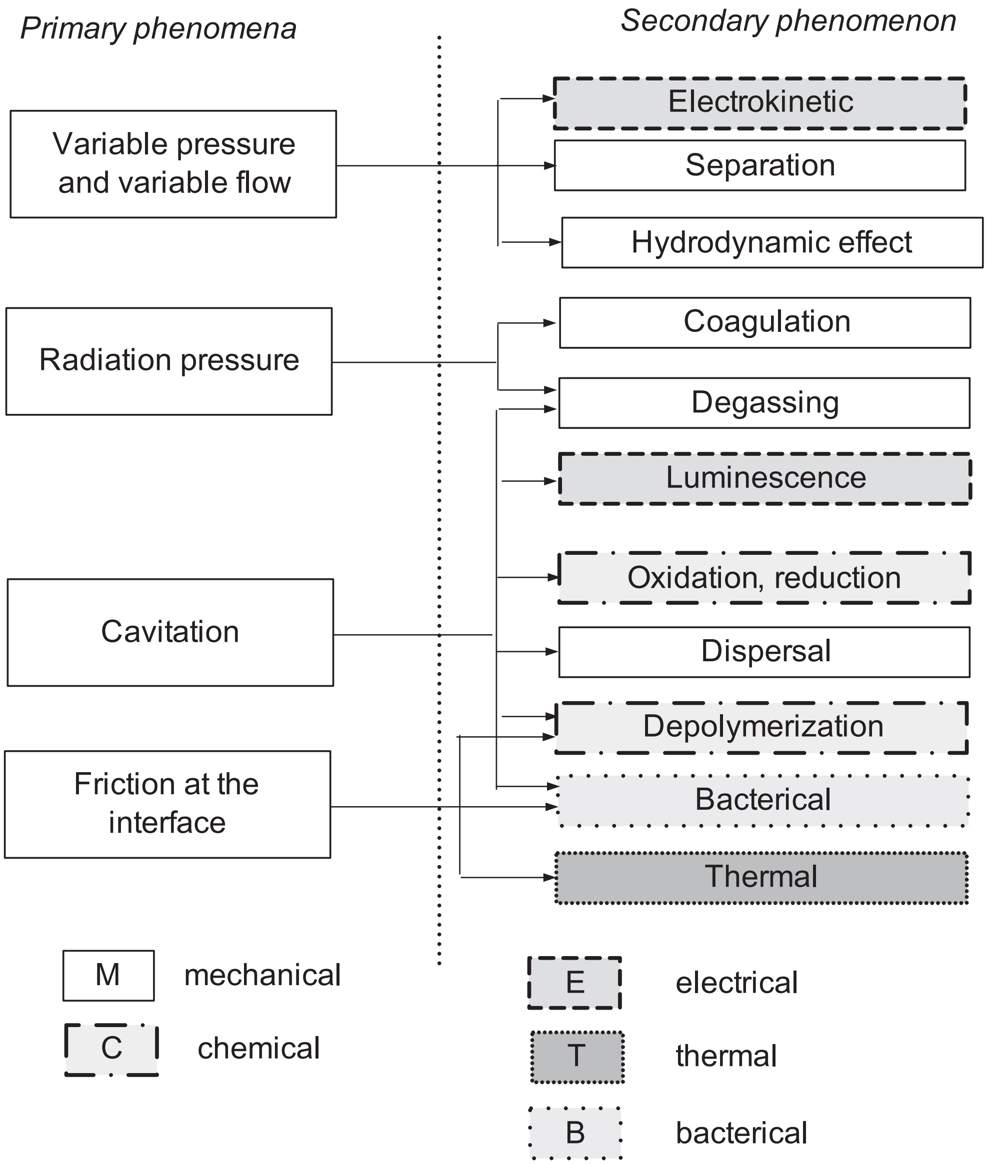

Figure 3.2. The various phenomena which accompany the application of ultrasound.

ultrasonic dispersion and coagulation, oxidation and reduction, heat phenomena, depolymerisation as well as others (Śliwiński, 2001, Gierczycki et al., 2006).

Previous research has shown that cavitation is observed after a certain intensity level of the ultrasonic wave has been exceeded, known as the cavitation threshold. The appearance and intensity of the process is dependent on temperature, surface tension, medium viscosity, hydrostatic pressure, degree of gas saturation and type of gas. Due to the particular cavitation process, conditions on the phase transition boundary, the presence of gas bubbles and pollutants suspended in the medium (cavitation nuclei), the medium's immunity is reduced to the manifestation of this phenomena.

The following will influence the overall phenomena and effects resulting from the interaction of the ultrasonic wave: frequency of the ultrasonic wave, intensity, the medium's physical structure and chemical constituents, and in particular its acoustic coupling efficiency (Elpiner 1968, Śliwiński 2001, Bień et al., 1995, Suslick i in., 2008).

Interest in ultrasound is a result of the various phenomena and effects which arise from it. On account of this, depending on its source parameters and the propagation medium, ultrasound is applied in industry to modify the chemical, physical and biological properties of different media whilst in medicine for diagnostic and treatment purposes. Macromolecular chemical compounds in an ultrasonic field can undergo an accelerated degradation and depolymerisation. Ultrasound can catalyse or cause reactions, as a result of which new complex chemical compounds are created. The process is dependent on many factors, which are influenced by the ultrasonic field parameters and the initial physicochemical characteristics of the treated compounds.

3.4 SONOCHEMICAL REACTIONS UNDER THE INFLUENCE OF ULTRASOUND

The influence of ultrasound on the behaviour of liquids was first confirmed by A.L. Louis in 1927, but the turbulent development of sonochemistry arose from the moment when relatively inexpensive ultrasonic generators were used in 1980 (Suslick, 1989). The majority of published works in sonochemistry make use of low frequency ultrasounds.

The important phenomena which appear during cavitation are the sonochemical reactions, which take place inside the cavitation bubbles and on the phase transition boundaries. The cavitation liquid environment is conducive to the energy effects associated with the formation, development and implosion of bubbles to accelerate the rate of chemical reaction.

The introduction of high acoustic energy into a liquid affects the occurrence of physical and chemical reactions, which can significantly change the nature of the decomposition of the compounds present in the solution. Such reactions are the result of the creation and destruction of cavitation bubbles which form under the influence of acoustic conditions. Previous research has shown (Feng, 2002, Colusii et al., 1998, Elpiner, 1968) that under the influence of ultrasound the following processes can happen:

- acceleration of conventional reactions
- polymer degradation
- decomposition and reactions in organic solvents.

Sonochemical reactions occur mainly in the cavitation bubbles and on the phase transition borders, explaining why the cavitation process plays an important role here.

Amongst the physicochemical phenomena an important role is assigned to the interaction of ultrasound on macromolecular compounds. Depending on conditions, it is possible to observe the acceleration of monomer polymerisation or the depolymerisation of macromolecules, or an intermediate effect dependent on the creation of mixed polymers. For polymers with a high molecular weight, ultrasound exhibits a depolymerisation action—large molecules, in particular "threads" undergo decomposition in the solution (Mason et al., 2004, Petrier et al., 1996). In this case a mechanical degradation of macromolecules occurs under the influence of significant shearing forces.

In the process of creating these reactions, local pressure changes cause local temperature changes, which in the final stage of collapse can reach thousands of atmospheres and thousands of kelvins respectively (Figure 3.3). At such high temperatures processes conducive to specific chemical reactions can occur. The cause of the creation of ions and free radicals in the compression stage of the cavitation bubbles is the thermal dissociation of the molecules.

As shown by the research carried out (Suslick, 1990, Suslick et al., 2008), during bubble collapse, large shearing forces are created, and even rigid structures can undergo damage. During bubble implosion in the gaseous phase

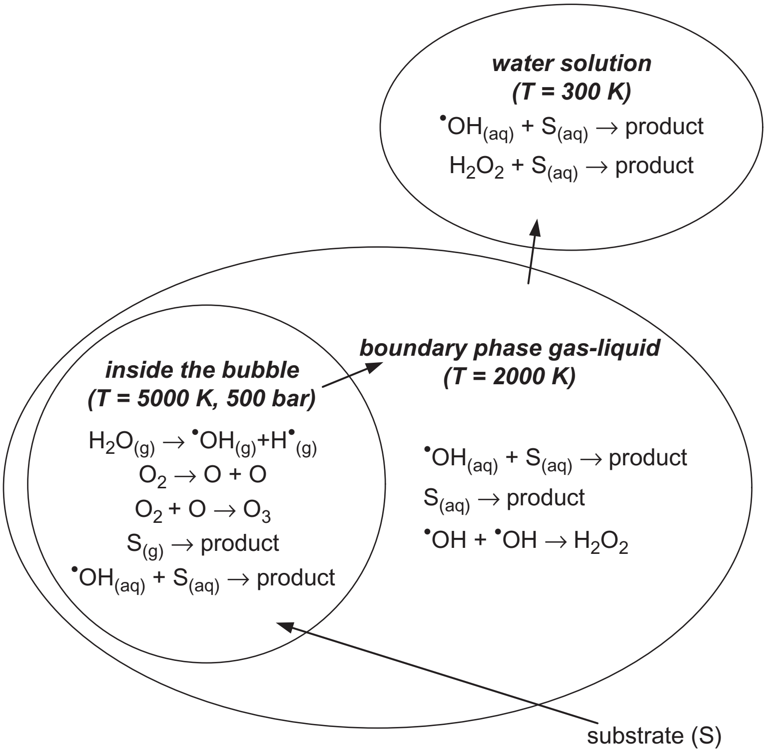

Figure 3.3. Sonochemical reaction zones (based on Adewuyi, 2001).

extreme conditions prevail; very high temperatures (~5000 K) and high pressures (~600 bar). These specific conditions lead to sonochemical reactions which cause amongst others, the creation of $H^{\bullet}$ and $^{\bullet}OH$ radicals, and the start of chemical changes to organic compounds.

In the cavitating liquid medium, hydroxyl and hydrogen peroxide radicals are created according to the following reactions (Masson et al., 1998):

$$HOH \xrightarrow{\text{cavitation}} H^{\bullet} + {}^{\bullet}OH \tag{R1}$$

$$H^{\bullet} + O_2 \rightarrow HOO^{\bullet} \tag{R2}$$

$$O_2 \rightarrow O^{\bullet} + O^{\bullet} \tag{R3}$$

$$HOO^{\bullet} + HOO^{\bullet} \rightarrow H_2O_2 + O_2 \tag{R4}$$

$$H^{\bullet} + O_2 \rightarrow HOO^{\bullet} \tag{R5}$$

$${}^{\bullet}OH + {}^{\bullet}OH \rightarrow H_2O_2 \tag{R6}$$

Reactions R3 and R5 are disadvantageous from the free radical reactions' viewpoint, as they reduce the number of hydroxyl radicals being created in the medium.

Taking advantage of ultrasound, the technologies of environmental engineering (Figure 3.4) can be fundamentally divided into two parts dependent on their actions: high frequency ultrasonic waves (2–10 MHz) and low frequency ultrasonic waves (20–100 kHz).

Research carried out (Petrier et al., 1997) has shown that sonochemical reactions appear not only in the presence of low frequencies but also between 100 and 1000 kHz. The optimal frequency depends on the type of reaction substrate. In the case of frequencies above 1 MHz it is extremely difficult to create conditions suitable for cavitation, since the wave intensity which should be used to create these conditions, increases with frequency. In the high frequency range (above 1 MHz) the dominant action is mechanical.

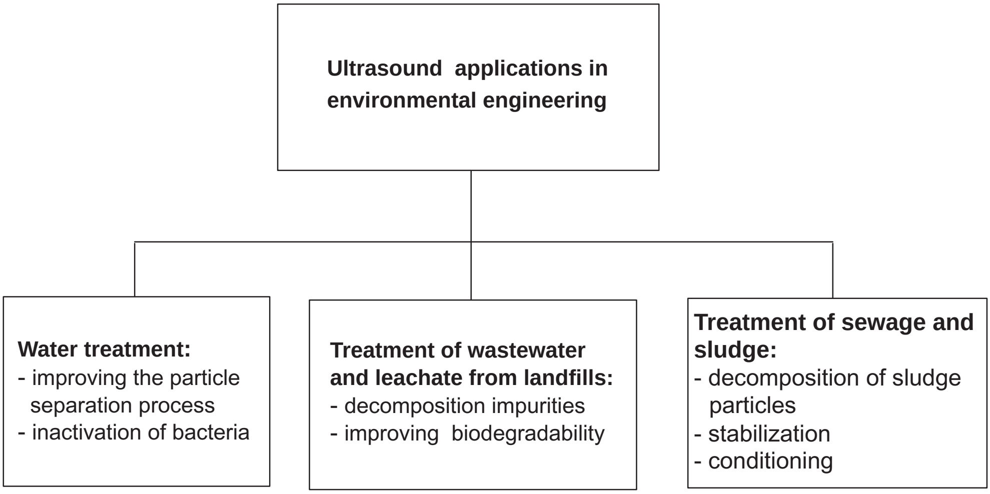

Figure 3.4. Ultrasound applications in environmental engineering.

Sonochemical reactions occurring in a cavitating liquid medium can be divided into the following groups (Elpiner 1968, Kang et al., 2001):

- reactions occurring directly in the vapour phase i.e. in the cavitation bubble
- chemical reactions occurring on the phase transition boundary of the cavitation bubble and the liquid, resulting in an interaction between the free radicals and atoms created inside the bubble, and the molecules in the single molecular layer
- chemical reactions appearing as active molecules, created in the vapour phase and penetrating into the surrounding liquid (usually water) with a resultant implosion of the cavitation bubbles
- chemical reactions initiated by the action of shock waves whose source is the collapsing cavitation bubbles.

In the last twenty years there has been a rise in the interest shown in the utilisation of ultrasound to degrade mainly organic pollutants in water and sewage (Hao et al., 2003). In comparison to other technologies of decomposition/removal of organic pollutants, such as ozone, hydrogen peroxide, ultraviolet radiation or the action of catalysts, ultrasound has important advantages of being a simple process, of lower energy consumption and a lack of secondary pollution (Teo et al., 2001).

Published data confirms that the combined use of ultrasound and ozone has a greater impact on the degradation process than simply just using ozone by itself or just ultrasound.

Combining the sonochemical process with ozonation produces a source of $^{\bullet}OH$ radicals from:

- sonochemical decomposition of water
- ozone decomposition
- thermal decomposition of ozone in the cavitation bubble.

However effective the sonochemical processes are in the decomposition of organic compounds, in many instances it is impossible to achieve a high degree of degradation due to, amongst others, the high polarisation of organic compounds, restricted access to hydroxyl radicals or an insufficient amount of delivered (dispersed) energy. To overcome these disadvantages sonochemical processes are frequently combined with advanced oxidation processes. In many cases taking advantage of ultrasound also enables the effectiveness of other degradation processes to be increased.

3.5 SUMMARY

The effectiveness of the advanced oxidation processes essentially depends upon the number of reactive molecules produced, including hydroxyl radicals. A knowledge of which reactive molecules are produced can be of help in identifying the dominant degradation reactions, which enables the appropriate, most realistic chain of AOP reactions to be worked out, and makes the decision about the practical implementation of a given process easier.

Researching through the rich literature regarding the degradation of different pollutants found in the treated waters and sewage it can be concluded that these methods seldom appear individually in the final stages of sewage treatment, but usually aid the biological cleaning processes. It is no doubt related to the cost of producing hydroxyl radicals using AOP methods. Besides, only the integration of chemical and biological oxidation methods has the greatest chance of being implemented practically in sewage treatment. Full degradation of pollutants in sewage using the advanced oxidation approach is not always possible, and above all relatively expensive. On the other hand, many pollutants found in sewage, particularly industrial are non-biodegradable, therefore this integration of both chemical and biological methods is necessary and beneficial.

Implementing advanced oxidation processes quite often leads to a high degree of pollution degradation in water and sewage, whilst partial oxidation produces simpler organic compounds. These methods are characterised by the very fast degradation of pollution, versatility and high effectiveness, but are also associated with significant cost of reagents and energy consumption when implementing the process.

The introduction of high energy into the liquid medium influences the physical and chemical reactions, which can significantly intensify the decomposition of the low biodegradable substances in water, sewage and leachate from landfills (Chowdbury et al., 2009, Kang et al., 2001, Ince, 1998, Colussi et al., 1998).

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CHAPTER 4

Problems and conditions in the generation of hydrodynamic cavitation

The intensity of the technological processes in hydrodynamic cavitation devices is associated with a range of physicochemical and mechanical effects (shock waves, cumulative microstreams, self-excited oscillations, turbulence), caused by the implosion of cavitation bubbles. In turn, this leads to a concentration of bubbles and an increase in their energies, located near the centre of the cloud. Under such conditions, during an implosion, the pressure rises to almost an order of magnitude greater than during the implosion of a single bubble (Litwinienko et al., 2005, Wójs, 2004). Intensive shock waves in the system also lead to an increase in the pressure at the centre of the bubble and a significant increase in the surface area of the phase transition boundary, which when repeated, lead to changes in the chemical composition of the system. These effects, due to the large concentration of cavitation bubbles, lead to favourable conditions for the initiation of physicochemical processes, which under normal conditions are complex or difficult to conduct.

4.1 PARAMETERS AFFECTING CAVITATION INTENSITY

The main factors which determine the formation of the hydrodynamic cavitation field and the effectiveness of the cavitation process can be divided into three groups (Figure 4.1).

The first group consists of parameters which determine the structural characteristics of the reactor; the size and shape of the cavitation inducer and the flow chamber. The second group includes parameters characterising the properties of the liquid medium, in the main: viscosity, density, surface tension and the dissolved gas contents. The third group includes parameters that are associated with the characteristics of the technological process; the "processing" time (the number of times the medium passes through the cavitation region), the interdependence between the process's temperature and pressure.

The technological effectiveness of the cavitation process depends on the cumulative effect of the above mentioned parameters.

The range of parameters which describe the cavitation process, in particular the number of cavitation bubbles generated and their implosion conditions (pressure and temperature during bubble collapse), is thus quite extensive.

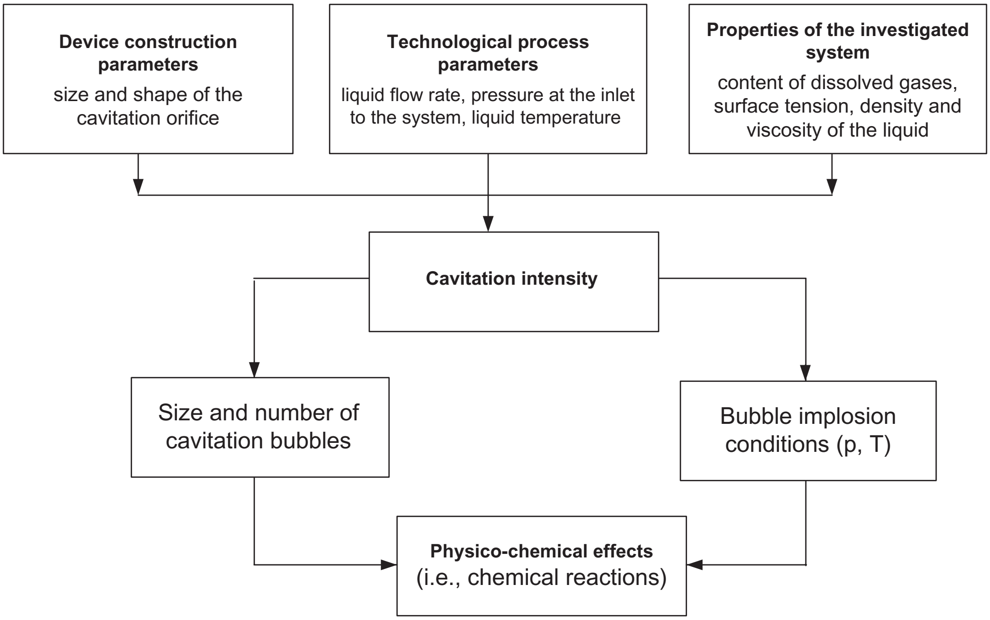

Figure 4.1. Basic factors influencing the intensity of the cavitation process.

The appearance of cavitation in the liquid can be written in the following form (Bagieński, 1998):

$$f\left(\frac{l_1}{l}, \ldots, \frac{l_n}{l}, K, Re, We\right) = 0 \tag{4.1}$$

where:

$l, l_1, l_2, \ldots, l_n$ – Linear values defining the size, shape, location of the body, and in addition its surface condition, microbubble dimensions and solid particles constituting the cavitation nucleus.

K, Re, We – Numbers (Cavitation, Reynolds and Weber) characteristic of cavitation.

Increasing the Reynolds number (Re) is usually accompanied by an increase in the Cavitation number (K). This may be the result of an increase in the flow rate or a decrease in the coefficient of kinematic viscosity, which also leads to local increases in velocity by reducing the thickness of the boundary layer. Increasing the Weber number (We) is usually accompanied by an increase in the Cavitation number. Like the Reynolds number, it is the result of an increase in the velocity or a decrease in the coefficient of surface tension. Surface tension forces tend towards minimising the bubble being formed in water, and in particular make it difficult for the cavitation nuclei to pass through bubbles of finite dimensions.

The deciding factor in the cavitation process is the shape of the cavitation inducer, the liquid flow velocity and its pressure. This process can be viewed as the sum of interactions between individual bubbles or as a cavitation cloud of bubbles (Figure 4.2). This second method gives a true reflection of the process, particularly for a higher cavitation bubble density (Braeutigam et al., 2010). The number of bubbles (cavitation events), size and temperature during the pulse, can be estimated experimentally (sonoluminescence) and/or by the effect of a chemical reaction and theoretically (computer simulation).

In addition to the number of cavitation bubbles, the intensity of their implosions is also important, as well as local pressure increases instigated during this process. Studies into cavitation produced during liquid flow through round nozzles (Gogate and Pandit, 2000, 2001) helped to determine the magnitude of the imploding cavitation bubble pressure (p_c), as a function of the supply pressure (p_{we}) in the cavitation region, the diameter of the cavitation orifice (d_0), the percentage free area of the holes (A), and the initial diameter of the bubble R_0 in the form:

$$p_c = 7527 \cdot A^{-2.55} \cdot p_{we}^{2.46} \cdot R_0^{-0.8} \cdot d_0^{2.37} \; [bar] \tag{4.2}$$

for $R_0 = 0.01–0.10$ mm, $p_{we} = 1–8$ bar, $d_0 = 1–3$ mm and $A = 1–20\%$.

Making use of this correlation and assuming: $R_0 = 0.05$ mm, $p_{we} = 1$ bar, $d_0 = 2$ mm, $A = 5\%$ the magnitude of the pressure, during the implosion of a cavitation bubble, can be calculated which comes out at more than 5000 bar.

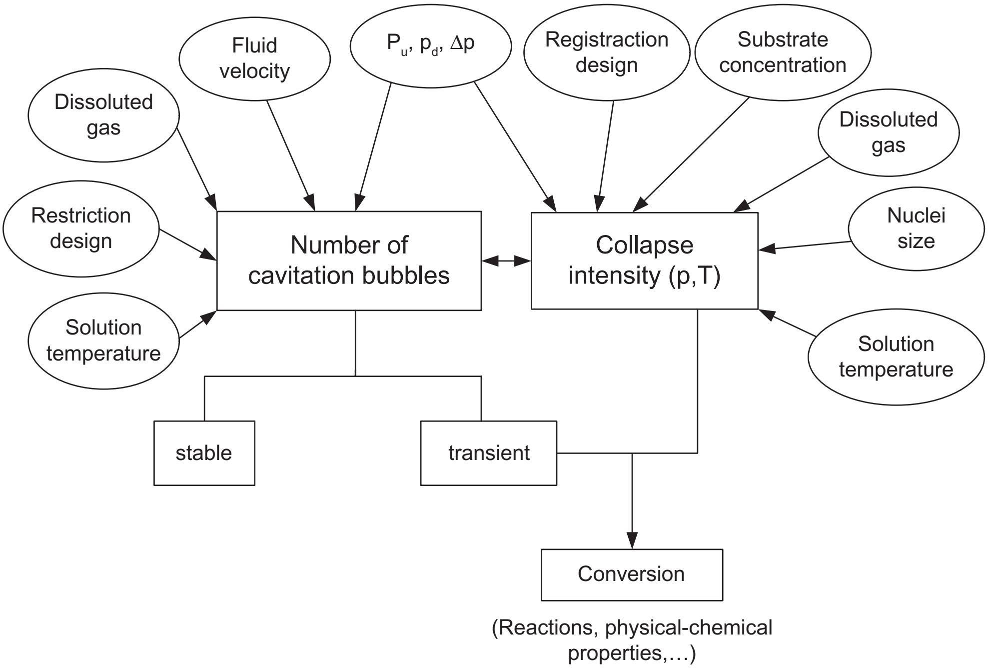

Figure 4.2. An overview of the effective parameters in hydrodynamic cavitation (Braeutigam et al., 2010).

4.2 CAVITATION DEVICE CLASSIFICATION

In the patent literature, information regarding cavitation devices is categorised into nearly 30 classes and subclasses of the International Patent Classification. A lack of an unambiguous classification for this group of devices causes difficulties when selecting device construction for a particular technological process. Assuming a method of generating cavitation in the device (reactor), all known cavitation devices can be divided into three groups (Figure 4.3).

The first group includes devices in which cavitation is generated as a result of hydrodynamic processes associated with a sudden change in flow geometry. As a result of a change in the flow conditions, there is a local reduction in the pressure which favours hydrodynamic cavitation. The change in the flow geometry is achieved by selecting the appropriate shape for the component in the device, located in the path of liquid flow—the cavitation inducer. The energy needed to induce cavitation is fed through the liquid (static matching) or by the help of a rotating inducer (dynamic alignment). These devices are distinguished by their relative simplicity, certainty and convenience of use, high output (up to 100 m^3/h) and significant technological capabilities.

The second group includes devices in which cavitation is generated by periodically changing the liquid pressure hydrodynamically. These are flow devices with ultrasound transducers and impellers of various types (rotational, pulse-rotational and pulse-rotational with a modulated stream), simple by design with an output not exceeding 50 m^3/h.

The third group of cavitation devices are those in which cavitation is caused by pressure oscillations from ultrasound transducers. This group includes cavitation reactor devices which were first implemented in industry. The most

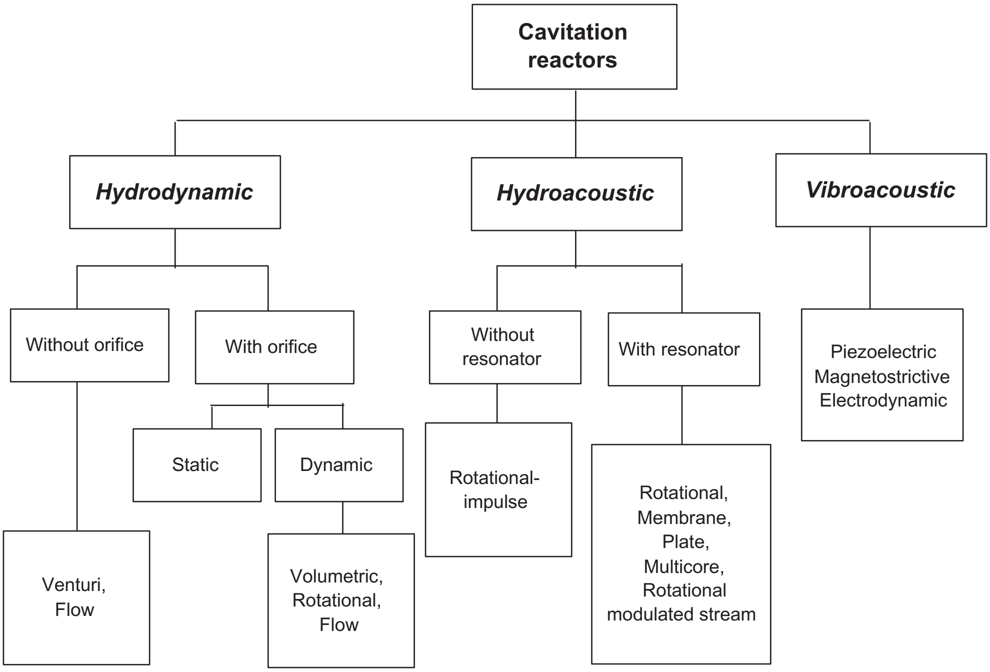

Figure 4.3. Cavitation reactor classification.

common type of ultrasonic devices include: ultrasonic baths, ultrasonic flow devices, and high pressure ultrasonic baths. The disadvantage of these devices is their low output (up to 30 m^3/h) and the need for complex, expensive accessories in the form of ultrasonic generators.

Structurally the simplest and most convenient, in practical applications, are the static hydrodynamic devices. They are characterised by certainty (stability) and a long operating life, resulting mainly from a lack of moving parts. Their simple construction results in lower energy consumption compared to other devices.

In each case, when choosing a cavitation device, it is necessary to perform an appropriate technical and economic analysis. It should be emphasized that hydrodynamic and hydroacoustic equipment is used for flow processes, whilst vibroacoustic most often, when cavitating small amounts of liquid (samples) in laboratories.

The most widely used technology, and therefore with the greatest prospects for industrial application, are the dynamic and static hydrodynamic cavitation devices. In the static type of device, the energy required to induce cavitation is supplied directly by the liquid, whilst in the dynamic device, by the help of rotating elements in the inducer. There is a significant difference in the construction of such devices depending mainly on their technological destiny and working conditions (Litwinienko et al., 2005, Wang et al., 2010, Braetigam et al., 2010, Kumar et al., 2007, Capin et al., 2006).

The main factors which determine the conditions for the initiation of the hydrodynamic cavitation field and the effectiveness of its use can be conventionally divided into three groups (Gogate et al., 2000, Litwinienko et al., 2005).

The first group consists of parameters which characterise the design of the device: the size, the shape of the cavitation inducer and the flow chamber. The second group includes factors which characterise the properties of the system being subjected to cavitation. In the main this concerns: the viscosity, density, surface tension and the amount of dissolved gases. The third group includes parameters that are associated with the characteristics of the technological process: the processing time (the number of times the medium passes through the cavitation region), the interaction between the system stages, the interdependence between the process's temperature and pressure. The effectiveness of the cavitation process depends on the cumulative effect of these factors.

Static hydrodynamic cavitation devices stand out mainly by the shape of the working chamber, the design of the cavitation reactor and inducer, and its size relative to the working chamber (Gogate 2008, Braeutigam et al., 2010, Gogate et al., 2005, Litwinienko et al., 2005).

The diversity of designs used to generate hydrodynamic cavitation does not allow us to consider all the reactor details.

4.3 HYDRODYNAMIC CAVITATION REACTOR SELECTION CRITERIA

The magnitudes of the pressures and temperatures during bubble collapse, as well as the number of free radicals generated at the end of cavitation, are strongly dependent on the operating conditions and configuration of the hydrodynamic cavitation reactors. Investigations into bubble dynamics can help in obtaining guidelines regarding the selection of an optimum set of parameters.

The most important parameters which affect the intensity of the cavitation process are shown in Table 4.1 (Gogate, 2008).

The aim should be to use liquids or conditions which favour the process of cavitation inception and which produce cavities with a lower initial size. These will grow to a larger extent, producing a more violent collapse, and hence greater cavitational activity. Table 4.2 lists some guidelines for the selection of a liquid, based on its physicochemical properties.

Table 4.1. Optimum operating conditions for hydrodynamic cavitation reactors (Gogate, 2008).

Item	Property	Favorable conditions
1	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
2	Diameter of the constriction used for the generation of cavities e.g., hole diameter on the orifice plate	Optimisation 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
3	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)	Smaller free areas must be used for producing high intensities of cavitation and hence the desired beneficial effects

Table 4.2. Guidelines for the selection of a liquid, based on its physicochemical properties (Gogate, 2008).

Item	Property	Affects	Favourable conditions
1	Liquid vapor pressure (range: 40–100 mm of Hg at 30°C)	Cavitation threshold, cavitation intensity, rate of chemical reaction	Liquids with low vapour pressures
2	Viscosity (range: 1–6 cP)	Transient threshold	Low viscosity
3	Surface tension (range: 0.03–0.072 N/m)	Size of nuclei (cavitation threshold)	Low surface tension
4	Bulk liquid temperature (range: 30–70°C)	Collapse intensity, rate of reaction, threshold/nucleation, almost all physical properties	Generally lower temperatures are preferable
5	Dissolved gas A. Solubility B. Polytropic constant and thermal conductivity	Gas content, nucleation, collapse phase, cavitation event intensity	Low solubility Gases with higher polytropic constant and lower thermal conductivity (monoatomic gases)

It is also important to make some recommendations for the selection of a particular type of reactor desirable for a specific application. Moholkar and Pandit (2001) conducted a study modelling the effect of selected parameters on the cavitation intensity in liquid flow for two different flow geometries: venturi constriction and a multiperforated orifice plate.

In the case of a venturi, a large fraction of the stabilised oscillatory radial bubble motion is due to a linear pressure recovery gradient. In the case of an orifice the flow is a combination of both stabilised oscillatory radial bubble motion and transient cavity behaviour, due to an additional oscillating pressure gradient caused by turbulent velocity fluctuations. In addition, the magnitude of the permanent drop in pressure across the orifice is much higher compared with that across a venturi, resulting in a larger fraction of the energy being available for cavitation. Thus, the cavitation intensity will be higher (due to a higher contribution from the transient cavitation) for an orifice system compared with a classical venturi. Bubble dynamics simulations, using various operating/design parameters for the hydrodynamic cavitation reactor, have enabled definite trends to be established for the generated cavitation intensity. This can form the basis for their optimisation in a targeted application. The model also enables the temperature and pressure pulse magnitudes to be quantified for a given set of design parameters. In this investigation the following important strategies have been established for the design of hydrodynamic cavitation reactors:

1. An orifice flow configuration is more suitable for applications requiring intensive cavitation conditions. A venturi configuration is more suitable and energy efficient for milder processes requiring collapsing pressure pulses, typically between 15 and 20 bar, and for transformations based on physical effects.
2. In the case of a venturi flow, the most economical technique for increasing cavitation intensity is to reduce the length of a venturi, but for higher volumetric flow rates there could be a limitation, due to the possibility of flow instability and super-cavitation. A similar argument can be used when reducing the venturi constriction to pipe diameter ratio.
3. In the case of an orifice flow configuration, the most convenient way of controlling the cavitation intensity is by controlling the orifice to pipe diameter ratio (basically throttling the pump discharge through a valve), or the cross-sectional flow area by varying the number and the diameter of the perforations on the orifice plate. However, indiscriminate growth of bubbles downstream from the orifice can lead to splashing and vaporisation (supercavitation).
4. To intensify the cavitation effects, increasing the pipe size downstream from the orifice (which offers a faster pressure recovery) is another option. However, using pipes of a larger size requires higher volumetric flow rates in order to carry out the process using the same cavitation number, resulting in higher processing costs.

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CHAPTER 5

The study of hydrodynamic cavitation in the laboratory

5.1 INTRODUCTION

The basic arrangement for the creation of cavitation, both in the laboratory and in the target technology is the cavitation unit. The cavitation reactor is a physicochemical reactor of a relatively simple build, but the properties of its individual components have a significant impact on the processing of the cavitation liquid. The basic condition for the creation of a diverse cavitation bubble field is the attainment of collapsing cavitation bubbles, of different shapes and sizes, over a period of time. This condition is realised through equipment design.

In order to use the hydrodynamic cavitation process in environmental engineering technologies, it is advisable to make a preliminary analysis of the subprocesses in relation to the proposed technological line of pollutant degradation and then as a result of this analysis to narrow the focus of the laboratory tests.

The results of published research (Litwinienko et al., 2005, Gogate 2008, Cai et al., 2009, Breuitigam et al., 2010) show that the cavitation phenomenon brings with it many desirable physicochemical effects, which can be used in the decomposition and oxidation processing of impurities present in water and sewage.

In order to determine the effects of hydrodynamic cavitation on the decomposition processes of low biodegradable compounds in the laboratory, the following assumptions have been adopted:

1. Cavitation bubbles—caverns appearing during cavitation intensify the physico chemical processes. Rapid changes in temperature and pressure inside the bubble medium and the formation of hydroxyl radicals contribute to the oxidation processes and initiate chain reactions. The contact surface area of the reagents also increases in the chemical reactions. Thus, in order to take advantage of cavitation in water and sewage treatment technologies, it is necessary to generate cavitation in suitable equipment—a cavitation reactor—in such a way that the cavitation region occupies as much space as possible, through which a stream of pollutants can pass and undergo degradation. This also applies to systems in the laboratory.
2. In environmental engineering technologies cavitation should be used in a hybrid form (associated), namely in conjunction with known oxidation methods, which should effectively lead to a more intensive treatment, without the need for excessive expansion of treatment works.
3. Among the various methods of generating cavitation for the needs of sewage treatment, the most appropriate is the hydrodynamic method. It is justified

both for economic reasons (the lowest cost of generating cavitation) and also for construction and operational; namely: simple cavitation reactor constructions (for industrial applications) and easy operation.

The analysis presented in the examples on the use of hydrodynamic cavitation to decompose low biodegradable organic compounds (Arrojo et al., 2008, Sivakumar et al., 2002, Gagate et al., 2010, Szulżyk-Cieplak et al., 2005) allows for the clarification of parameters influencing cavitation intensity. Figure 5.1 is a schematic diagram of a hybrid method for the removal of low biodegradable compounds, utilising cavitation and oxidising agents in the context of the system. The method's concept involves two stages of implementation: cavitation and oxidation and the destruction of pollutants by chemical means.

It should be emphasized that the hybrid method (oxidation assisted by hydrodynamic cavitation) provides the opportunity to use new reaction mechanisms such as sonochemical effects; it also allows for the oxidants to be intensified—in the case of ozone, by a greater mixing of the liquid and gas in regions of the cavitating liquid.

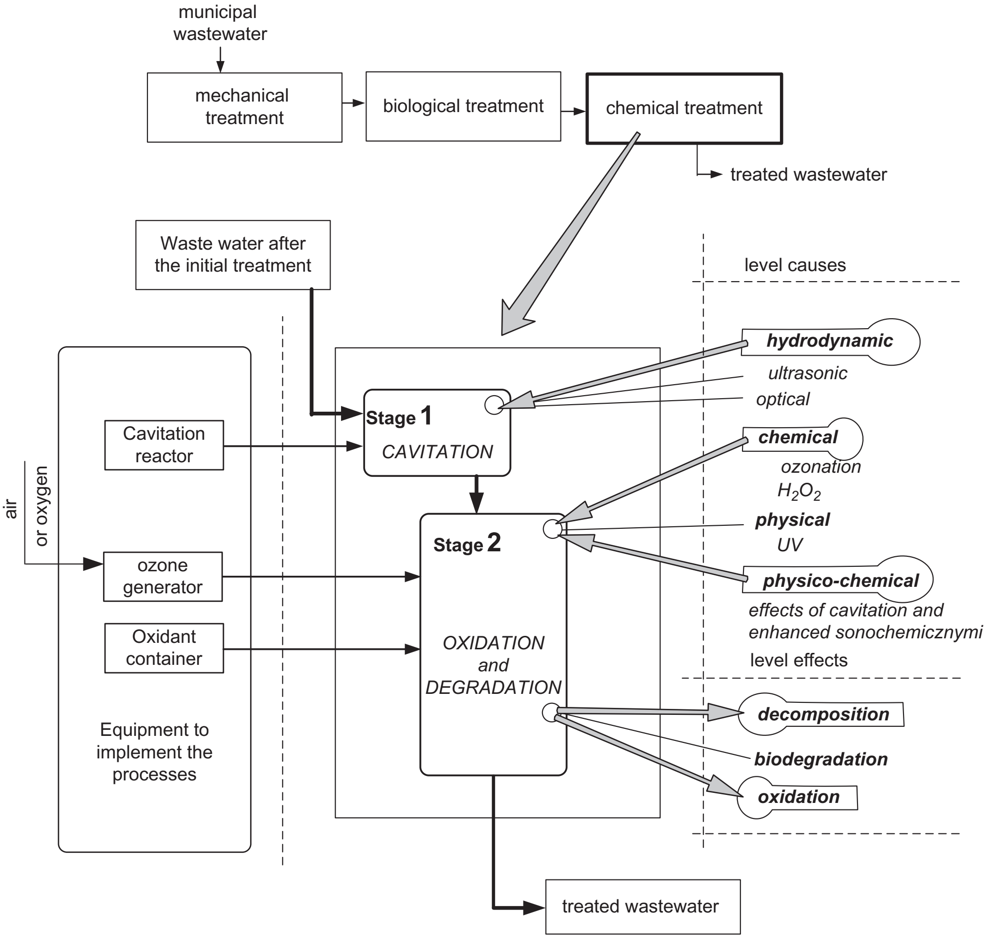


Figure 5.1. Schematic diagram of hybrid methods for the removal of low biodegradable compounds with use cavitation and oxidizing agents.

5.2 THE CHARACTERISTICS AND DESCRIPTION OF THE RESEARCH FACILITY

During laboratory research, use was made of a cavitation reactor, operating on the principle of hydrodynamic cloud cavitation. This cloud was generated in the constriction of a venturi and formed in the region beyond the orifice (cavitation inducer).

Studies were conducted to determine the effect of significant parameters including geometric and hydrodynamic, and to determine the effect of process conditions on the intensity of cavitation. These included research into:

- determine the effect of pressure and flow rate of the liquid on the cavitation intensity
- the effect of the cavitation inducer shape on the cavitation process
- determine the hydrodynamic characteristics of the cavitation reactor

5.2.1 *The research facility*

Figure 5.2 is a schematic diagram showing the facilities used to study hydrodynamic cavitation in the laboratory. The cavitation reactor (1) is connected via pipes to the circulation tank (3) and a Wilo centrifugal pump (2). In the piping, the following valves have been incorporated: Z1—the liquid cut-off valve to the

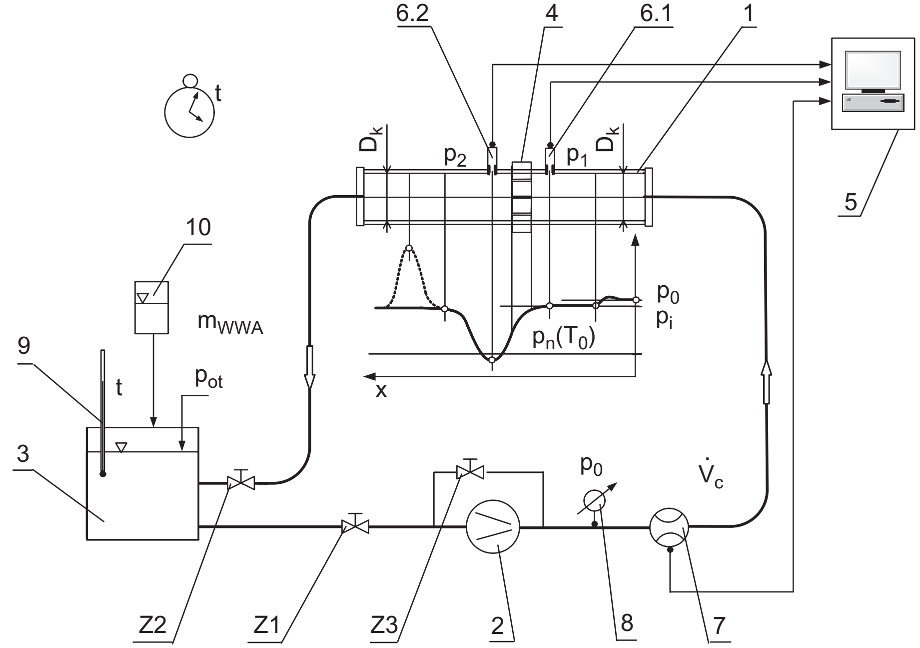


Figure 5.2. The experimental set-up for the generation of hydrodynamic cavitation: 1 – hydrodynamic reactor, 2 – centrifugal pump, 3 – circulation tank, 4 – interchangeable orifice plates with holes (cavitation inducers), 5 – measurement and acquisition system, 6.1 and 6.2 – Keller piezoelectric pressure gauges, 7 – electromagnetic flow meter, Z1, Z2 – valves, Z3 – control valve, 8 – pressure gauge, 9 – thermocouple, 10 – test substance dispenser.

cavitation reactor, Z2—the cut-off valve for the outflow test solution from the reactor to the circulation tank, Z3—control valve. The setup is equipped with a measuring system comprising of: Keller PR-35X piezoelectric pressure gauges (6.1 and 6.2) with a 1 mbar resolution, connected via a databus to a computerised data measurement and acquisition system and a M1500 AA electromagnetic flow meter from Badger Meter Inc. with a resolution of 0.05 dm^3min^{-1} also connected via a databus to the computer system. Temperature readings during cavitation were measured with a thermocouple.

In the model, the solution subjected to cavitation was driven by a pump (2) from a circulation tank (3), of 30 dm^3 capacity, to the cavitation reactor (1), and then returned to the circulation tank (3). Photograph 5.1 shows the liquid supply into the cavitation reactor at a higher pressure along with the liquid flow rate measurement system using an electromagnetic flow meter.

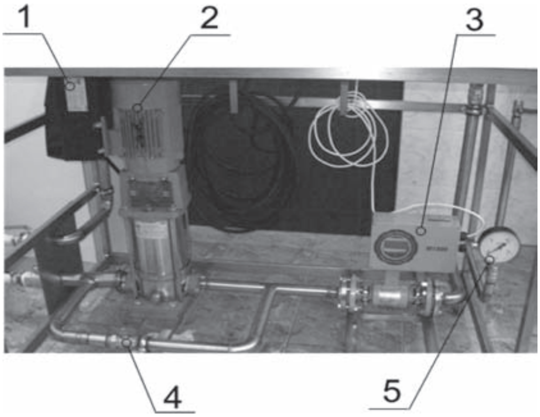
The pressure in the system is generated by a 200–1/16/E/3–2–2G MVIE centrifugal pump manufactured by Wilo. Control is through varying the speed of the electric motor, which drives the pump by means of a thyristor regulator, and hence pump output. The pump output is measured using the M1500 AA flow meter.

5.2.2 *The hydrodynamic cavitation reactor*

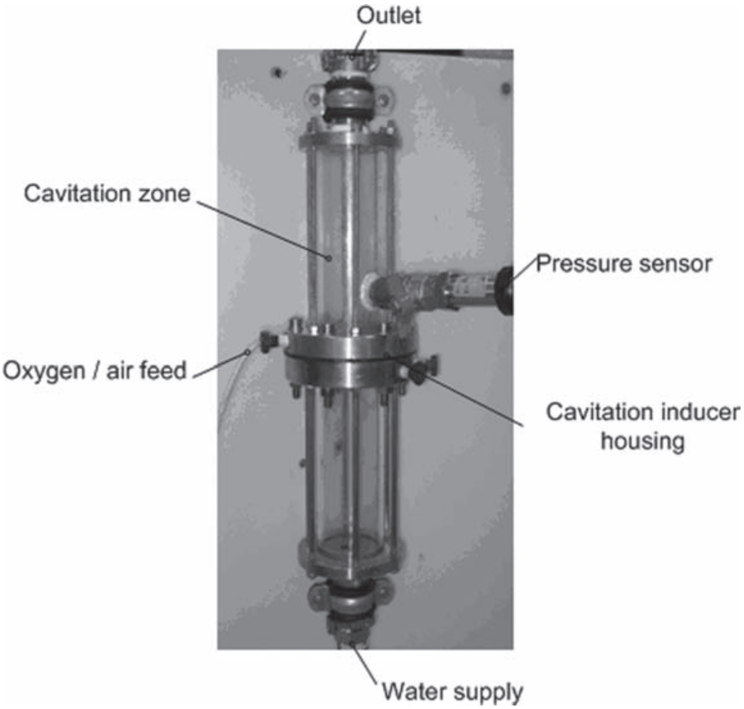
This type of cavitation reactor used in research belongs to a group of devices in which cavitation is generated as a result of hydrodynamic processes associated with a sudden change in flow geometry (Ozonek et al., 2009). Photograph 5.2 and Figure 5.3 show the design schematic and implementation of the experimental reactor during research.

The hydrodynamic cavitation reactor consists of a cavitation inducer (5) and casing. The casing consists of two steel discs (3, 4), bolted together (7) which house the cavitation inducer, tubes of poly (methyl methacrylate) (PMMA) (2, 6) enclose the cavitation region and two tappings (1, 8) enable connection to the system.

In the expansion part of the reactor, the tappings were connected to a measuring device (a Keller pressure sensor) for recording pressure and temperature



Photograph 5.1. The pressure generation and flow rate measurement configuration, 1 – thyristor regulator for pressure control in the cavitation reactor, 2 – MVIW208–1-/16/E/3–2–2G Wilo pump, 3 – electromagnetic flow meter, 4 – ball valve regulator, 5 – pressure gauge control.



Photograph 5.2. Experimental cavitation reactor in the laboratory.

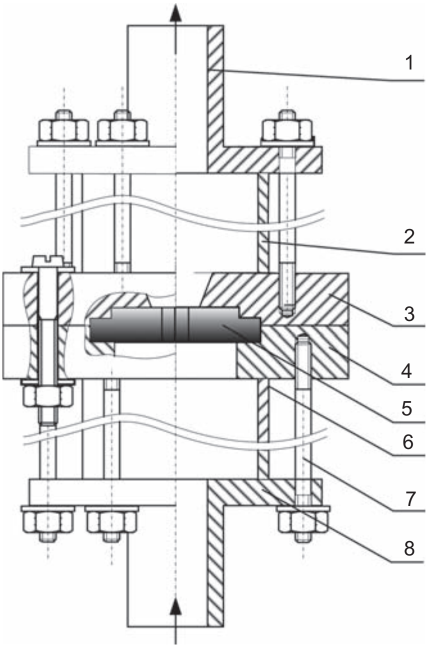


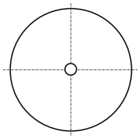
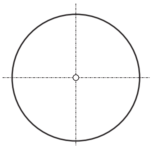
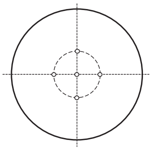
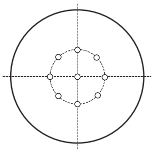
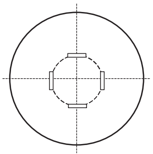
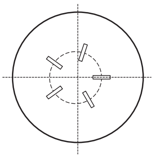
Figure 5.3. Schematic diagram of a cavitation reactor: 1, 8 – tappings, 2, 6 – acrylic glass tube, 3, 4 – steel discs connecting the casings, 5 – cavitation inducer, 7 – bolts connecting the cavitation reactor components, 8 – flashings.

changes in the cavitation region. Cavitation inducers used in the studies were in the form of a steel disc (orifice plate), of 64 mm external diameter with holes, mounted in the body of the cavitation reactor. The cavitation reactor design allows for the quick replacement of cavitation inducers. The cavitation reactor walls are made of organic glass. This allows for continuous observations of the cavitation process. The reactor elements are made of stainless steel, characterised by high chemical resistance and high resistance to erosion and abrasion. Table 5.1 summarises the dimensions of the various cavitation inducers used during the studies.

The following cavitation inducers were used during the studies:

- Inducer 1 – Orifice plate with a 3 mm diameter cylindrical bore located on its axis.
- Inducer 2 – Orifice plate with a 1 mm diameter cylindrical bore located on its axis.

Table 5.1. Design details of the orifice plates (cavitation inducers) used in the study.

Orifice plate number	Orifice plate pattern	Hole characteristics and dimension [mm]	α [mm^{-1}]	β
1		1 hole Φ 3	4.0	0.0042
2		1 hole Φ 1	4.0	0.0013
3		5 hole Φ 1	4	0.0023
4		9 holes Φ 1	2.0	0.0066
5		4 rectangular holes 5 × 1	2.4	0.0021
6		5 rectangular holes 5 × 1	2.4	0.0026

- Inducer 3 – Orifice plate with five 1 mm diameter cylindrical holes, one located on the axis and the remainder evenly spaced around the disk half way out to the circumference.
- Inducer 4 – Orifice plate with nine 1 mm diameter cylindrical holes, one located on the axis and the remainder evenly spaced around the disk half way out to the circumference.
- Inducer 5 – Orifice plate with four holes of rectangular cross-section (1 mm × 5 mm) evenly but tangentially spaced around the disk half way out to the circumference.
- Inducer 6 – Orifice plate with five holes of rectangular cross-section (1 mm × 5 mm) evenly but radially spaced around the disk half way out to the circumference.

The intensity of the generated cavitation significantly depends on the geometry of the component causing the cavitation. The geometry can be described by the geometric numbers characteristic of the hydrodynamic flow conditions. These are parameterised as follows (Sivakumar et al., 2002, Jyoti et al., 2004, Braeutigam et al., 2010):

$$\alpha = \frac{\textit{total sum of all the hole circumferences}}{\textit{the cross sectional area of the pipe}} \ [\mathrm{mm}^{-1}] \tag{5.1}$$

$$\beta = \frac{\textit{sum of the hole area(s) on the orifice plate}}{\textit{the cross sectional area of the pipe}} \tag{5.2}$$

The value β is often referred to as the flow number, its magnitude significantly affects the cavitation number and thus determines the intensity of the resulting cavitation.

For orifice plates used in the studies, equations 5.1 and 5.2 take on the following form:

a) An orifice plate with circular holes

$$\alpha = \frac{4}{d_0} [\mathrm{mm}^{-1}] \tag{5.3}$$

$$\beta = n \cdot \left(\frac{d_0}{D} \right)^2 \tag{5.4}$$

b) An orifice plate with rectangular holes

$$\alpha = \frac{2a + 2b}{ab} \tag{5.5}$$

$$\beta = n \cdot \frac{4ab}{\pi \cdot D^2} \tag{5.6}$$

where:

d_o – diameter of the holes in the orifice plate
a, b – dimensions of the holes of rectangular cross section
D – diameter of the cylindrical part of the cavitation reactor
n – the number of holes in the orifice plate.

5.3 THE EFFECT OF CERTAIN PARAMETERS ON THE CAVITATION INTENSITY

In recent years the conditions necessary to induce hydrodynamic cavitation have been studied intensively. The creation of cavitation bubbles is related to the change in liquid velocity and drop in static pressure. The Bernoulli equation takes these changes into account (Franc et al., 2004, Bagieński, 1998):

$$p_{stat} + p_{dyn} = const = p_{stst} + \frac{\rho}{2} w^2 \qquad (5.7)$$

where:

p_{stat} – static pressure
p_{dyn} – dynamic pressure
ρ – fluid density
w – liquid flow velocity

Bernoulli's equation implies that the sum of static and dynamic pressures is constant. If the liquid velocity increases, dynamic pressure also increases thus lowering the static pressure. If the static pressure reaches the cavitation threshold, cavitation bubbles form. The shape of the cavitation inducer plays an important role on pressure changes during the cavitation process.

Figure 5.4 shows the influence of pressure on changes in the liquid flow rate depending on the shape of the cavitation inducer. At a constant liquid pressure at the cavitation reactor inlet, the flow rate depends significantly on the shape of the cavitation inducer, and increases with a rise in the flow number, β characterising the degree of throttling of the outflow liquid surface area from the orifice plate.

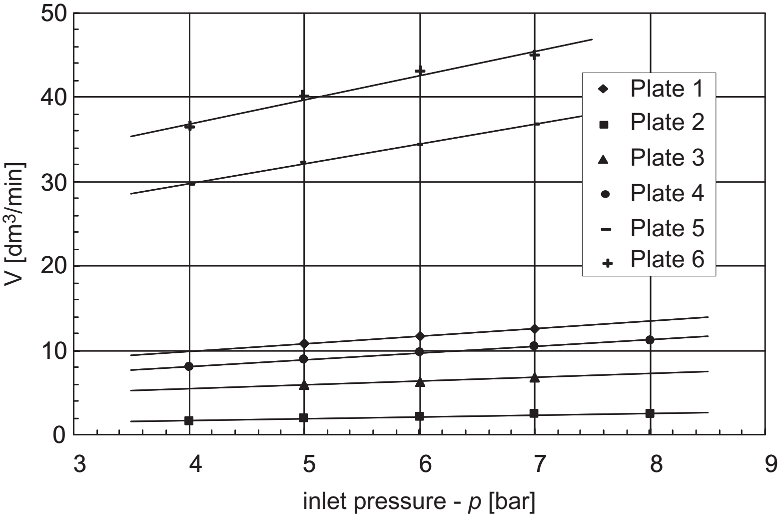


Figure 5.4. Hydraulic characteristics of the orifice plates: the effect of the inlet pressure on the flow rate depending on the shape of the cavitation inducer.

5.3.1 *The shape of the cavitation inducer*

As mentioned earlier, the cavitation inducer design, as well as the number and distribution of holes in the orifice plate, is an important factor for the intensity of the cavitation process.

The important parameters for the hydrodynamic cavitation process are: the pressure (p_1) powering the cavitation reactor, the pressure developed on the expansion side, the saturated vapour pressure of the liquid as well as its density, and the velocity of the liquid flow through the cavitation holes. For smaller cavitation numbers, the number of bubbles produced per unit time increases as well as the intensity of the cavitation process.

Figure 5.5 shows the effect of the inlet pressure to the hydrodynamic reactor on the value of the cavitation number, depending on the shape of the cavitation inducer.

Figure 5.6 shows the effect of the flow number β on the value of the cavitation number at constant inlet pressure to the cavitation system. Smaller values for the cavitation number are achieved by orifice plates with smaller β values.

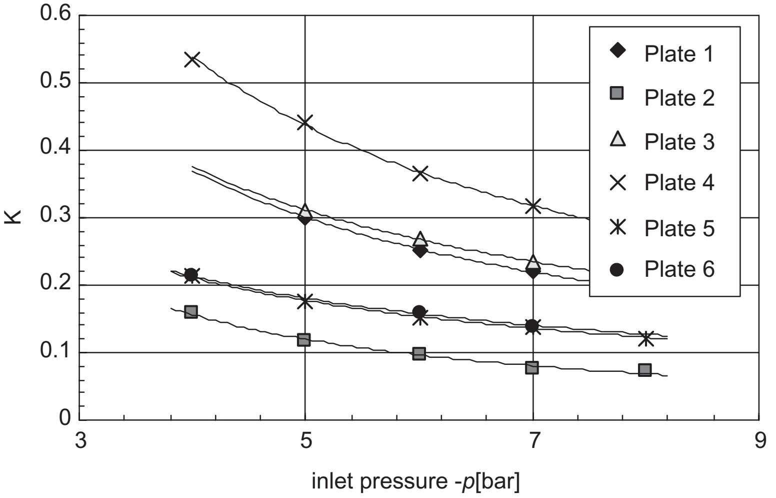


Figure 5.5. The effect of the inlet pressure to the hydrodynamic reactor on the cavitation number depending on the shape of the cavitation inducer.

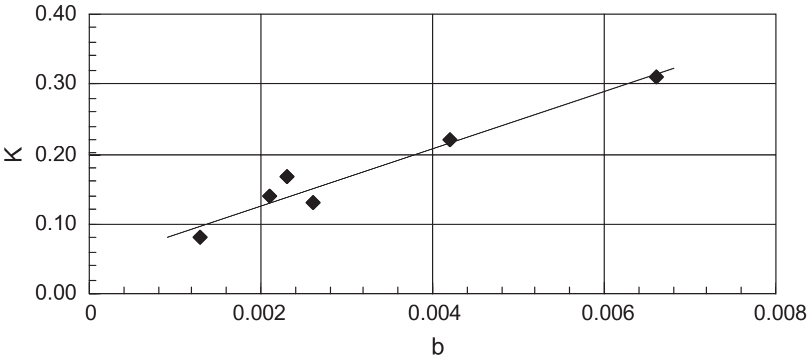


Figure 5.6. The effect of the flow number β on the cavitation number, $p = 7$ bar.

Studies have confirmed that the geometry of the cavitation inducer significantly affects the cavitation number (K), increasing almost linearly with an increase in the cross-sectional area of the cavitation holes compared with the cross-sectional area of the pipe feeding the cavitation reactor. The cavitation number varies in the range 0.1–0.6 and depends on the shape and size of the cavitation inducer (Figure 5.6) and the supply pressure to the hydrodynamic cavitation reactor.

Figure 5.7 shows the effect of the flow number β on the cavitation inducer's outlet liquid flow velocity, with the cavitation reactor powered under constant pressure. An increase in the flow number β decreases the cavitation number and simultaneously intensifies the cavitation process.

5.3.2 *Pressure variations in the cavitation region*

During cavitation studies, pressure variations on the expansion side of the cavitation reactor were recorded using Keller's PR-35X piezoelectric pressure gauge. Figure 5.8 shows for different supply pressures, the pressure variations in the

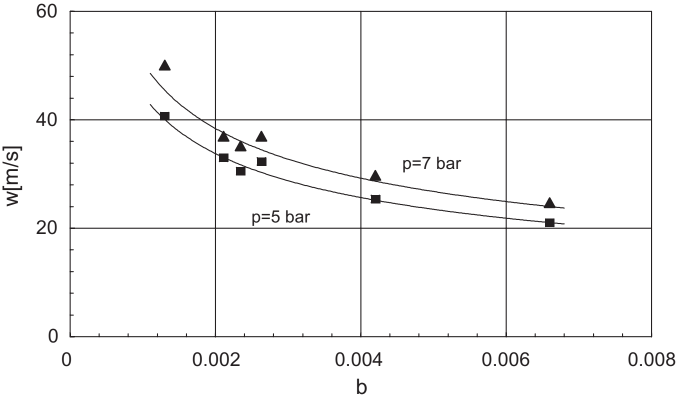


Figure 5.7. The effect of the flow number β on the flow velocity in the cavitation region under various constant pressures.

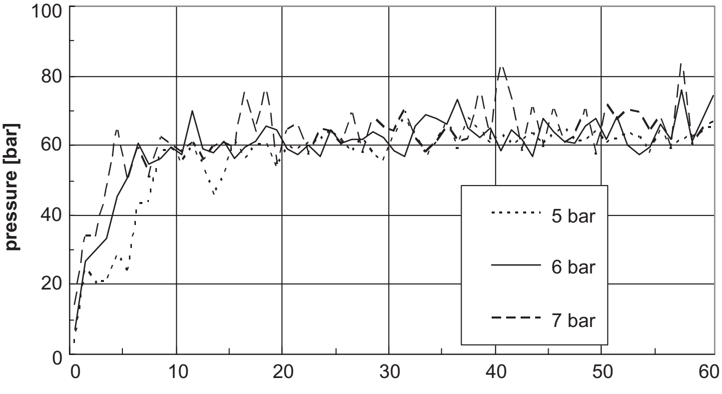


Figure 5.8. Pressure changes during cavitation for orifice plate No. 3.

cavitation region for orifice plate number 3 at a distance of 45 mm from the cavitation inducer.

During the first 7–8 minutes the pressure rises in the cavitation region, which then stabilises regardless of the supply pressure to the cavitation reactor.

Figure 5.9 shows pressure variations in the cavitation region, over short time intervals. The pressure variations occur within a 15% window. It mainly affects the cavitation noise intensity.

Figure 5.10 shows changes in temperature and pressure on the expansion side of the cavitation reactor as a function of the supply pressure at a distance of 40 cm beyond the orifice plate for various supply pressures to the cavitation reactor.

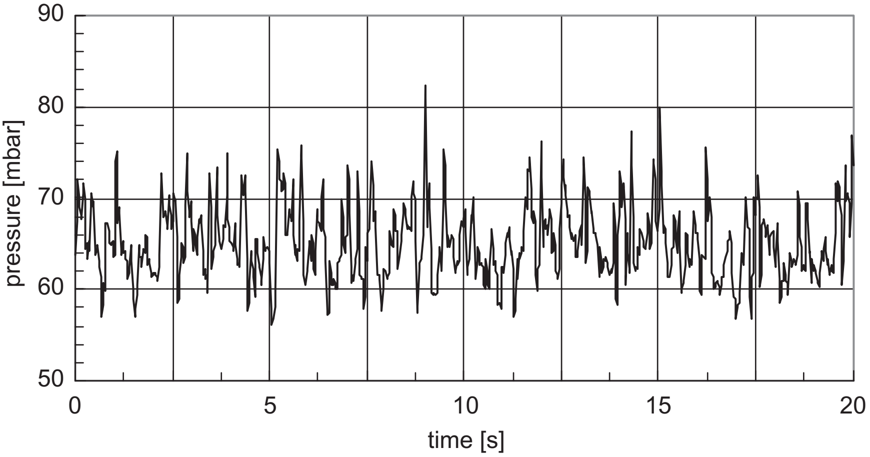


Figure 5.9. Pressure variations at a distance of 45 mm from the cavitation inducer.

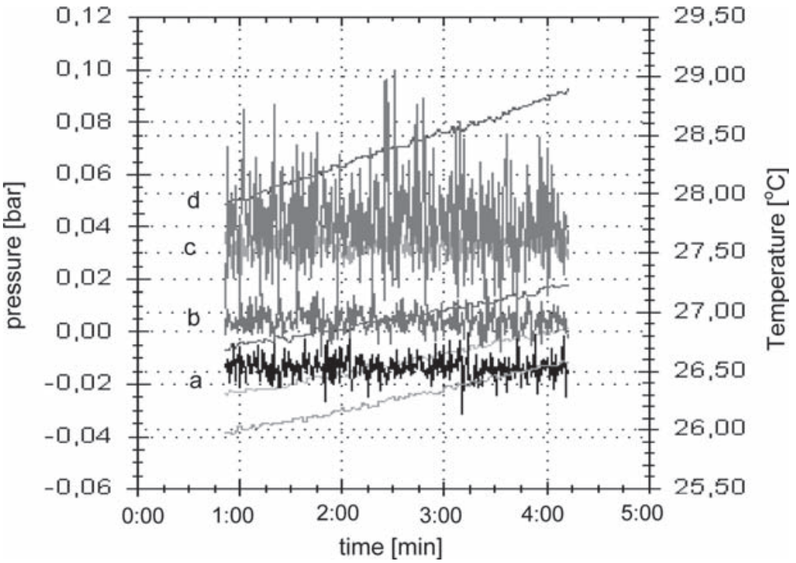


Figure 5.10. Changes to the pressure in the cavitation region and temperature in the cavitating liquid at different supply pressures: a) 6 bar, b) 7 bar, c) 8 bar, d) 9 bar using orifice plate number 3.

During research, in order to determine the extent of the cavitation region the expansion section of the hydrodynamic cavitation reactor was extended to 1 m and Keller piezoelectric pressure sensors were arranged over the entire length. Figure 5.11 shows the pressure change over distance along the expansion side of the reactor for various supply pressures using orifice plate number 3.

The energy efficiency of the cavitation process is an important parameter which affects the energy cost of pollutant degradation. For its evaluation, it is essential to measure the electrical real power consumption in relation to the pressure of the liquid supplied into the cavitation system.

The amount of real power consumed by a centrifugal pump in order to produce the appropriate pressure can be measured with the Kyoritsu KEW 6310 Power Quality Analyser. Figure 5.12 shows the real power measurements over a range of pressures for various orifice plates.

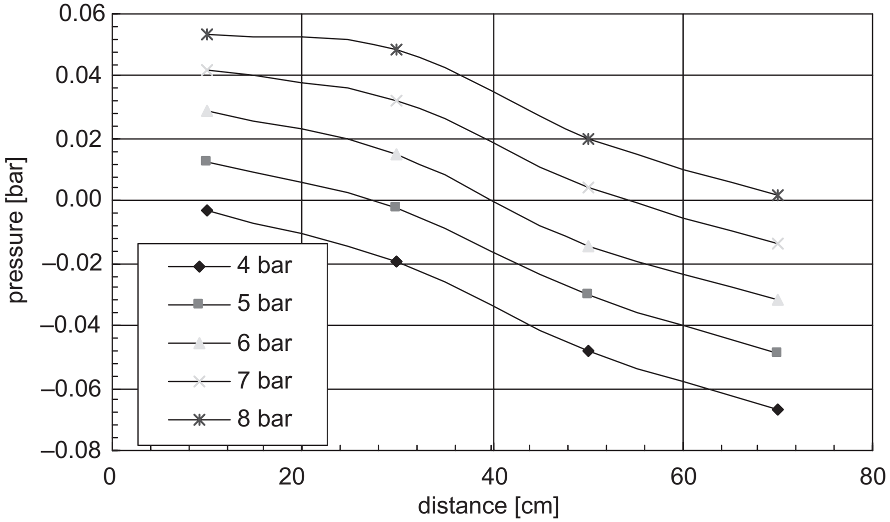


Figure 5.11. Pressure variations over distance from orifice plate number 3 along the expansion side of the cavitation reactor for various supply pressures.

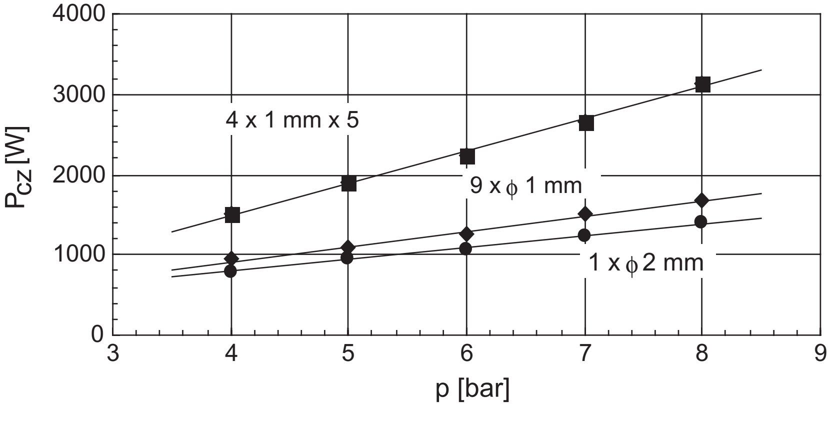


Figure 5.12. The effect of pressure on the real power consumed by a centrifugal pump for different types of cavitation inducers.

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CHAPTER 6

The use of cavitation to aid the water treatment process and effluent decontamination

6.1 INTRODUCTION

The implementation of new technological processes, the intensive application of fertilisers and pesticides, as well as the scarcity and limitations of treatment facilities leads to a reduction in the quality of water resources, which is essential to the proper functioning of the economy. A significant proportion of the toxic organic chemical compounds and biological pollutants (industrial effluents and municipal waste) ends up, in a more or less uncontrolled fashion, in the natural water basins. Purification methods, used to date, do not always produce the desired effects. The new sewage treatment technologies are frequently multistage processes.

With the aim to improve the quality of water and sewage treatment, it is necessary to improve the effectiveness of each of the components in the treatment process. This also applies to the possibility of exploiting the latest treatment methods, and improvements to their effectiveness, because they can contribute to increasing the intensity of these processes.

The most widespread effluent treatment methods are:

- Chemical – dependent on the addition of reactants, adsorbents etc. into the wastewater.
- Technological – which take into account and justify the addition of reactants and improve the required conditions for the reactants to mix with water.
- Physical – associated with ultrasound, magnetic and electric fields, and ultraviolet radiation, etc.
- Biological – the utilisation of compatible bacterial flora.

Making use of each of these methods requires adopting a specific technological process and achieving the required quality standards of the treated effluent.

In all of the water and sewage treatment technologies, the deciding factor are the critical conditions required for the mixing of the reactants. The operating conditions for each of the technologies should ensure for the reactants, contact with the maximum amount of pollutants in the shortest possible time. This requires the search for new technological solutions which ensure high effectiveness, productivity, and reduce energy consumption.

To a large extent cavitation devices fulfil this requirement. As a result of the specific conditions prevailing in the cavitating liquid—localised high temperature and pressure—processes aided by hydrodynamic cavitation, in recent years have been increasingly investigated, with the intention of applying them to water and sewage treatment technologies (Chakinala et al., 2008, Capin, 2006, Kalumuck et al., 2000, Arrojo, 2008, Suschka et al., 2007). The effectiveness of the cavitation process increases significantly when linked to oxidation processes or when used with catalysts (Gogate, 2008). During the sewage treatment process, products such as chlorinated hydrocarbons, aromatic compounds, dyes, phenols and esters are decomposed (Jyoti et al., 2001, Mezule et al., 2009, Vasilieva et al., 2007).

The application of hydrodynamic cavitation in sewage treatment may be considered in two aspects:

- The breakdown of various pollutants as a result of the specific conditions inherent in the cavitating liquid.
- The combined interaction of the mechanical effects of hydrodynamic cavitation and oxidation, through the joint action of cavitation with the oxidants.

6.2 WATER TREATMENT AND DISINFECTION

The purpose of disinfecting water is the removal of pathogenic organisms and their means of survival. Therefore, the disinfection process primarily serves to minimise the epidemiological risk. In practice, to disinfect water on an industrial scale, various chemical and physical methods are applied (Nawrocki, 2010, Biń, 2005). The essence of these methods is the irreversible destruction of the microorganisms' protective wall and then, of the semipermeable membrane that surrounds them. The methods applied to date have certain disadvantages e.g., chlorine, which is commonly used as a disinfectant, at the same time causes the formation of carcinogenic and mutagenic (trichloromethanes) compounds in treated water. In addition, in other chemical methods, higher doses of disinfectants are used, due to the limited mass transfer. Some colonies of bacteria and spores remain in many cases undestroyed. The effectiveness of whichever method depends on several factors, including temperature and turbidity, and the variable resistance of organisms to become inactive. The effectiveness of some techniques, such as UV radiation is limited in technical solutions which cause scattering of UV light (Parker and Darby, 1995). That is why there is a need to develop other techniques for water disinfection. Cavitation, due to its spectacular effects, such as the creation of highly reactive free radicals and intensive mass exchange, offers a very effective tool for water disinfection.

The use of ultrasonic reactors for water disinfection has been fairly well researched and documented in the review journals (Gogate et al., 2004, Goncharuk et al., 2008, Andreozzi et al., 1999). Although hydrodynamic cavitation was considered more effective compared with acoustic cavitation, however, in recent years many studies have been carried out clarifying the nature of the hydrodynamic cavitation process (Gogate et al., 2005, Braeutigam et al., 2010, Arrojo et al., 2008).

An example of the use of cavitation in water disinfection is the research carried out by (Ptoszek et al., 2003) into the application of ozone inside cavitation tunnels. Figure 6.1 shows the laboratory setup for the treatment of water using ozone as an oxidising agent in the cavitation tunnel. The main part of the installation is the cavitation apparatus powered by water pumped from the tank. The cavitation apparatus is equipped with a pipeline of 80 dm^3 capacity. Control points located after the cavitation tunnel, as well as on four points on the pipeline, were used to measure the residual ozone and for obtaining samples.

As a source of ozone, a generator with a capacity of about 8 g/h and a concentration of 1% in air was used. During the study, water was used, after being dechlorinated by sorption on activated carbon. Chlorine compounds, manganese, iron and organic pollutants, in the main, substances that cause turbidity and colour, were removed from the water. The water had the following properties: pH value of 7.3, 3.5 mg O_2/dm^3 oxidation and an overall basicity of 1.8 $mMol/dm^3$. Table 6.1 shows the effect of ozonation, in conjunction with hydrodynamic cavitation, on the residual values of selected pollutants during the study.

Studies confirm that the effectiveness of the oxidation of pollutants depends on the ozone dosage. During ozonation, in the case of water samples containing both manganese and iron compounds, iron compounds were oxidized to a greater extent, whilst manganese was removed to a small extent (2–20%). When manganese was oxidised alone, the degree of removal ranged from 40% to 90%.

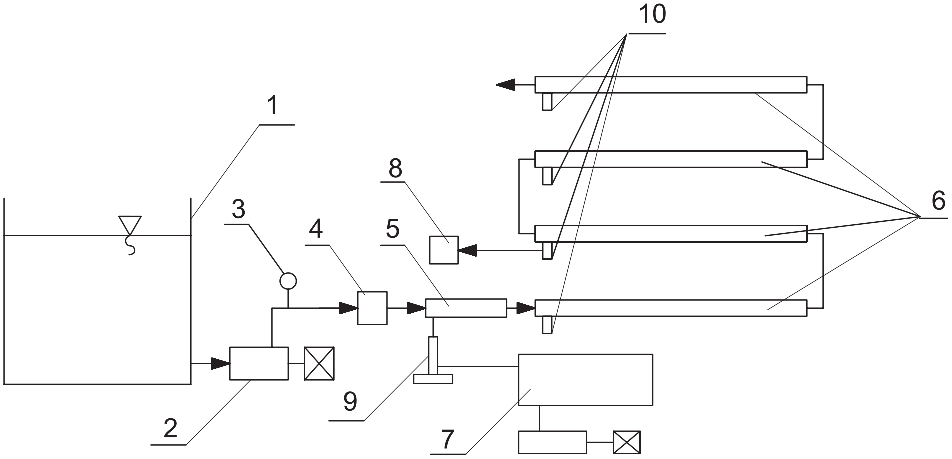


Figure 6.1. Setup schematic: 1 – tank, 2 – pump, 3 – pressure gauge, 4 – flow meter, 5 – cavitation reactor, 6 – pipeline, 7 – ozone generator, 8 – ozone analyzer, 9 – rotameter, 10 – sampling points (1, 2, 3 and 4).

Table 6.1. The effect of ozone dosage on the residual values of selected pollutants from water in conjunction with hydrodynamic cavitation (Ptoszek et al., 2003).

Ozone dose [g O_3/m^3]	0.0	0.3	0.5	0.7	0.9	1.1
Iron [mg Fe/dm^3]	9.1	7.7	6.6	5.2	3.5	1.2
Manganese [mg Mn/dm^3]	1.12	0.79	0.58	0.38	0.19	0.04
Nitrites [mg NO_2^-/dm^3]	0.98	0.82	0.62	0.44	0.29	0.06
Phenol [mg/dm^3]	0.83	0.62	0.52	0.42	0.30	0.22

In cited studies, the manganese oxidation reaction proceeded to yield about 98% after ozone injection. Analysis of the demand for ozone in relation to 1 mg of the removed substance highlights a large uptake of the injected ozone. During the oxidation of phenol, manganese compounds and nitrites, the rate of demand fluctuates near the theoretical values, which are calculated based on the reaction stoichiometry. In the case of samples using iron and a mixture of manganese and iron compounds, this parameter has a value lower than the theoretical demand for ozone. Studies confirm that the oxidation of pollution using ozone in conjunction with cavitation is complex, but using this method, favourable results for the breakdown of selected pollutants in water can be obtained (Ptoszek et al., 2003).

Using ozone assisted hydrodynamic cavitation achieves a greater oxidation intensity of the impurities, with a reduction in ozone consumption. It was confirmed that using ozone assisted hydrodynamic cavitation, the oxidation of pollutants takes place immediately after the injection of ozone, which leads to the elimination of the contact columns. A lack of moving parts in the cavitation tunnels ensures a high reliability, whilst the assembly does not necessitate changes to the technological systems. The distribution of the cavitation tunnels and traditional technological equipment in a single installation expands its technological capabilities. The equipment can be run intermittently or continuously.

The work of (Litwinienko et al., 2005) quotes studies confirming that hydrodynamic cavitation can also exhibit bactericidal activity during water treatment. The use of cavitation for the biological disinfection of water, polluted with 10^6–10^{10} colonies of micro organisms per 1 dm^3 eliminates them with 97–99% effectiveness. Hydrodynamic cavitation also has a destructive effect on yeast, bacteria and even viruses. The neutralisation of micro organisms is caused both by the shockwaves, during cavitation bubble implosions, causing a tearing of the cell membrane, as well as by the production of hydrogen peroxide (Margulis, 1995).

Jyoti and Pandit (2001, 2004) have studied the effectiveness of using ultrasound, hydrodynamic cavitation, ozone and their combined effects to disinfect water. Ultrasound at a 22 kHz frequency and 240 W power was used. Cavitation was carried out at a pressure of 2–6 bar and ozone dosages of 1–4 mg/dm^3 in water jets directed towards the cavitation region. The obtained results confirmed that the hybrid technique for water disinfection is much more effective in comparison to individual methods. The combination of hydrodynamic cavitation and ozonation proved to be the most effective method of disinfecting water from deep-well waters. Using this method means, that the treated water meets the required quality standards and at the same time reduces the amount of disinfectant required. In addition, the amount of ozone used in the process is reduced by half.

The effect of hydrodynamic cavitation on neutralising Escherichia coli was also studied by Mezule (Mezule et al., 2009) on a laboratory scale. The study used a cavitation reactor with a rotating rotor in the form of a disc (Figure 6.2).

Cavitation occurs in the space between the motorised disk and stationary flat surface. The rotor revolved between 9,000–23,000 rpm, the experiment's duration ranged between 3–9 min. Under these conditions, the study confirmed that hydrodynamic cavitation significantly reduces the ability of bacteria to reproduce. An exposure time of 3 minutes at 490 W/dm^3 power reduces the number of E. coli cells by 75%. This method can be used to disinfect drinking water in rural areas.

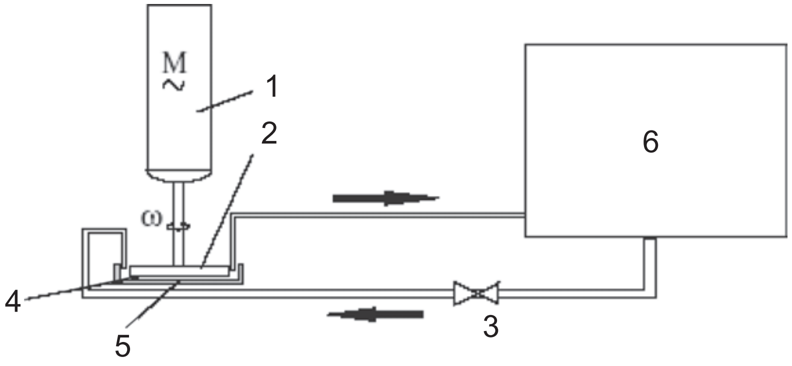


Figure 6.2. Experimental setup of the cavitation system, 1 – electric motor, 2 – rotor, 3 – valve, 4 – liquid layer undergoing cavitation, 5 – plate, 6 – circular tank (Mezule et al., 2009).

In the work carried out by (Arrojo et al., 2008) the study concentrated on the impact of different cavitation inducer designs and cavitation process variables on the rate of E. coli inactivation. During the study various discs were used:

- 1 hole of 5 mm diameter (1 × 5)
- 6 holes of 2 mm diameter (6 × 2)
- 25 holes of 1 mm diameter (25 × 1)

The disk with 1 mm diameter holes removed E. coli to the greatest extent, after 40 minutes of cavitation at 2 bar pressure.

The research confirmed that in a hydrodynamic cavitation environment, disinfection is caused both by chemical and physical processes which lead to cellular dys functionality. The simultaneous interactions of ultrasonic cavitation, ozonation and UV irradiation disinfects water highly effectively. In the work carried out by (Jyoti et al., 2001, 2004b), results were presented confirming that the use of UV radiation allows for the ozonation rate to be increased, ozone consumption to be reduced, and the effectiveness in removing organic pollutants from surface water increased. At the same time, UV radiation may exhibit a catalytic action, accelerating hydrogen peroxide's oxidation of pollutants dissolved in aqueous solutions.

6.3 SEWAGE TREATMENT

Advanced oxidation processes are characterised by a rapid rate of pollutant decomposition, versatility and high effectiveness, but they are also associated with significant reactant costs and energy outlay for their implementation (Naumczyk et al., 2006).

Numerous studies have shown that hydrodynamic cavitation, induced by fluid flow in channel constrictions, or in a cavitation inducer, produces similar effects to those of advanced oxidation processes (Gogate, 2002, Chakinala et al., 2009, Sivakumar et al., 2002).

Amongst the research conducted worldwide, on the use of advanced oxidation processes, particularly thorough investigations were carried out on oxidation using the Fenton's reaction. Under these conditions, a 60% reduction in COD is achieved from an initial value of around 10,500 mg O_2/dm^3 (Lopez, 2004). Bae et al., (1997) obtained a reduction in COD of 63%, whilst in a three stage system: biological treatment with nitrification, Fenton's reaction and biological treatment, a reduction down to 97%. The use of ultrasound (50–150 W) reduced the COD value between 11–16%, from an initial concentration of 4,770 mg O_2/dm^3 (Wang et al., 2008). In processes involving ozone, H_2O_2 and UV radiation, reductions in COD of 42%, 15% and 15% respectively were achieved, whilst the most effective turns out to be the combination of several methods such as H_2O_2/O_3. The O_3/UV and H_2O_2/UV processes helped to reduce the COD value by 54%, and as a result of applying the H_2O_2/O_3/UV process, the COD value was reduced by 79% (Ince et al., 1998).

Recently, intensive research is being carried out into using ultrasound and hydrodynamic cavitation, as well as their application in conjunction with various oxidation methods in sewage treatment.

The works of Margulis (Margulis, 2004, Margulis et al., 2004) confirmed ozone production in a high-intensity ultrasonic field, under cavitating conditions. This effect is the result of cavitation bubble deformation and the placement of ions of opposite polarities on opposing surfaces. For imploding bubbles of 5 μm diameter, the electric field may reach 10^6 V/m. Under such conditions, electrical discharges occur and ozone is produced.

The results from studies into sewage treatment, involving hydrodynamic cavitation, were presented by Mołchanov and colleagues. The study (Mołchanov et al., 2002) investigated the possibility of generating ozone in a cavitating liquid environment and using it to oxidise the pollutants in sewage and to disinfect water in a circular system.

The cavitation reactor (Figure 6.3) is constructed in the shape of a pipe (1) enclosing a conical obstacle (2) mounted on ribs (3), at a distance (δ) of 2 mm from the pipe wall. When the liquid flows behind the obstacle (cavitation inducer), a cavitation region of reduced pressure occurs, into which air is sucked through a nozzle (4).

Tables 6.2 and 6.3 show the results of studies conducted for selected sewage in a circulation system, using a pump of 7 m^3/h capacity in a 17 mm diameter cavitation reactor. The cavitation effectiveness on municipal sewage, oily and dairy effluents relating to pollutant concentrations expressed as COD is summarized in Table 6.2, whilst changes to the amount of E. coli bacteria in municipal sewage are summarised in Table 6.3.

These results demonstrate the practical possibilities of using cavitation to generate traces of ozone for oxidation and/or decomposition of pollutants in sewage.

Magnum Water Technology Inc. (USA) is the only company in the world making use of hydrodynamic cavitation on an industrial scale, incorporated in the CAV-OX system for industrial trade effluent (Figure 6.4). The adopted hybrid system combines hydrodynamic cavitation with UV radiation and hydrogen peroxide to oxidise organic compounds present in water and sewage at concentrations of a few $\mu g/dm^3$. Such a system is characterized by a high degree of decomposition of volatile organic compounds, in the main: chloroform, benzene, toluene, phenol and xylene. Hydrogen peroxide, along with the polluted water is directed into the cavitation reactor, after which the cavitated effluent is subjected to UV radiation. During cavitation, additional hydroxyl radicals

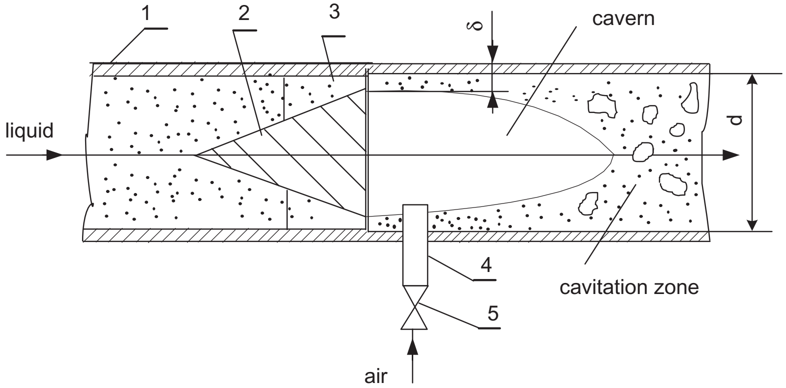


Figure 6.3. Schematic of the hydrodynamic ozonizer: 1 – pipe, 2 – conical obstacle, 3 – rib, 4 – nozzle, 5 – valve (Mołchanov et al., 2002).

Table 6.2. The effectiveness of a hydrodynamic ozonizer in a circulation system at a temperature between 20–23°C and 3 bar pressure.

	COD [g O_2/m^3]				
Circulation time t [mins]	0	30	60	90	120
Municipal sewage sample 1	590	515	430	415	365
Municipal sewage sample 2	590	320	200	150	90
Municipal sewage sample 3	590	475	390	350	250
Oily effluent	1200	900	600	420	230
Dairy effluent	2250	1650	1350	1125	900

Table 6.3. Changes in the number of E. coli bacteria in municipal sewage at 3 bar pressure and temperature between 20–23°C.

Time [min]	0	20	30	40	50	85	110
E. coli [No/dm^3]	$2.2 \cdot 10^6$	$2.2 \cdot 10^5$	$2.2 \cdot 10^4$	$2.2 \cdot 10^3$	$2.2 \cdot 10^2$	45	25

are produced, which increase the degree of decomposition. Under UV radiation, the number of free radicals also increases, mainly due to hydrogen peroxide decomposition. The extent to which organic pollutants present in the effluent are removed ranges from 20% to 99% (Gogate, 2008).

Investigations into the effect of hydrodynamic cavitation on the effectiveness of treating communal sewage at the “Hajdów” sewage treatment works in Lublin are presented in the work carried out by (Korniluk and Ozonek, 2010). Effluent samples were taken following mechanical cleaning but before the biological stage. These effluents are characterized by relatively high COD values and are devoid of large floating pollutants which could hinder cavitation. The effluent used in the analysis was pre-filtered through a filter fabric. Figure 6.2 in Chapter 6 shows a schematic diagram of the study undertaken.

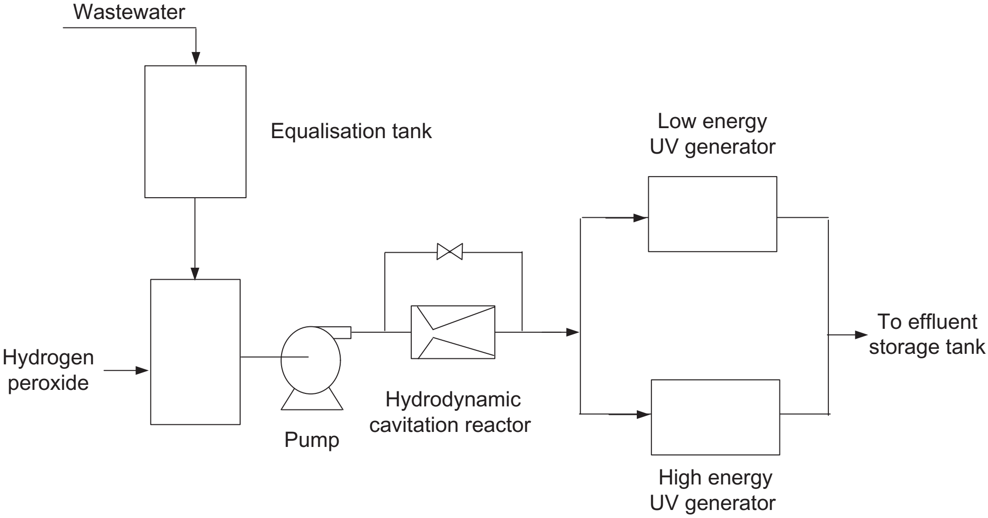


Figure 6.4. Schematic diagram of the CAV-OX process.

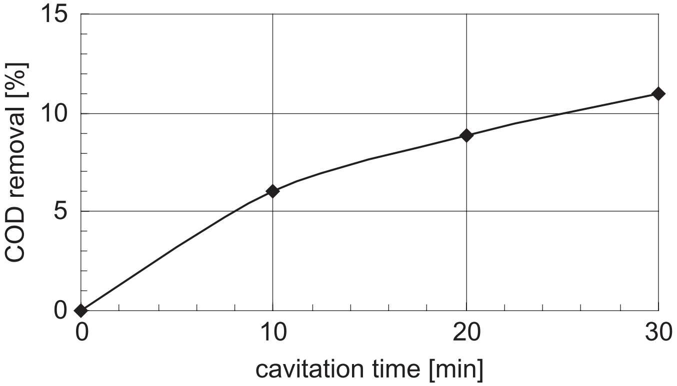


Figure 6.5. The effect of hydrodynamic cavitation on COD removal from sewage.

The efficiency of the sewage treatment with respect to COD can be determined according to the formula:

$$\eta = \frac{ChZT_o - ChZT}{ChZT_o} \tag{6.1}$$

where:

$ChZT_o$—The initial COD value for filtered effluent.

Figure 6.5 shows changes in the COD value over time for sewage in a cavitation system.

Sewage, after filtration, had a COD value of 240 mg O_2/dm^3, which after 30 minutes of cavitation was reduced by around 10%. It can be assumed that

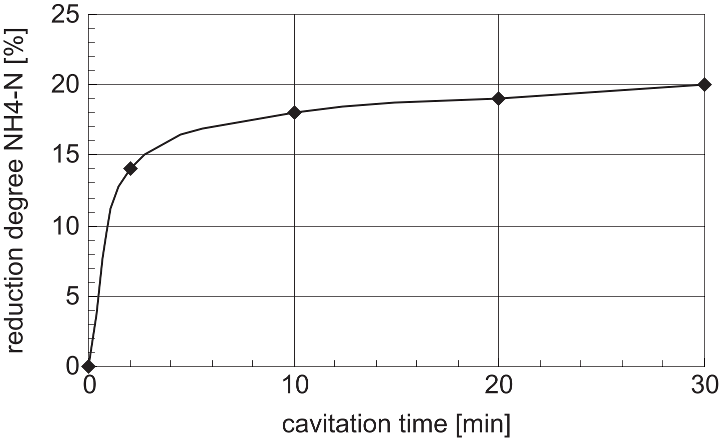


Figure 6.6. The effect of hydrodynamic cavitation on the reduction of NH_4-N in sewage.

increasing the processing time will lead to further reductions in the COD value of the cavitated liquid, but it is also associated with an increased energy demand for the process. Therefore, in order to optimise and improve the efficiency of the process, the aim will be to combine cavitation with another oxidation technology.

During the study, changes in the concentration of ammonium nitrogen were analysed (Figure 6.6). Starting with an initial value of 50.5 mg/dm^3 of ammonium nitrogen, after 30 minutes of cavitation an 18.5% reduction was noted. A significant reduction in this parameter's value was noted in the first minutes of the process.

6.4 CLEANING LEACHATE FROM MUNICIPAL LANDFILLS

Leachates are the result of rainwater percolating through the landfill, which wash out organic compounds and minerals resulting from changes occurring in the stored waste. Both the quantity and composition of the leachate are subject to change, depending on amongst others, the type of waste, the age of the landfill and the quantity of waste (Renou et al., 2008, Derco et al., 2010, Surmacz-Górska, 2001). The result is that at each landfill the leachate composition is different and over the landfill's lifetime undergoes significant changes. Consequently, the development of universal and effective leachate purification methods, on many landfills, remains an unresolved problem.

Leachate from landfills are generally characterised by high concentrations of organic matter (COD on average 3,000–10,000 mg O_2/dm^3) and total nitrogen, mostly in the form of ammonium nitrogen (on average 400–3,100 mg/dm^3) (Renou et al., 2008). These effluents also contain toxic refractive compounds such as BTEX, PAHs, PCBs and heavy metals (Renou et al., 2008, Paxeus, 2000, Surmacz-Górska, 2001).

The susceptibility of the leachate to biodegrade is characterised by the ratio of BOD_5/COD. In the case of leachates from landfills, this ratio also depends on the age of the landfill; for young landfills (3–5 years) it is about 0.7, whilst after

10 years of operation can even reach a value of 0.1, indicating that the organic substances present are mainly in the form of low biodegradable compounds.

Most importantly, in leachate from landfills, organic compounds very often considered to be dangerous are present, causing endocrine system disorders in living organisms. Numerous studies conducted over the past two decades confirm that these types of compounds interact with the endocrine system and cause adverse effects in humans, animals, fish and birds. These types of compounds interact with the endocrine system in many ways. The endocrine system is in fact, one of the most sensitive communication networks in each organism. It affects all aspects of our health such as cognitive functions, reproductive potential, metabolism, digestion, and hormone balance.

Research conducted by Paxéus (2000) on three old municipal and industrial landfills in the surrounding area around Gothenburg, in Western Sweden (two landfills operational, one closed down) allowed for more than 200 organic compounds to be identified in concentrations ranging from 1 $\mu g/dm^3$ to more than a few hundred $\mu g/dm^3$. Amongst the compounds analysed, the presence of approximately 40 potentially dangerous organic substances was confirmed. These included:

- Organochlorines – chlorobenzene (0.1–62 $\mu g/dm^3$)
- Aromatic alkyl hydrocarbons – toluene (1–17 $\mu g/dm^3$), xylene (0.3–310 $\mu g/dm^3$)
- Polycyclic aromatic hydrocarbons – naphthalene (0.4–400 $\mu g/dm^3$), phenanthrene (0.6–52 $\mu g/dm^3$), pyrene (3 $\mu g/dm^3$)
- Phthalates – diethyl phthalate (0.1–4 $\mu g/dm^3$).

For the treatment of leachate from municipal landfills, biological, physicochemical, and combined (hybrid) methods are used. The choice of treatment method largely depends on the susceptibility of the organic compounds in the leachate to biodegrade.

Biological methods are usually applied to leachate from young landfills, characterised by a high BOD_5/COD ratio. Literature data shows that the effectiveness of removing organic compounds using biological methods, is significantly reduced when the leachate comes from old landfills and contains mainly low biodegradable organic compounds. In such cases physicochemical methods, such as advanced oxidation processes (Naffrechoux et al., 2000) and membrane (Bodzek, 2002, Kulikowska, 2009), turn out to be effective.

To decompose refractory compounds present in effluents, advanced oxidation processes are becoming more widely employed. Fenton's reaction is very often used by those researching into the application of advanced oxidation processes. Under these conditions, with an initial COD value of around 10,500 mg O_2/dm^3, this value is reduced by 60% (Lopez et al., 2004). Bae et al. (1997) obtained a COD reduction of 63%, whilst for a three stage system: biological treatment with nitrification, Fenton's reaction, and biological treatment leads to a COD reduction of 97%. The use of ultrasound (50–150 W) reduced the initial COD concentration of 4,770 mg O_2/dm^3 by 11–16% (Wang et al., 2008).

Examples of photochemical oxidation using the O_3/UV method (WEDECO) can be found in the cited literature. When the leachate was retained for 4.3 hours and a 686 g O_3/m^3 dose of ozone, a reduction in the COD value from 377 to 77 g O_2/m^3 was achieved. With a retention time of 7.5 hours and a 560 g O_3/m^3 dose of ozone, the reduction was down to 32 g O_2/m^3 (Kulikowska, 2009).

In the subject literature there are many reports on the use of acoustic cavitation, with its associated processes, in water and sewage treatment technologies (Gogate et al., 2005, Kulikowska, 2009). However, the use of hydrodynamic cavitation to decompose and/or oxidise the pollutants in the leachate from municipal landfills is still an unexplored area, despite knowing about this process for many years.

Korniluk and Ozonek (2011) conducted a study into the pre-treatment of leachate from the municipal landfill at Leczna, near Lublin. Table 6.4 shows some of the characteristic parameters for the leachate used in the study. Samples were analysed for pH, total suspended solids (TSS), Turbidity, COD, BOD_5 and TOC.

This leachate has a high concentration of recalcitrant organic matter, as indicated by its COD value, and low biodegradability with a BOD_5/COD ratio of around 0.1. According to the literature (Wu et al., 2004) the leachate falls into the stabilised form category.

The study concentrated on the efficiency of COD removal. Figure 6.7 illustrates the decrease in COD values for the landfill leachate samples as a function of reaction time. The reduction achieved in the first 30 minutes of treatment, using solely cavitation, is about 5.8%. However, when ozone is used in combination with cavitation, the COD value reduces by 10.3%. The maximum

Table 6.4. Characteristics of the landfill leachate used in the experiment.

Parameter	Value
pH	6.7–6.9
COD	3300–3600 [mg O_2/L]
TOC	470 [ppm]
BOD_5/COD	0.09–0.1
TOC/COD	0.15
TSS	1050–1200 [mg/L]
Turbidity	570–640 [NTU]

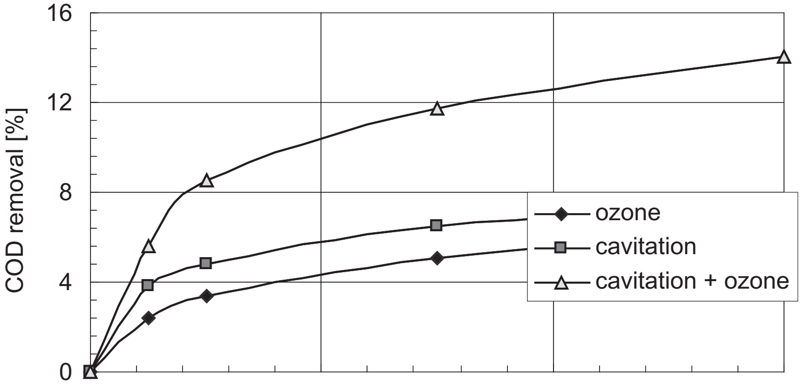


Figure 6.7. The effect of hydrodynamic cavitation and ozone on COD removal.

reduction for sole cavitation is about 6.8%, whilst for cavitation with ozone it is about 13.5%. From Figure 6.7, it can be seen that cavitation with ozone is a more effective process for COD removal than for sole cavitation.

Comparing the results obtained for ozone and cavitation individually, shows that they are similar over the treatment time. Ozonation as a single process is not considered to be very effective at COD reduction since it is about 6%.

6.5 SLUDGE DIGESTION

Sewage treatment processes are associated with the formation of sludge, whilst its quantity depends on the purification method. The most commonly used biological method for the purification of municipal sewage is sludge treatment, which is also used in the treatment of industrial trade effluent (Bień et al., 1995). Despite the fact that sludge is less than 5% sewage by volume, sludge disposal often consumes more than 50% of the operational costs at each treatment works. Conventional activated sludge treatment processes are accompanied by a relatively high production of sludge in relation to the removed pollution load (BOD_5). Hence, with ever increasing costs of sludge disposal, increasing attention is being paid to ways of reducing the growth of biomass at the sewage treatment stage. The physical processes which minimise sludge and make use of cavitation, such as ultrasonic (Muller, 2000) or hydrodynamic (Moholkar et al., 1999, Suschka et al., 2007) decomposition, require additional equipment (ultrasound generators, specially designed nozzles or pumps), which make them very energy and cost consuming processes.

Sludge digestion is the process of destroying the sludge structures (rupturing cell membranes included), accelerating cell hydrolysis by releasing the cells' contents into the water present in the sludge, and allowing the initiation and increasing the level of biological decomposition (Zhang, 2007). The application of a sludge digester facilitates the hydrolysis stage producing methane (which is the essence of this process), and impacts on minimising the quantity of sludge remaining for final disposal. Sludge digestion can be used to improve the effectiveness of the biological decomposition processes for sludge (including accelerating methane production, increasing gas production, increasing the digestion level, shortening the digestion time) by increasing the cells' hydrolysis rate and increasing the decomposition of low biodegradable substances (Gronroos et al., 2005). Another advantage derived from sludge digestion is the possibility of utilising substances released from cells, as a source of easily absorbable organic carbon in the denitrification process, when it is deficient in the incoming effluent.

Favourable results for sludge digestion were obtained using cavitation nozzles (Suschka et al., 2007). A high technological effectiveness allows for the use of hydrodynamic cavitation to intensify biogas production. The studies used recycled activated sludge from the sewage treatment works, using advanced biological processes in the treatment of effluent, dependent on the simultaneous removal of organic compounds as well as nitrogen and phosphorus compounds.

Samples of activated sludge were supplied by a worm pump (Figure 6.8) at a pressure of 12 bars to the cavitation nozzle, at the outlet, where so-called fog cavitation occurred.

During the digestion (destruction) of the activated sludge cells, under cavitation conditions, into the solution of the surrounding liquid, the accumulated organic compounds and enzymes inside the cells are released, which impact the COD value (by raising it) and the products of hydrolytic decomposition.

Comparing the digestion results for activated sludge (Figure 6.9) it can be seen that the amount of biogas produced rose by 20% when hydrodynamic digestion was used.

The study results confirmed that digestion strongly affects the amount of biogas produced, resulting in a lower dry solid content, and consequently less sludge for final disposal. The positive effect of digestion is a greater susceptibility of the sludge to drain (Suschka et al., 2007).

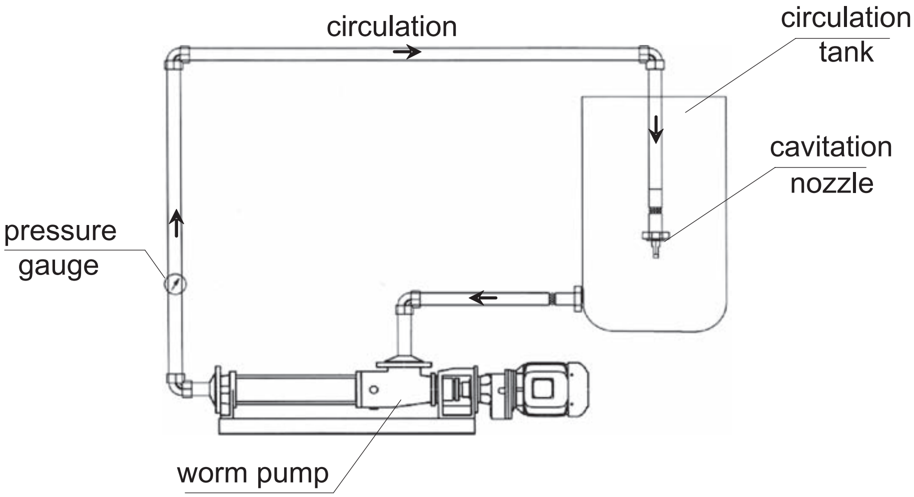


Figure 6.8. Schematic of the experimental configuration of activated sludge disintegration.

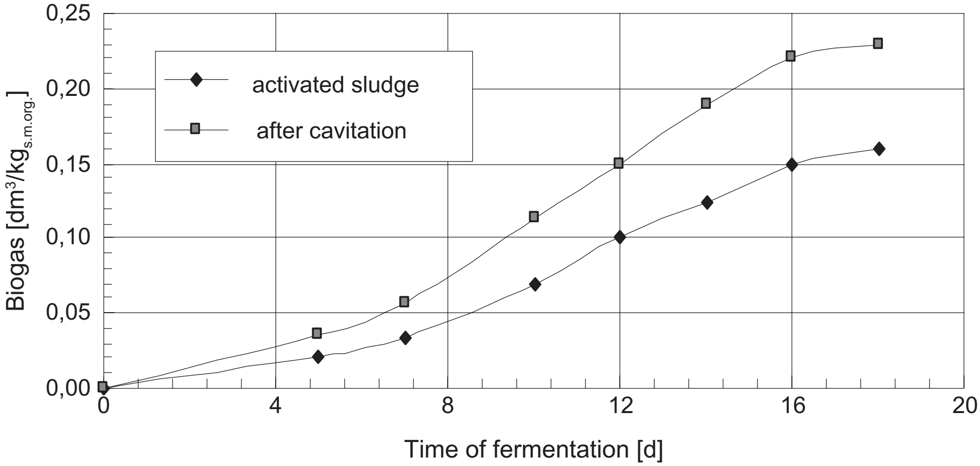


Figure 6.9. Biogas production over time using anaerobic digestion (Suschka et al., 2007).

6.6 THE DEGRADATION OF ORGANIC COMPOUNDS IN AQUEOUS SOLUTIONS

Many organic compounds that are found in sewage are of low biodegradability and very toxic. Most commonly, they are mixtures of different organic compounds such as dyes, surfactants, halides, aromatic compounds, polycyclic aromatic hydrocarbons (PAHs), etc. The traditional treatment methods do not give satisfactory results. Modern sewage treatment technologies are multi-stage processes. Following the mechanical processes, a variety of physicochemical or chemical processes are used, followed by biological decomposition. The aim is to develop methods that are effective and cheap. Of particular interest are advanced oxidation methods (AOPs), including processes using ultrasound (Margulis, 2004) and hydrodynamic cavitation (Gogate, 2010, Capin et al., 2006, Cravotto et al., 2010).

Sewage treatment technology involving ultrasound and hydrodynamic cavitation is becoming more widely used in the textile industry (Gogate et al., 2005). Dyes are particularly difficult to remove from the textile effluent. Dyes used in the textile industry are mainly low biodegradable products of chemical synthesis, whose formula is often undisclosed by the manufacturer. Their removal and decomposition during chemical and biological treatment is particularly difficult and poses the greatest problems (Ledakowicz et al., 2001, Lifka et al., 2003).

One of the most difficult to decompose is the effluent produced in textile factories. The main sources of post-production effluent are all the so called wet processes, in which the water, in terms of quantity, is a basic component of the technology. These include washing, bleaching, dyeing, rinsing, printing and ennobled finishing. The specifics of this type of effluent is generally very high pollutant concentrations, and consequently raised values for parameters such as COD, BOD_5 or total organic carbon (TOC).

Currently, there are more than 3,000 different types of dye used throughout the world. Approximately 600,000 tonnes of dye are introduced annually into the various parts of the global environment. Even low concentrations of dye in natural waters significantly reduce light transmission. This increases the risk of oxygen deficiency, as it hinders photosynthesis carried out by algae and plants present in the aquatic environment. In many cases, microorganisms cannot metabolise all the pollutants present in the effluent, due to the cell wall structure and also, often because of the toxicity of these compounds.

Dyes, as persistent compounds, present in the effluent (usually industrial), are difficult to decompose, both by physicochemical as well as biological methods. Most are absorbed by the activated sludge biomass, and along with it are removed from the effluent.

The Pandit team (Sivakumar et al., 2002, Mishra et al., 2010), using rhodamine B as an example on a laboratory scale, investigated the use of hydrodynamic cavitation to decompose dyes in aqueous solutions.

The impact of the reactor geometry, including the shape of the cavitation inducers on the degree of degradation was analysed. Figure 6.11 shows a schematic of the laboratory test rig. Cavitation was carried out in a closed circuit through a buffer tank of 50 dm^3 capacity. The main system elements are: centrifugal pump, control valves and a cavitation inducer with interchangeable plates.

The research used six types of discs, made from stainless steel (SS316), whose characteristics are summarized in Table 6.5, along with values for coefficients α and β. The diameter of each disc was 40 mm.

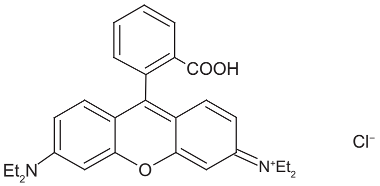


Figure 6.10. The chemical structure of rhodamine B.

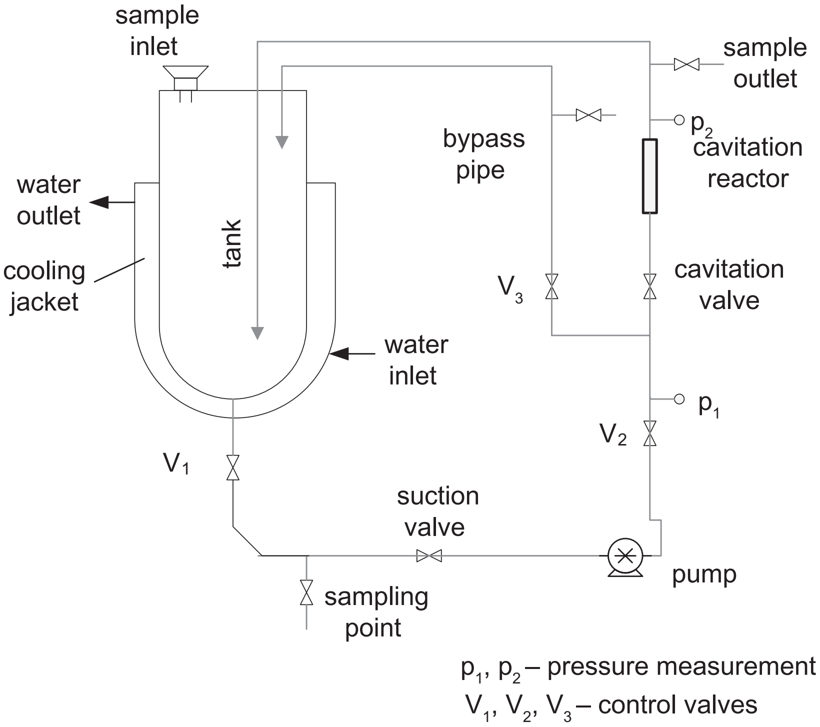


Figure 6.11. Schematic diagram of the hydrodynamic cavitation set-up (Gogate et al., 2005).

Table 6.5. Parameters for the cavitation inducers used in the research.

Disc id	Number of holes	Hole diameter [mm]	α [mm^{-1}]	β
1	33	1	4.00	0.023
2	8	2	2.00	0.022
3	8	5	0.80	0.139
4	20	3	1.33	0.124
5	33	2	2.00	0.091
6	16	3	1.33	0.100

The research used an aqueous solution of the rhodamine B dye at a concentration of 5–6 μg/ml. Experiments were conducted between 35–40°C. The degree of decomposition was determined using a Hitachi U1500 spectrophotometer using cuvettes with an optical path length of 10 mm. The change in the absorption of the cavitating dye solution was examined at a wavelength of 533 nm.

Samples were collected after 15, 30, 40, 45, 50, and 60 minutes of circulation in the cavitating system under a constant input pressure of 2 bars. Figure 6.12 shows the degree of decomposition of rhodamine B as a function of time. Figure 6.13 shows the change in the reaction rate constant depending on parameter α.

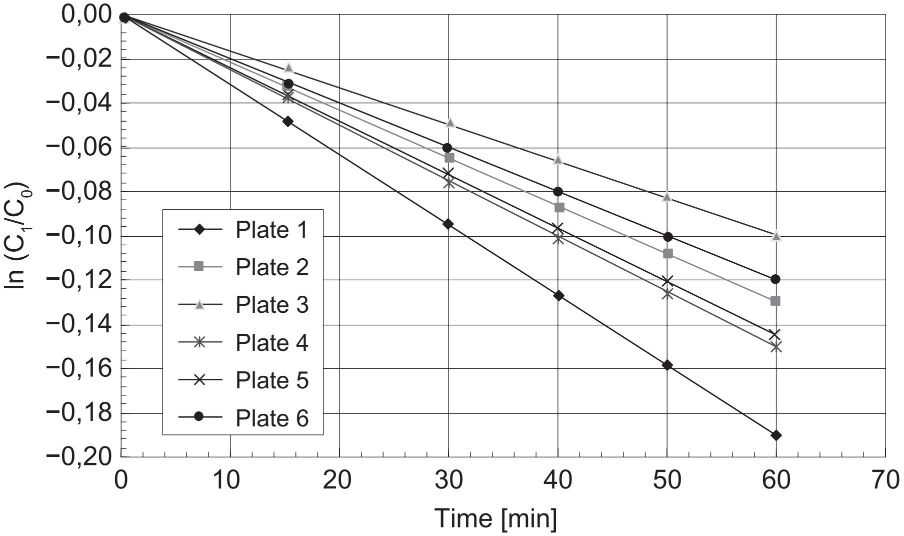


Figure 6.12. The effect of hydrodynamic cavitation over time on the degree of decomposition of rhodamine B, at 2.1 bar pressure (Sivakumar et al., 2002).

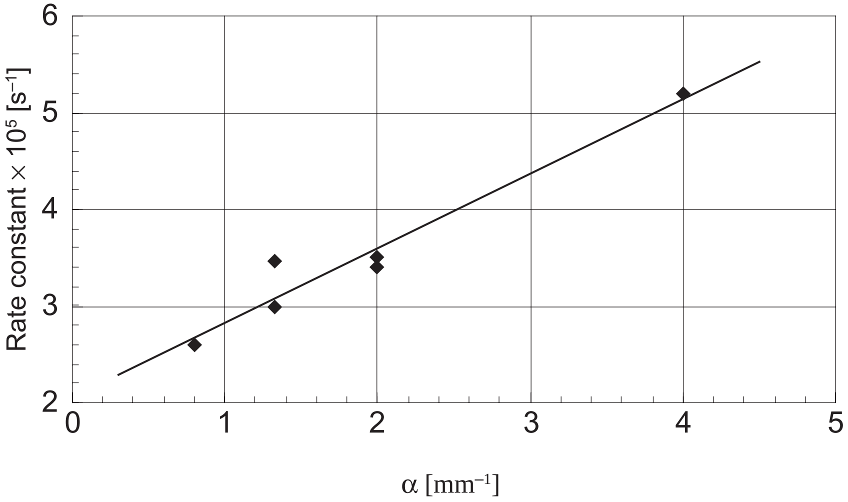


Figure 6.13. The effect of parameter α on the first-order rate constant of rhodamine B (Sivakumar et al., 2002).

The decomposition of dyes (organic compounds of complex structure) using hydrodynamic cavitation, as shown in the works of Wang (Wang et al., 2009, 2008), concerns in the main, the decomposition of rhodamine B and Reactive Brilliant Red K-2BP (Figure 6.14).

For the study, a laboratory test rig (Figure 6.15), exploiting the *swirling* type of vortex cavitation (Figure 6.16), was used. Cavitation was initiated in the circulation system using a centrifugal pump (3,000 rpm, 3.5 kW).

Figures 6.17 and 6.18 show the effects of the various methods on the degree of decomposition of rhodamine B in aqueous solution over time.

Studies on the decomposition of Reactive Brilliant Red K-2BP were carried out for varying values of pH, temperature, initial dye concentration, and cavitation inception pressure. To evaluate the effect of cavitation, a series of studies were conducted involving ultrasonic and hydrodynamic cavitation with the addition of H_2O_2.

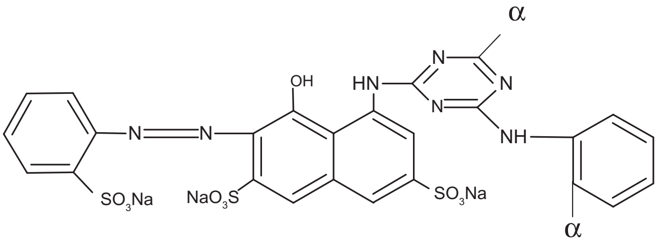


Figure 6.14. The chemical structure of Reactive Brilliant Red K-2BP.

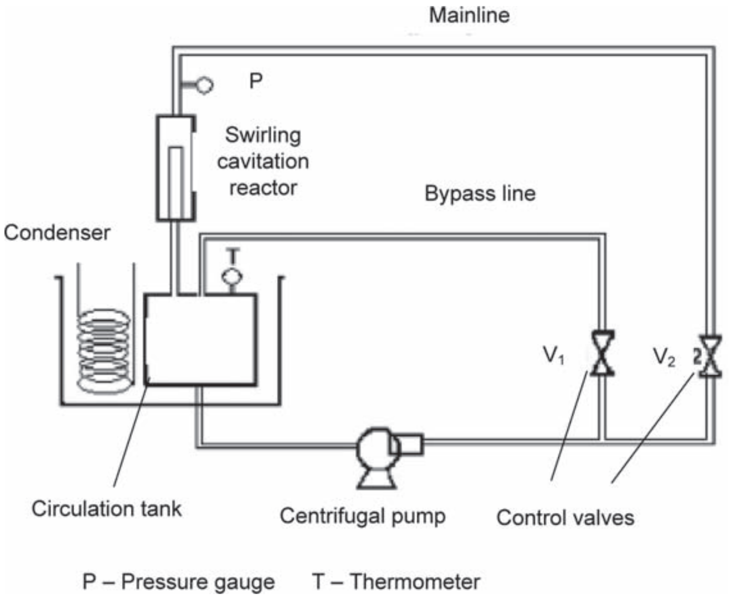
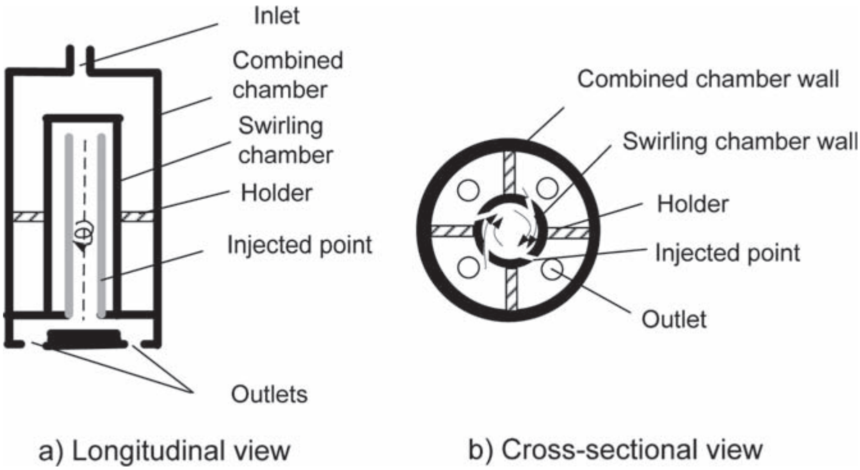


Figure 6.15. Schematic representation of the swirling cavitation reactor setup (Wang et al., 2008).



a) Longitudinal view

b) Cross-sectional view

Figure 6.16. Views of the swirling cavitation reactor (Wang et al., 2009).

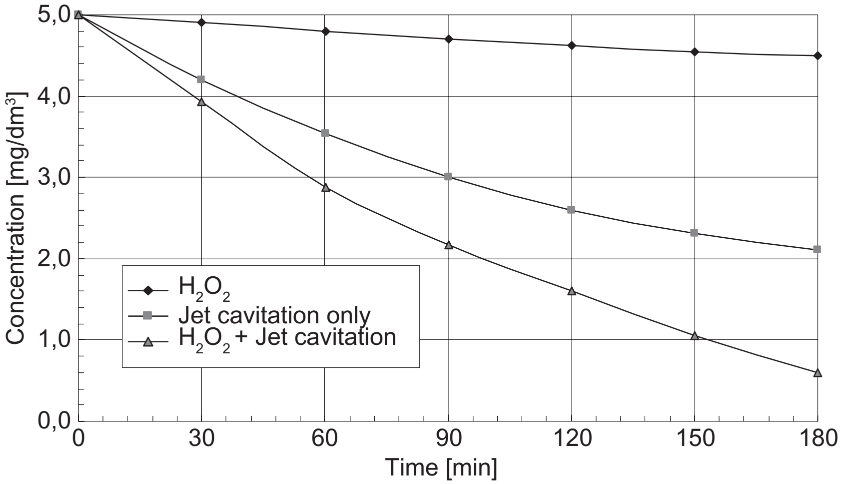


Figure 6.17. The effect of H_2O_2 on the degradation of rhodamine B at a pressure of 0.6 MPa, temperature 40°C, pH 5.4, $[H_2O_2]$ 100 mg/dm^3 (Wang i in., 2008).

Figure 6.19 shows the changes in the concentration of Reactive Brilliant Red during the decomposition process involving H_2O_2, ultrasound, vortex cavitation and their combinations.

A study of the hydrodynamic cavitation system conditions, as shown in Figure 6.15, have confirmed that in this environment, oxidation takes place under the influence of $^{\bullet}OH$ radicals generated during the collapse (implosion) of cavitation bubbles. The presence of hydrogen peroxide molecules intensifies this process, since the O–O bond strength in H_2O_2 is 210 kJ/mol, which is much smaller than the O–H bond (463 kJ/mol) in water molecules, and the C–C bond (413 kJ/mol) in organic compounds. Thus, it is easier for H_2O_2 to decompose into radicals in the cavitating liquid environment.

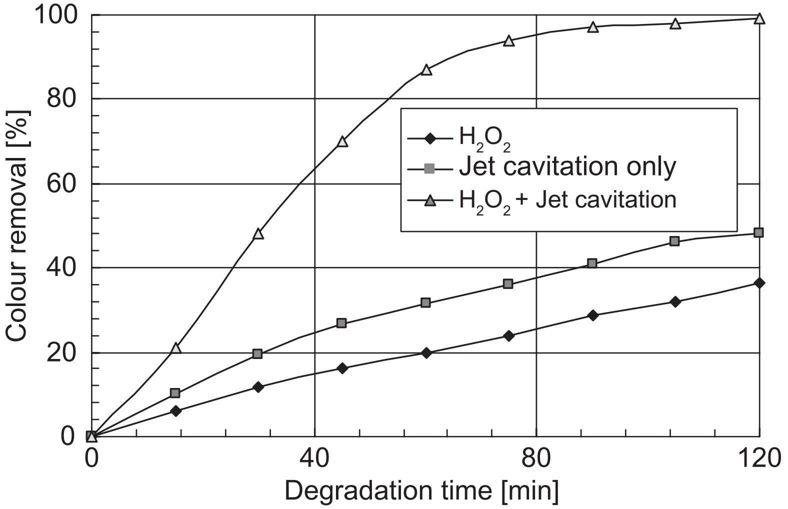


Figure 6.18. The effectiveness of color removal over time for rhodamine B, for various methods. Operating conditions: pH 5.4, temperature 40°C, pressure 0.6 MPa.

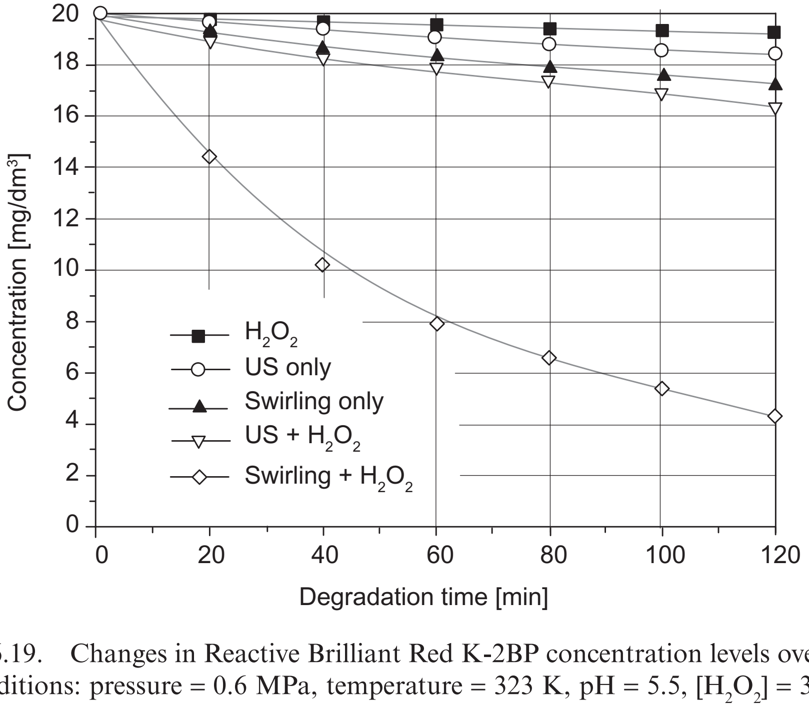


Figure 6.19. Changes in Reactive Brilliant Red K-2BP concentration levels over time; test conditions: pressure = 0.6 MPa, temperature = 323 K, pH = 5.5, $[H_2O_2]$ = 300 mg/dm³, initial concentration (20 mg/dcm³) (Wang et al., 2008).

The paper by Vasilieva et al. (2007) presents the results of studies carried out into the oxidation of nitrophenol using hydrogen peroxide in the presence of Fe^{2+} ions in a cavitating liquid environment, in a hydrodynamic reactor consisting of a toroidal chamber.

Nitrophenol is a toxic compound, which on entering into the human body, even in small quantities, causes damage to the liver, kidney or the central nervous system. It appears in the effluent from the production of herbicides, insecticides, and synthetic dyes (Vasileva et al., 2007, Batoeva et al., 2010). Its high stability and significant solubility in water are the causes of many difficulties in its decomposition during effluent treatment. The application of cavitation reactors, for this purpose, where oxidation processes are enhanced in the presence of hydroxyl radicals, is a promising technique for the decomposition of nitrophenol and other phenols.

Figure 6.20 shows a schematic diagram of a cavitation reactor which consists of a cylindrical body (1), inlet (2), toroidal chamber (3), conical diffuser (4), niches in the form of turnings (5) surrounded by a ring (6). Air or liquid is supplied by a conduit (7). The pressurized operational liquid is fed into the inlet (2) where part of its flow is redirected into the toroidal chamber (3), whilst the remainder moves around the axis of the conical diffuser.

The pressure in the cavitation system was 2 bars at a flow rate of 0.5 m^3h^{-1} and a solution temperature of 20°C. The initial concentration of 4-nitrophenol was 9.3 mg/dm^3 and the pH value of the solution was 3.4. Figure 6.21 shows the results for the oxidation of 4-nitrophenol:

1. With hydrogen peroxide in a cavitation stream
2. With Fenton's reagent
3. With hydrogen peroxide in a cavitation stream and dissolved Fe^0
4. With Fenton's reagent in a cavitation stream.

After 20 minutes of cavitation with Fenton's reagent phenol decomposition reached 98%.

Braeutigam et al (2009) studied the use of hydrodynamic cavitation in the decomposition of BTEX (benzene, toluene, ethyl benzene and xylenes) in aqueous solutions. Their studies included the inlet pressure to the cavitation reactor,

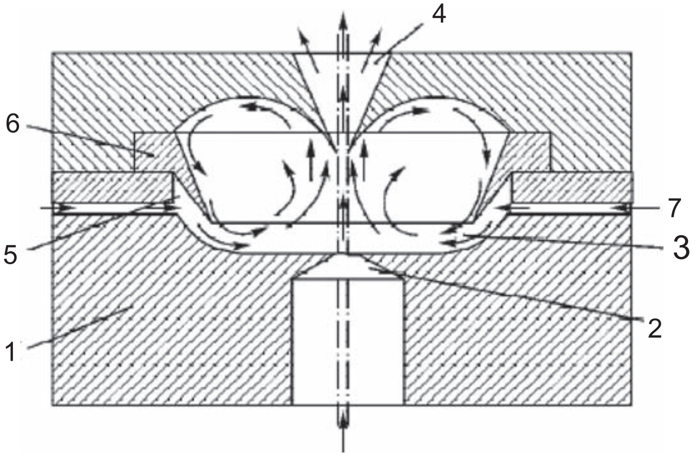


Figure 6.20. Schematic diagram of a cavitation reactor: 1 – cylindrical body, 2 – inlet, 3 – toroidal chamber, 4 – cone diffuser, 5 – niche in the form of turnings, 6 – ring, 7 – conduit for air (gas) or liquid feed (Vasilieva et al., 2007).

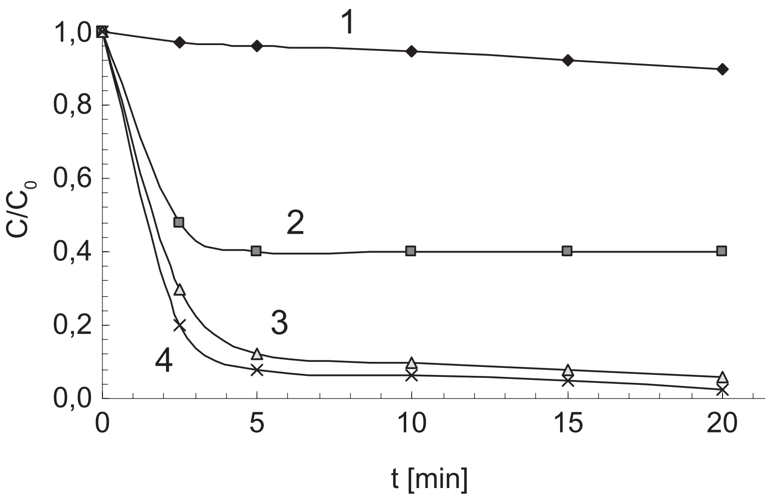


Figure 6.21. Oxidation kinetics for 4-nitrophenol using various methods (see text above). Initial concentration, mol/dm^3, [4-nitrophenol] = $6.7 \cdot 10^{-5}$, [H_2O_2] = $4.02 \cdot 10^{-4}$, [Fe^{2+}] = $1.66 \cdot 10^{-4}$, temperature 20°C, pH = 3.4.

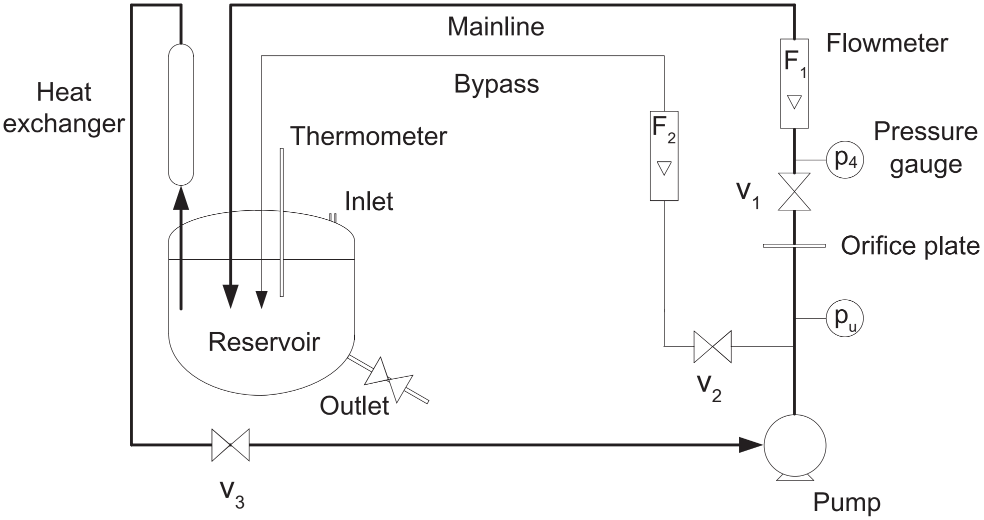


Figure 6.22. Schematic diagram of the hydrodynamic cavitation setup (Braeutigam et al., 2009).

solution temperature and the initial concentration of selected compounds from the BTEX group. Figure 6.22 shows a schematic diagram of the device used.

It has been observed that BTEX can be decomposed with moderate conversion, whereas toluene shows the highest and ethyl benzene the lowest conversion. The optimum operating pressure and temperature values have been reported; multiple hole orifice plates produce decomposition to a greater extent compared with the single hole orifice plate.

Wang and Zhang (2009) have investigated the use of swirling jet induced hydrodynamic cavitation for the decomposition of alachlor aqueous solution at an operating capacity of 25 dm^3. The results showed that it can be successfully decomposed. It was found that the decomposition can be described by pseudo first-order kinetics, with a decomposition rate constant k value of $4.90 \cdot 10^{-2}$ min^{-1}, for a 50 mg/dm^3 loading of alachlor in aqueous solution, at an operating temperature of 40°C. The effects of the operating parameters such as liquid pressure, solution temperature, initial alachlor concentration, and pH value of the medium on the alachlor decomposition rates have also been established. The results showed that the alachlor degradation rates increased with increasing pressure and decreased for an increase in the initial concentration. There is an optimum temperature of 40°C for the maximum decomposition rate, which also depends slightly on the pH value of the medium.

Kalumuck and Chahine (2000) investigated the decomposition of p-nitrophenol using a hydrodynamic cavitation reactor, based on a closed loop circuit with pollutants being pumped using a triplex positive displacement pump (17 dm^3/min and 69 bars pressure). Multiple orifice plates in the re-circulation line were used serially in order to produce intense cavitation. The total capacity of the reactor was 6.5 dm^3, operating in re-circulation mode. Reports have indicated that the cavitating jet setup gives an oxidation efficiency (mg decomposed per unit energy supplied) which is about 25 times more compared with the sonochemical reactor i.e., ultrasonic horn (frequency of 15.7 kHz and power density of 0.36 W/mdm^3). The optimum operating temperature was reported to be 42°C. Lower pH values and also lower cavitation numbers (higher inlet pressure at the same pressure drop across the nozzle) favours decomposition and increases the oxidation efficiency for the hydrodynamic cavitation setup.

6.7 SUMMARY

Due to the constant increase in the drinking water quality standards, an important technological problem is how to adapt to the requirements dictated by the standards. This applies primarily to the different types of micropollutants present in untreated water. Currently, advanced research is being carried out on implementing methods of disinfecting water which do not require the use of chemicals (oxidants).

Numerous studies, conducted on a laboratory scale, have shown that hydrodynamic cavitation and advanced oxidation processes (AOPs) involving cavitation enable a fairly effective decomposition, and removal of such pollutants, in treated water.

Literature reviews and studies confirm that hydrodynamic cavitation can be used to reduce the basic pollutant levels in municipal sewage, but combined with a dose of other oxidising agents (O_3, H_2O_2) in the reaction environment, it can increase the effectiveness of the purification process (Jyoti et al., 2000, 2004a).

The effectiveness of pollutant decomposition in sewage, by means of hydrodynamic cavitation, largely depends to a certain degree on the type of sewage undergoing treatment and the processing time. Published experimental results from studies (Capin et al., 2006, Gogate, 2002, 2010, Sivakumar et al., 2002, Korniluk and Ozonek, 2010), in addition to experiential results, are a premise for continuing research into the application of cavitation into the decomposition of organic compounds in the aqueous environment, including the removal of organic pollutants in municipal sewage and leachates from municipal landfills.

Dye decomposition using hydrodynamic cavitation also gives promising results, although to date, it is easier to remove dyes using activated carbon adsorption in combination with ozonation or the membrane method. Energy consumption unit costs for such methods are still relatively high (Gogate, 2007).

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CHAPTER 7

The decomposition of persistent organic pollutants using hydrodynamic cavitation

7.1 INTRODUCTION

For a long time now there has been a growing interest in a specific group of environmental pollutants, namely POPs (Persistent Organic Pollutants). These compounds, released into the environment, mainly from anthropogenic sources are characterised by their high toxicity, persistence and ability to bio-accumulate (Kot-Wasik et al., 2001). This group of organic pollutants include, amongst others: polycyclic aromatic hydrocarbons (PAHs), chlorophenols, polychlorinated biphenyls (PCBs), dioxins PCDD (Polychlorinated Dibenzodioxins) and PCDF (Polychlorinated Dibenzofurans), and some pesticides. These compounds, depending on the part of a given ecosystem in which they occur (soil, benthal sludge deposits, surface water and groundwater) may undergo slow changes due to various physical, chemical, biological or even photochemical processes (Walton et al., 1998, Pehkonen et al., 2002).

Depending on the compound and medium in which they are found, as well as the environmental factors specific to the medium, decomposition processes occur at different rates, and the newly created compounds can create a burden on the environment to a greater or lesser extent.

Particularly burdensome for the natural environment are the polycyclic aromatic hydrocarbons. The importance of this ubiquitous and rich family of organic chemical compounds (more than 300 different PAHs are known) is taken into account, because of the carcinogenic and mutagenic properties of some of its members (Martinez, 2004). The reference here is, of course, to the 16 representative PAHs listed by the U.S. Environmental Protection Agency (US EPA) as hazardous organic compounds.

The reason for their presence in the environment are both natural sources and anthropogenic, which can include: forest fires, volcanic eruptions, biosynthetic processes, organic matter humification, geothermal reactions, industrial processes associated with the processing of coal and oil (Psillokalis et al., 2003).

In the case of the atmosphere, these cyclic organic compounds, consisting of two or more fused aromatic rings are released in the form of steam which is adsorbed on dust particles (Marty, 1992). Especially dangerous, is the situation when the PAHs adsorption occurs on particles with a diameter less than 2.5 μm (PM 2.5), since the dust particles, of such a size, settle slowly, and the rain does not remove them effectively, which leads to their long persistence in the air, inhalation by the human body and because of the depth of penetration, are not completely removed from the body (Jacob, 1984). Released from the sources described above, 90% of the PAHs can be found in soils and 9% in benthal sludge deposits. The remainder remains retained in air (0.5%) and surface water (0.5%).

In principle, the occurrence of PAHs in every part of the environment, means that human exposure to their effects is widespread. Due to their high affinity for solid surfaces, poor water solubility, low vapour pressure, and aromatic characteristics, these compounds are currently present in water and air in the form they were adsorbed on the surface of the particle matter, which certainly favours their deposition in benthal sludge deposits (Marty, 1992).

The contamination of the human body by the PAHs compounds is primarily through inhalation (usually in the form of aerosols adsorbed on dust particles, typically respiratory—this relates to the less volatile hydrocarbons including benzo[a]pyrene), through consumption of contaminated food and dermal exposure including contact with such substances as tar, oil and soot. PAHs and their metabolites, present in blood and urine, serve as evidence that these compounds are absorbed into the body, where they undergo metabolic changes associated with the creation of carcinogenic agents. The most harmful PAHs are those containing 4–7 aromatic rings. Differences in PAHs absorption by the body is related to differences in their lipophilicity. As inactive compounds and highly soluble in fats, they diffuse through the protein-lipid cell membranes. The greater the lipophilicity and the more fats in the digestive system, the greater the absorption. Bio-concentration of these persistent organic pollutants as factors which initiate mutagenic and carcinogenic changes has been demonstrated in the case of water flora and fauna (Onuska, 1989).

The toxic effects of PAHs means, that many countries restrict the PAHs concentrations in selected parts of the environment. For this purpose, the so-called relative carcinogenicity factor (RCF) was introduced, based on the carcinogenicity of benzo[a]pyrene, which was assigned a value of 1, enabling the systematic toxicological evaluation of all PAHs exhibiting carcinogenic properties.

The permissible PAHs concentration levels in water have been set depending on the water purity class (from I to V) as classified in the Regulation of the Minister of the Environment dated 20th August 2008. This document deals with water classification for the assessment of surface water and groundwater, monitoring methods and how to interpret results and assessments of the state of these waters. This content (defined as the sum of benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenzo[a,h]anthracene, benzo[g,h,i]pyrelene and indeno[1,2,3-cd]pyrene) takes on a value from Table 7.1, depending on the water purity class.

Table 7.1. Maximum PAHs summated concentration levels in surface and ground water.

	Purity class				
	I	II	III	IV	V
Surface water, μg/dm^3	0.01	0.05	0.2	1.0	>1.0
Groundwater, μg/dm^3	0.01	0.02	0.03	0.05	>0.05

The permissible PAHs concentration levels in drinking water are given in Directive 98/83/EC which governs the permissible concentration of benzo[a] pyrene in drinking water to a maximum value of 0.01 μg/dm^3, whilst the permissible summated concentration level of four PAHs (benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[g,h,i]pyrelene and indeno[1,2,3-cd]pyrene) cannot exceed 0.1 μg/dm^3.

The degree to which the PAHs are removed in conventional sewage treatment systems varies and depends on the PAHs type and concentration, as well as the stage processes used. Polycyclic aromatic hydrocarbons are resistant to biodegradation. Previous studies have confirmed that bicyclic and tricyclic PAHs are biodegradable (Juhasz et al., 2000). Microbiological resistance to PAHs decomposition is due, amongst others, to the hydrophobic structure of the molecule, poor aqueous solubility and thermodynamic stability (Traczewska, 2003).

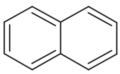
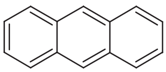
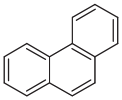
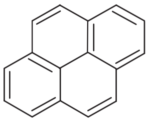
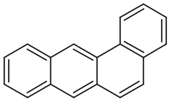
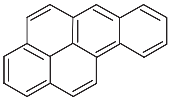
Chemical oxidation (Kornmuller et al., 2003), coagulation, natural infiltration, reverse osmosis, nanofiltration with the use of appropriate membranes, adsorption (Bilek, 2004, Traczewska, 2003) and the use of ultrasound (Manariotis et al., 2011) are some of the most commonly recommended methods which may be helpful in the decomposition of PAHs. The decomposition reaction rate constant depends on the number of rings in the molecule. Hydrocarbons of good solubility in water are characterised by a greater susceptibility to the actions of oxidants. Currently, it is believed that the most effective is the application of highly effective multistage technologies in which, amongst others, advanced oxidation processes are used based on reactions involving very highly reactive hydroxyl radicals, leading to the decomposition of the majority of organic compounds in aqueous solutions (Ledakowicz et al., 2001).

7.2 THE DECOMPOSITION OF PAHs IN AQUEOUS SOLUTIONS

Ozonek et al., conducted studies into defining conditions for, and the possible removal of polycyclic aromatic hydrocarbons from sewage using hydrodynamic cavitation (Szulżyk-Cieplak et al., 2005, Ozonek et al., 2009). Tests were carried out on a laboratory scale using the setup shown in Figure 5.2 using variable cavitation system operating parameters.

The PAHs decomposition studies involving hydrodynamic cavitation, used substances modelled on the selected polycyclic aromatic hydrocarbons: phenanthrene (97%, Fluka Analytical), anthracene (99%, Acros Organics) which represented the tricyclic PAHs, pyrene and benzo[a]anthracene (98% and 99% purity respectively, Acros Organics) having four fused aromatic rings, whose selection properties are summarised in Table 7.2. These substances were distinguished by their high purity level and were not subjected to further purification processes. The preparation of aqueous solutions of PAHs at a concentration of 500 ppb was conducted in two stages. Firstly, 15 mg (± 0.5 mg) of the given hydrocarbon was dissolved in 50 ml acetonitrile (produced by POCH with a purity level suitable for HPLC). Secondly, the modelling solutions were transferred to the 50 dm^3 circulation tank. The degree of the PAHs decomposition was monitored for pressures of 5, 6, and 7 bar over a 60 minute duration. Before monitoring began, the PAHs aqueous solutions were mixed with the water contained in the measuring system (9.5 dm^3) for 10 minutes at a pressure of about 3 bar.

Table 7.2. Chemical structures and properties of selected PAHs used in the study.

Item	Name of compound	structure	M_{mol} [g/mol]	ρ [g/cm^3]	t_{mp} [°C]	t_{bp} [°C]	$S(H_2O)$ [g/100 g]
1	Naphthalene		128.17	1.168	80.3	218.0	0.0031
2	Anthracene		178.23	1.25	216.3	340	$7 \cdot 10^{-6}$
3	Phenanthrene		178.23	1.182	101	340	0.00012
4	Pyrene		202.26	1.27	150.7	370	$1.4 \cdot 10^{-5}$
5	Benzo[a]anthracene		228.3	1.274	158.9	437.5	$1 \cdot 10^{-6}$
6	Benzo[a]pyrene		252.32	1.35	176	495	$8 \cdot 10^{-7}$

During the course of the monitoring, samples were taken after 5, 10, 15, 20, 30 and 60 minutes and changes in the pH value, temperature and pressure in the working chamber of the cavitation reactor were recorded. The samples taken from the aqueous PAHs solutions were extracted in an ultrasonic bath in order to isolate the hydrocarbon fraction. The extraction time was 45 minutes with dichloromethane as the solvent, of which 10 ml were added to each sample. After extraction, the organic phase was collected from each flask and a qualitative and quantitative analysis was performed using a gas chromatograph coupled to an Ion Trap Mass Spectrometer (Finnigan Mat GCQ), equipped with an A220S Finnigan Mat autosampler and a RTX-5MS capillary column of 60 m length and 0.25 mm diameter. The injector (type split-splitless) temperature was 275°C whilst the volume of the injected sample was 2 μl. The initial column temperature (80°C) was maintained for two minutes, after which it rose at a rate of 8°C/min up to 300°C where it was maintained for 25 minutes. The carrier gas was helium whose flow rate was 40 cm/s. The chromatograms were recorded by scanning ions in the range 80–305 m/z, with recording beginning 10 minutes into the analysis.
where:

M_{mol} - Molecular mass [g/mol]
ρ - Density at 25°C [g/cm^3]
t_{mp} - Melting point [°C]
t_{bp} - Boiling point [°C]
S - Solubility in water [g/100 g].

The degree of PAHs decomposition (η), as a function of the process conditions during the study can be determined from the relationship:

$$\eta = \frac{C_0 - C}{C_0} \cdot 100\ C_0\,[\%] \tag{7.1}$$

where:

C_0 - The initial concentration
C - Concentration after time *t* during cavitation

The effectiveness of PAHs decomposition was determined chromatographically.

Based on the obtained fragmentograms of compounds tested (anthracene, phenanthrene, benzo[a]anthracene and pyrene), their degree of decomposition was determined. Figures 7.1 to 7.5 show selected chromatograms of PAHs decomposition dependent on the cavitation operating conditions.

Figure 7.6 shows the effect of changes in the supply pressure to the cavitation region on the degree of anthracene decomposition.

The obtained results confirm that the rate of anthracene decomposition is dependent on the supply pressure at the input to the hydrodynamic cavitation

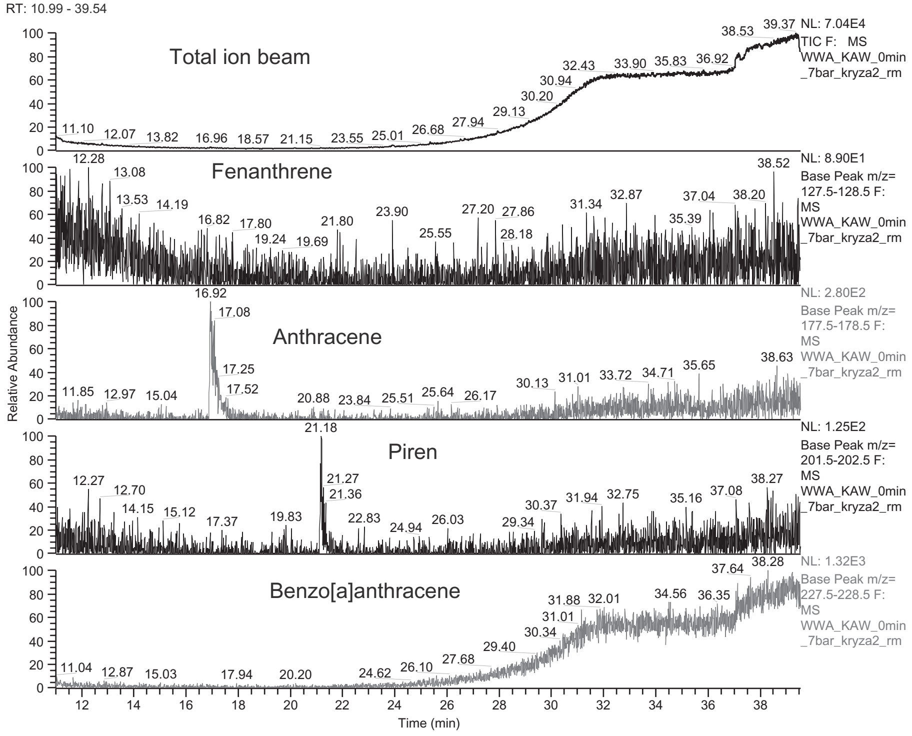


Figure 7.1. Mass fragmentograms of PAHs extracted from samples after 5 minutes of cavitation using orifice plate number 2 at 7 bar pressure. From top to bottom: Total ion beam, Phenanthrene, Anthracene, Pyrene, Benzo[a]anthracene.

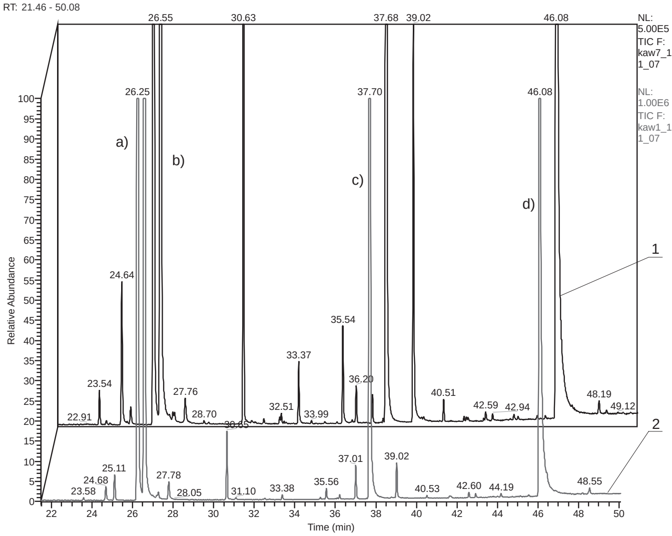


Figure 7.2. Chromatograms for the PAHs mixture: a) phenanthrene, b) anthracene, c) fluorene, d) indeno[1,2,3-cd]pyrene, using orifice plate No. 2, at a pressure of 7 bar. 1 – before cavitation, 2 – after cavitation.

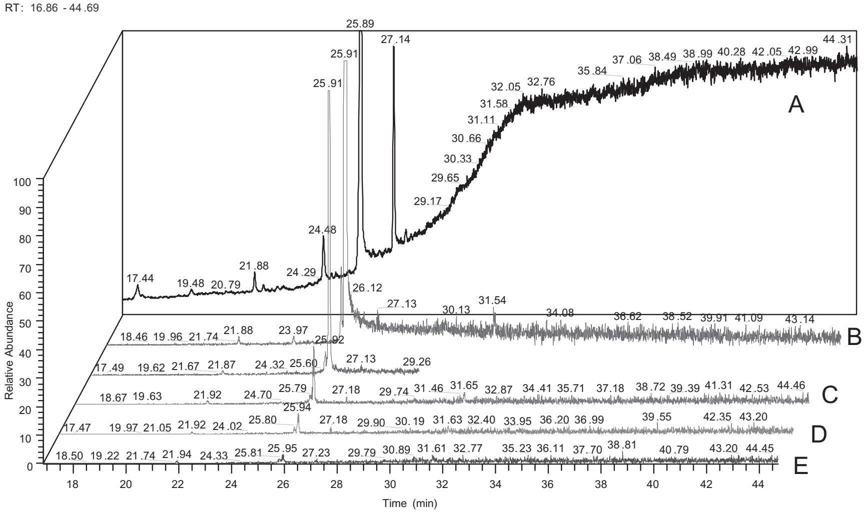


Figure 7.3. Chromatogram for the total ion beam (A) for anthracene, and mass fragmentograms for the ion at m/z 178 during cavitation after: B – 0 min, C – 15 min, D – 30 min and E – 60 min, for orifice plate number 2 at a pressure of 7 bar.

reactor. At an initial supply pressure of 9 bar, over 75% of the anthracene was decomposed. This result was achieved after 10 minutes of cavitation.

Dynamic pressure changes during liquid flow through the cavitation inducer mainly depend on the changes in liquid velocity through the holes on the orifice plate. With an increase in the liquid's flow velocity, the pressure drops at the

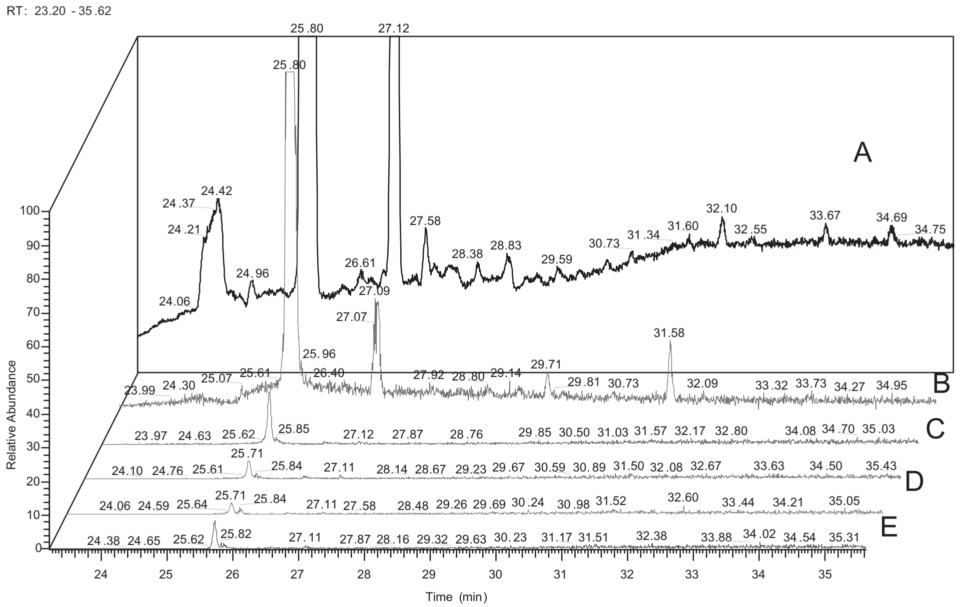


Figure 7.4. Chromatogram for the total ion beam (A) for phenanthrene, and mass fragmentograms for the ion at m/z 188 during cavitation after: B – 0 min, C – 15 min, D – 30 min and E – 60 min, for orifice plate number 2 at a pressure of 7 bar.

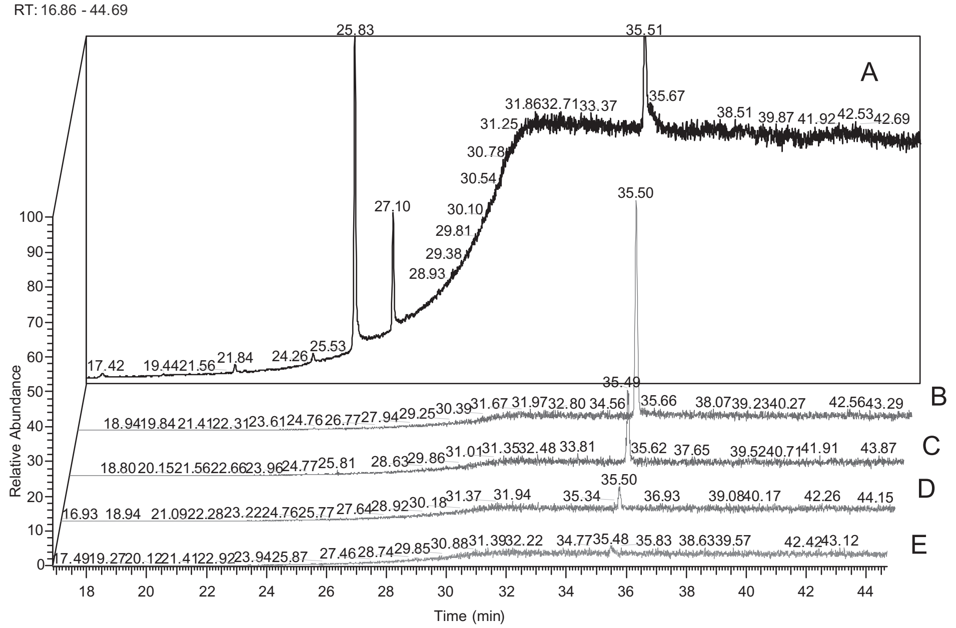


Figure 7.5. Chromatogram for the total ion beam (A) for dibenzo[a]anthracene, and mass fragmentograms for the ion at m/z 228 during cavitation after: B – 0 min, C – 15 min, D – 30 min and E – 60 min, for orifice plate number 2 at a pressure of 7 bar.

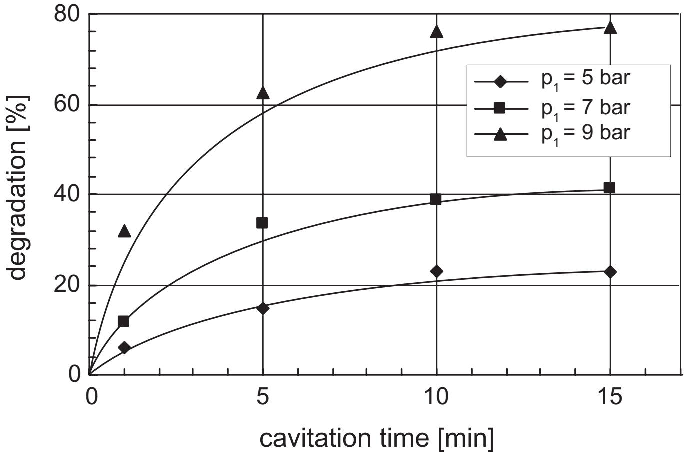


Figure 7.6. Degree of anthracene decomposition over time for different values of supply pressure to the cavitation region.

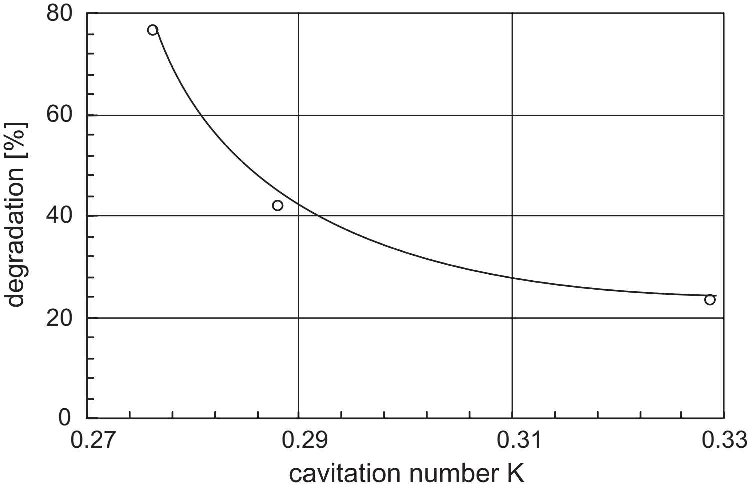


Figure 7.7. Degree of anthracene decomposition depending on the cavitation number K.

septum, thus decreasing the cavitation number, which causes an increase in the degree of anthracene decomposition.

Figure 7.8 shows the effect of the cavitation inducer geometry on the effectiveness of anthracene decomposition. Tests were carried out with an initial temperature and pressure of 12°C and 7 bar respectively, using orifice plates number 1 (a 3 mm diameter hole located on the axis) and number 3 (nine 1 mm diameter holes).

Figure 7.9 shows the effect of the supply liquid temperature to the hydrodynamic cavitation reactor on phenanthrene decomposition using orifice plate number 3 for an initial pressure of 9 bar and two initial temperatures, 12°C and 40°C.

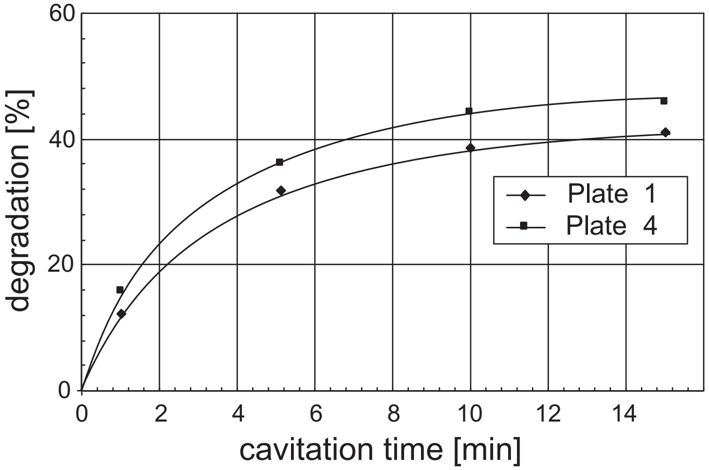


Figure 7.8. Degree of anthracene decomposition over time depending on two cavitation inducer geometries for an initial pressure of 7 bar and a temperature of 12°C.

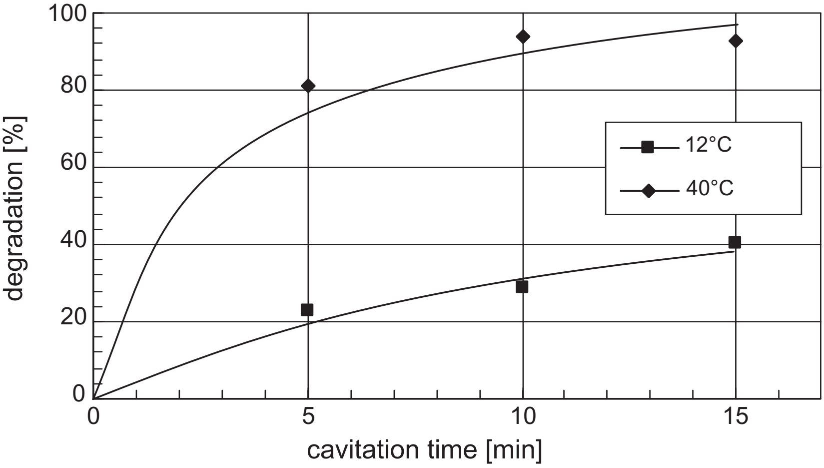


Figure 7.9. Degree of phenanthrene decomposition over time for two initial temperatures, 12°C and 40°C for orifice plate number 3.

For an initial temperature of 12°C, after 5 minutes of cavitation, the decomposition of phenanthrene reached almost 20%, compared to almost 80% for an initial temperature of 40°C. This shows that for an increase in the initial temperature the degree of decomposition increases.

Psillakis et al., (2004), studied the decomposition of naphthalene, acenaphthylene and phenanthrene, using ultrasound frequencies of 24 kHz and 80 kHz, under variable operating conditions (concentration 150–450 μg/dm^3, liquid temperature 20°C and 40°C). In most cases, all the PAHs underwent complete decomposition after two hours of cavitation. It was confirmed that a fall in the degree of decomposition was caused by an increase in the initial concentration or a decrease in temperature, power and frequency.

7.3 THE REDUCTION OF ODOUR EMISSIONS FROM COUNTER-CURRENT EXTRACTION WATER IN THE SUGAR INDUSTRY

Odours cause discomfort when the external environment is sensed; they are currently one of the most frequently mentioned by the public sources of sensory nuisance. This applies not only to cities, but to villages and protected areas, where together with the neighbouring agricultural areas, particularly breeding farms, undesirable smells, described as odours (malodorous compounds), spread. It should also be remembered that odours are inherent in the environmental processes. Malodorous compounds are introduced into the environment as a result of natural processes e.g. the planet's volcanic activity, the decomposition of matter by microorganisms, steppe and forest fires, the release of malodorous gases from marshland and as a result of weathering processes. The source of anthropogenic odours is the human economic activity, carried out mainly in the petrochemical, cellulose, food industries but also by public utilities (landfills and waste incinerators, sewage treatment works), agriculture and livestock (large-scale farms) and caused by motoring (combustion engines). They lead to the discomfort of ontic man. Breathing polluted air containing malodorous compounds can cause fatigue, drowsiness, hyperactivity, feelings of disgust (Szynkowska et al., 2009). Besides the negative effect on psychological comfort, individual malodorous compounds also have toxic, mutagenic and carcinogenic properties.

Given the chemical structure, malodorous compounds can be divided into two basic groups, gaseous inorganic compounds and volatile organic compounds. Inorganic compounds, odorous in character, include hydrogen sulphide, ammonia, sulphur oxides and nitrogen oxides. Malodorous organic compounds include a wide variety of carbon and hydrogen compounds, containing more than one heteroatom in their molecule. Heteroatoms are most frequently oxygen, nitrogen, sulphur, phosphorous, but also selenium, tellurium and others. This group can also include organic acids, aldehydes, ketones, amines, sulphides or polysulphides, and also heterocyclic compounds etc. Only in rare cases, is the odour caused by one or several malodorous compounds. In general, it is the result of a sense of smell of a mixture of many substances. It is estimated, that from amongst the most common odorants around 300 chemical compounds can be found.

The choice of an effective method of removing odours requires considering several factors, such as emission volumes, the nature of the compounds present in the waste gases causing the smell burden or the required degree of decomposition (treatment). The implementation of specific technology in real world conditions should be preceded by researching the literature, reviewing the adopted solutions in similar industrial works, as well as a series of laboratory tests.

Ozonek et al., (2009) conducted a study into reducing the smell burden in sugar refineries, using hydrodynamic cavitation. Water used to transport or to wash sugar beet passes through the cavitation reactor, in which partial decomposition of the organic compounds occurs which contributes to the formation of odours. It is then directed to the clarifiers.

The counter-current extraction water from washing the sugar beet, which is directed to the clarifiers, underwent laboratory investigations, making use of the test rig described in Chapter 5. Samples were taken for analysis, before, and after 30 minutes of cavitation (at a height of 20 cm above the liquid's surface in the circulation tank). An analysis of the odorous compound composition was performed using a gas chromatograph coupled to a Thermo Polaris Q (Trace Ultra) mass spectrometer.

Figure 7.10 shows the chromatogram of the total ion beam before and after 30 minutes of cavitation for the air-borne compounds above the liquid under test, sampled at the "Lublin" sugar refinery. The retention times are on the horizontal axis whilst the signal strength is on the vertical axis. The detection of the chemical compounds is carried out on the principle of assigning the right

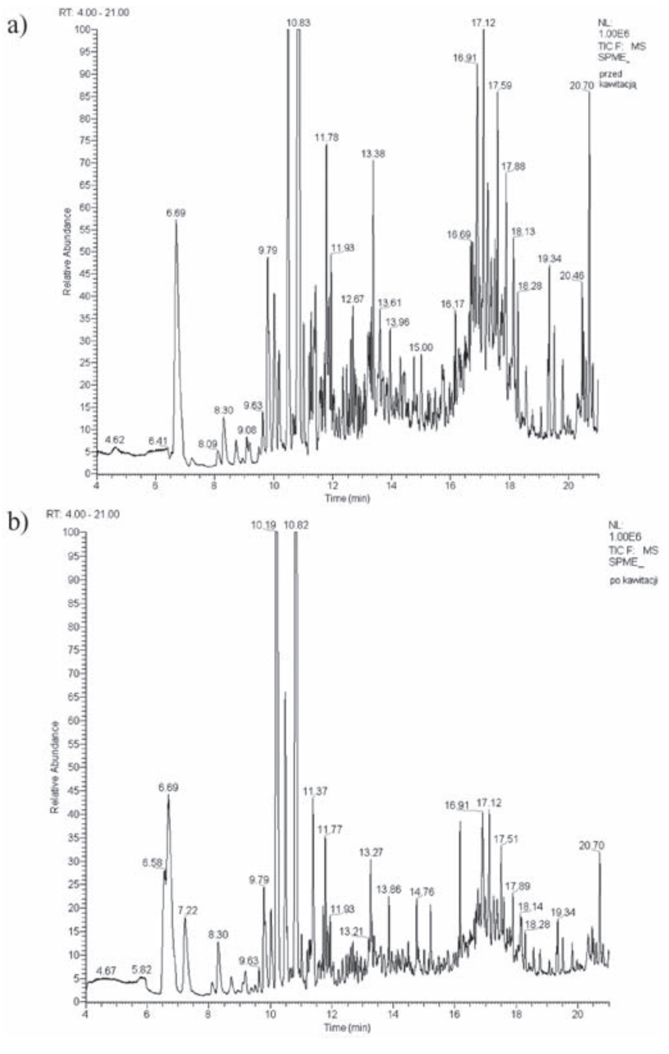


Figure 7.10. The results of chromatographic analysis of odorous liquid samples released from the "Lublin" sugar refinery: a) before cavitation, b) after 30 minutes of hydrodynamic cavitation.

substances to the retention times. Identification reference data is obtained from the NIST 2005 spectra library. The determination of the concentrations of individual substances is based on the summation of the area under the peak representing the specified compound. Amongst the peaks obtained, 11 compounds were identified, which have revealed carcinogenic properties. Table 7.3 summarises the characteristics of the identified compounds.

The greatest degree of decomposition was obtained for compounds containing heteroatoms such as oxygen and sulphur (Figure 7.11). However, the lowest

Table 7.3. Malodorous compounds identified in samples of counter-current extraction water from the "Lublin" sugar refinery before and after hydrodynamic cavitation.

				Concentration [ppb]	
Rt [min]	Compounds	CAS number	Smell	before cavitation	after 30 min cavitation
6.58	dimethyl disulphide	624-92-0	rotten onions, garlic	412	231
6.69	toluene	108-88-3	aromatic	736	698
7.22	tetrachloroethylene	127-18-4	sweetish	542	419
8.11	ethylbenzene,	100-41-4	sweetish	234	230
8.72	m-xylene	108-38-3	sweetish	229	216
	p-xylene	106-42-3	sweetish	367	211
10.19	dimethyl trisulphide	3658-80-8	rotten onions	240	130
10.55	p-menth-2-ene	13837-70-2	mint	346	211
10.83	dichlorobenzene	106-46-7	sweetish	564	532
10.87	trans 3-caren-2-ol	N/A	citrus fruits	2146	1349
11.91	2-Carene epoxide	20053-58-1	citrus	178	56
12.67	Pulegone	89-82-7	veined	613	124

Rt – Retention time [min], CAS – *Chemical Abstracts Service,* N/A – Not Available

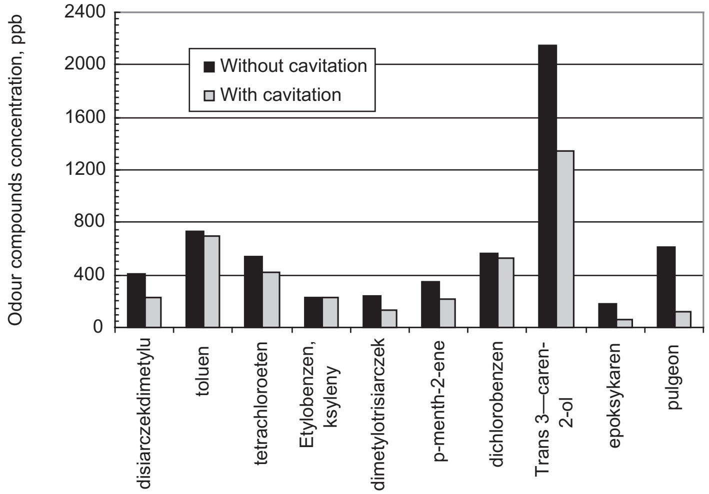


Figure 7.11. Odorous compound concentrations released from counter-current extraction water in the "Lublin" sugar refinery with and without hydrodynamic cavitation.

degree of removal was observed for mono-aromatic compounds with simple substitutions (dichlorobenzene, ethyl benzene and toluene).

7.4 SUMMARY

Polycyclic aromatic hydrocarbons, because of their carcinogenic and mutagenic effects, are among the group of compounds particularly dangerous to living organisms. Their removal, using traditional purification methods do not always give satisfactory results.

Methods which produce a high degree of degradation of PAHs in aqueous solutions are: ozonation, UV irradiation, and hybrid methods which combine ozone and H_2O_2 with photolytic processes.

The results of this study confirm that hydrodynamic cavitation can be used to degrade low biodegradable organic compounds including PAHs in aqueous solutions and wastewater.

The degree of degradation of compounds in systems using hydrodynamic cavitation is high in comparison with traditional methods of degradation. In addition, their energy demands are relatively low compared to other technologies used for the degradation of PAHs.

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CHAPTER 8

The application of cavitation to intensify technological processes

8.1 INTRODUCTION

Since the mid-1990s there has been an increase in the interest shown around the world regarding the use of hydrodynamic cavitation to remove toxic organic and biological pollutants, which find their way into natural water basins in a more or less uncontrolled manner. The positive results of many pilot studies and those conducted on a laboratory scale indicate a wide range of possibilities for its application. An increase in the effluent treatment quality standards means that, in the case of effluent of specific composition, the recommendation is to use more effective treatment technologies. One can include two or multi-stage purification systems, which achieve a manifold reduction of wastewater pollution, compared with that obtained when each of the processes is used separately. One of the options under consideration is the possibility of integrating into the sewage treatment system chemical oxidation processes, including those utilising hydrodynamic cavitation, acting upon the relatively low-cost biological processes.

The use of hydrodynamic cavitation is one possible method to improve the biodegradability of organic compounds in polluted water and effluent. The generation of hydroxyl radicals during this process, with the involvement of oxygen and/or air, can lead to the degradation of organic matter within the sewage and organic compounds in the polluted waters. In general, cavitation is one of the elements of an integrated treatment system, consisting of physical, chemical and biological processes.

8.2 THE USE OF CAVITATION IN THE FOOD AND PROCESSING INDUSTRIES

A comprehensive review of hydrodynamic cavitation usage, for the intensification of technological processes in the food and processing industries, is presented in the works of Gogate, 2011, Litwinienko et al., 2005, Milly et al., 2007.

Laboratory studies and industrial tests which have been carried out have shown that with the aid of hydrodynamic cavitation devices, a homogeneous composition in a variety of liquid systems can be obtained, particularly in heterogeneous systems (Litwinienko et al., 2005). Fruit and vegetable juices are subjected to homogenisation, which with the help of cavitation produces stable dispersions and emulsions thus improving the extraction of valuable constituents.

The homogenisation of milk and its products is one of the most energy-intensive operations in the dairy industry, which significantly affects the energy consumption during production. At the same time, as is known, the effective homogenisation determines the quality of the final product, so it is an important technological operation. Regularly used in the dairy industry, pressure homogenisers are relatively large and heavy pieces of equipment characterised by a high energy demand and not always of sufficient operational reliability. Litwinienko (2005) found that treating milk with the help of hydrodynamic cavitation allows for the fragmentation of the dispersion phase (fat molecules) down to 1 μm diameter, which is required to give it the appropriate consistency. The effectiveness of cavitational homogenization of dairy products has still not been sufficiently investigated.

The study by Litwinienko et al. (1988) presents the results of research into the homogenisation of milk in the industrial environment. During this research the impact of processing times and temperatures on the quality of products, which had been subjected to homogenisation, was analysed. The study included semi-skimmed and skimmed milk, and also cream. It was found that the optimal processing time for milk with a 2.5–2.7% fat content required it to be homogenised twice. The study confirmed that the use of hydrodynamic cavitation during milk homogenisation produces a measurable technological effect.

Milly et al. (2007) have investigated the application of a hydrodynamic cavitation reactor for the sterilisation of liquid foods such as tomato juice, apple juice and skimmed milk. It has been reported that hydrodynamic cavitation induced adequate destructive forces to inactivate the vegetative cells of bacteria, yeast, yeast ascospores and heat-resistant bacterial spores. Common spoilage microorganisms, such as lactic acid bacteria and yeast, can be eliminated at reduced temperatures, due to the synergistic effects of temperature and hydrodynamic cavitation.

Adequate lethality was obtained for commercial sterility of high-acid liquid foods. One of the main advantages of using a hydrodynamic cavitation reactor are the lower operating temperatures during sterilisation, and hence, foods such as acidic fruit juices, salad dressings and milk can be safely processed at reduced processing temperatures, which translates into superior products.

Milly et al. (2008) have also investigated the application of a shock wave reactor for the inactivation of Saccharomyces cerevisiae in apple juice. It has been reported that enhanced inactivation of S. cerevisiae (6.27 log cycles) can be achieved at reduced processing temperatures (65.6°C and 76.7°C) when subjected to sufficient hydrodynamic cavitation, compared to what can be predicted when using heat inactivation parameters. Comparison of the energy consumption, in the case of a hydrodynamic cavitation reactor to conventional and pulsed electric field processing technologies, indicated that energy consumption can be reduced significantly (173 compared with 215 and 258 kJ/kg respectively), and the effectiveness of the process can be significantly increased by using hydrodynamic cavitation in fruit juice manufacturing. It has also been reported that the hydrodynamic cavitation equipment can be easily scaled up for large industrial purposes, with improved energy savings and greater efficiencies (from 55% to 84%).

Favourable results were obtained in the sugar industry with the use of hydrodynamic cavitation during the defecation of diffusion juice (Litwinienko et al., 2005). The high effectiveness of the technology allows the use of hydrodynamic cavitation in complex thermal, chemical, and hydro-mechanical treatment of diffusion juice. During its treatment, deposition and coagulation processes are accelerated, physical and chemical properties of the rich juice are improved, whilst the energy demands associated with its treatment are reduced. It should be noted that these technological operations are performed in one device.

8.3 CHEMICAL SYNTHESIS

8.3.1 *The hydrolysis of vegetable oils*

Conventionally, the hydrolysis of vegetable oils, using steam or water, requires operating temperatures between 250–350°C, and pressures between 30–60 atmospheres. Pandit and Joshi (Pandit et al., 1993) studied the hydrolysis of castor oil and kerdi oil, using both acoustic (ultrasonic generator) and hydrodynamic cavitation (in a flow loop at a cavitation number less than that required for inception) under ambient operating conditions.

The hydrodynamic cavitation setup is a loop reactor with a gate valve, used as a throttling device, to cause cavitation. Oil-water mixtures, without any catalysts and of different proportions, totaling 200 dm^3, were subjected to cavitation conditions by circulating the liquid a number of times through the throttling valve in the reactor, under a constant ambient temperature held at around 25°C with the help of cooling coils. The extent of the hydrolysis was monitored by determining the acidic value of the oil-water emulsion in the tank. The decreasing acidic value traces for the hydrolysis reaction were similar for the two types of cavitation. Thus, the study was the first to show that the flow loop, with a constriction for the generation of cavitation conditions, produces similar results to that for acoustic cavitation. It also found that the required dissipation energy, for the same degree of hydrolysis, was 30% lower for hydrodynamic cavitation (1,080 J/cm^3 of emulsion) than for acoustic cavitation (1,384 J/cm^3 of emulsion). The work also clearly showed that the rate of hydrolysis increased with cavitation severity, when the cavitation number was reduced.

8.3.2 *The synthesis of biodiesel*

The term “bio-diesel” refers to simple alkyl esters, derived from fatty acids, used as an alternative energy source for oil or diesel.

The world’s biodiesel production is continuously growing. The use of this fuel is beneficial, not only because of its low price, but also because during its combustion the amount of CO_2 released into the atmosphere is equal to the amount needed to grow the plants in order to produce the fuel.

Refaat (2010) presented an interesting review of the technologies used in the production of biodiesel from waste vegetable oils, taking into account economic aspects, environmental protection and waste management.

The conventional techniques for the synthesis of biodiesel (Qiu et al., 2010, Gogate et al., 2009, Kelkar et al., 2008) refer to a catalysed chemical reaction involving vegetable oil and an alcohol to yield acids, alkalis, esters and glycerol. The conventional techniques typically utilise temperatures in the range 70–200°C, pressures in the range 6–10 bar, and reaction times of up to 70 hours, in order to achieve conversions in the range of 90–95%, based on the type of raw material used (usually mixtures of waste fatty acids). The reaction is usually limited by mass transfer rates and the mixing of the different phases due to their limited solubility. Hence, there exists a lot of potential for the application of cavitation reactors.

Kelkar et al. (2008) investigated the use of cavitation for the intensification of the biodiesel synthesis (esterification) reaction, which is a mass transfer limited reaction considering the immiscible nature of the reactants, i.e., fatty acids and alcohol. Esterification of fatty acid (FA) odour cut (C_8–C_{10}) with methanol in the presence of concentrated H_2SO_4 as a catalyst has been studied in the hydrodynamic cavitation reactor as well as in the sonochemical reactor. The different reaction operating parameters such as the molar ratio of acid to alcohol, and catalyst quantity have been optimised under acoustic as well as hydrodynamic cavitation conditions, in addition to the optimisation of the geometry of the orifice plate in the case of hydrodynamic cavitation reactors. A few experiments have also been carried out with other (lower and higher carbon) acid/methanol combinations viz. caprylic and capric acids with methanol, with the aim of investigating the efficacy of cavitation for giving the desired yields and also to quantify the degree of process intensification that can be achieved using the same.

It has been observed that the ambient temperature and pressure operating conditions and reaction times of less than 3 hours, for all the different (lower and higher carbon) acid/methanol combinations studied in the present work, were sufficient to give more than 90% conversion (mol%). This clearly establishes the efficacy of cavitation as an excellent way to achieve intensification of the biodiesel synthesis process.

Pal et al. (2010) presented the development details of a biodiesel production test rig based on hydrodynamic cavitation. This was followed by the results of an experimental investigation carried out on a four cylinder, direct injection, water cooled diesel engine, operating on diesel and a biodiesel blend of Citrullus colocyntis (Thumba) oil.

The experiment covered a wide range of engine rpm. Results show that the Thumba oil biodiesel, produced through hydrodynamic cavitation, can be used as an alternative fuel with a better performance and lower emissions compared with diesel.

The most significant conclusions are that:

i. biodiesel production, using the hydrodynamic cavitation technique, seems to be a simple, efficient, time saving, ecofriendly and industrially viable process.
ii. A 30% biodiesel blend of Thumba oil shows a relatively higher brake power, brake thermal efficiency, reduced BSFC (brake specific fuel consumption), and smoke opacity with a favourable p–q diagram compared with diesel.

Ji et al., (2006) presented the transesterification results for soybean oil, using both ultrasonic cavitation and hydrodynamic cavitation. Both methods had shorter reaction times and lower energy consumptions than the conventional mechanical stirring method. Hydrodynamic cavitation is a potential method that could be used for biodiesel production on an industrial scale due to its easy scale-up property.

8.4 THE APPLICATION OF CAVITATION IN ENVIRONMENTAL DECONTAMINATION PROCESSES

8.4.1 *Using cavitation to treat wastewater during mining*

An important environmental problem is the purification of water during mining. When drilling shafts, a typically fitted complex is not equipped with the means of reusing the water. For this reason low biodegradable pollution such as oil, surfactants, and lubricants are carried by the water to the surface and are collected in open settlement ponds (so-called sludge settlement tanks). They occupy considerable space, which for a long period of time are unsuitable for agricultural use, and require long rehabilitation.

Litwinienko et al., (2005) described/presented technology for the neutralisation of the drill wastewater produced when drilling shafts. The purification technology combines the physical and chemical interactions on water pollution and provides for the conversion of toxic constituents, dissolved in water, into insoluble precipitation. During the purification of water using filter separators, the solids are separated out whilst the clarified water is subjected to reagents/chemicals. The result is the binding of ions from the dissolved compounds into weakly soluble but strongly bound compounds. With the removal of the hazardous compounds the drill wastewater can be reused according to the technical needs and the excess discharged into natural or artificial water reservoirs.

To accelerate and secure the full course of chemical reactions, which cause problems under normal conditions, the authors proposed a two-stage hydrodynamic cavitation reactor. During the first stage of cavitation, chemicals (e.g. slaked lime) are introduced into the wastewater being processed whilst during the second, air or another oxidant (e.g. hydrogen sulphide) is injected. In contrast to typical industrial facilities, which require water to be heated in order to remove pollutants, the cavitation process is conducted at the ambient temperature, whilst the acceleration of the neutralisation reaction proceeds as a result of cavitation. Ozone can be used as an oxidant in the neutralisation of wastewater with a high organic pollutant content, especially in an alkaline environment which favours the precipitation of metal hydroxides. The end result, during the oxidation of organic compounds, can be the formation of CO_2 and H_2O, but the consumption of ozone is significantly increased.

Figure 8.1 shows a schematic diagram of the test rig for the treatment of drill wastewater with a capacity of up to 20 m^3/hr. It consists of devices for drill wastewater neutralisation and ancillary equipment (tanks for the collection and disposal of liquids, pipelines, control and measuring equipment). The arrangement consists of a pump, the hydrodynamic cavitation reactor, filter, separator, and the dosing unit.

The hydrodynamic cavitation reactor (5) is fitted to a pipeline that is connected to the reservoir (7) which collects the drill wastewater. The centrifugal pump (6) supplies the water to the cavitation reactor. The slaked lime inlet to the first stage of the cavitation reactor (or another chemical reagent) is dosed by a pump (9) from the chemical reagents tank (1) through a purification filter (10). The oxidant (air or ozone) is fed to the second stage of the cavitation reactor. The tuning of the hydrodynamic cavitation reactor for optimum operating conditions is done with the help of a valve (4), usually in terms of the circulation until the required purification level is reached. Consumption of slaked lime is not less than 2.5–3.5% CaO (by dry weight) per 1 m^3 of purified water and to

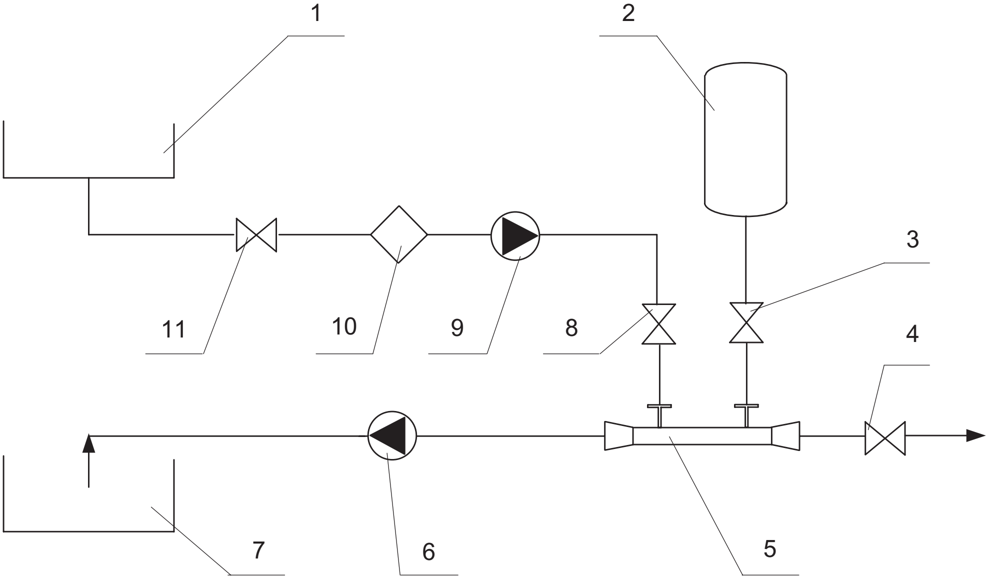

Figure 8.1. Schematic diagram of the drill wastewater treatment arrangement. 1 – tank containing chemical reagents, 2 – ozoniser, 3 – control unit, 4 – control valve, 5 – hydrodynamic cavitation reactor, 6 – pump number 1, 7 – reservoir containing drill wastewater, 8 and 11 – valves, 9 – pump number 2, 10 – filter.

attain a pH value between 8.0–8.5. The maximum oxygen/ozone mixture consumption is 2 m^3/hr. The use of ozone is dependent on the organic compound content present in the treated drill wastewater.

8.4.2 *Cavitation and flotation*

Hydrodynamic cavitation provides a practical method for an in situ generation of tiny bubbles in flotation systems. Although the cavitation phenomena in flotation has been considered in commercial applications from the beginning, intentionally applying hydrodynamic cavitation for improving the flotation performance has only been realised during the past decade or so. Recent developments and an understanding of cavitation, gas nucleation, and degassing due to cavitating conditions, have provided a scientific basis for the cost-effective application of hydrodynamic cavitation to flotation operations (Zhou et al., 2009).

Tiny bubbles created by low intensity hydrodynamic cavitation in flotation appear to offer the following:

a. an enhanced particle aggregation by tiny bubble bridging, giving rise to an increased collision probability of the enlarged particle aggregates with flotation-sized bubbles
b. an accelerated particle-bubble attachment through the coalescence of tiny bubbles frosted onto particle surfaces with larger bubbles, instead of direct particle-bubble contact
c. an increased contact angle and attachment force between particles and bubbles, through tiny bubbles frosted onto particle surfaces, and an increased recovery of fine and coarse particles at reduced reagent consumption

d. a cleaning of particle surfaces through the collapse of cavity bubbles (e.g. removal of slime coatings, oxidation films, and collector contaminated layers on the gauge particle surfaces).

Both fundamental analysis and experimental results have demonstrated the beneficial effect of hydrodynamic cavitation on flotation performance. Flotation incorporating hydrodynamic cavitation is still in its infancy, but is gaining broad interests among researchers, equipment manufacturers and flotation operators. One question of interest is: besides their small physical size and huge collapsing intensity, are there any other unique features of the cavitation-generated bubbles which distinguish them from the tiny bubbles generated by other means, e.g., electrolysis, chemical reaction, etc.

There are many reports indicating to the investigations related to understanding the effect of using hydrodynamic cavitation for improving the performance of flotation devices (Zhou et al., 2009, 1997).

Zhou et al. (1997) have studied the effect of a hydrodynamic cavitation reactor on the performance of a conventional flotation cell, on a larger operating scale, in the matte separation plant at Copper Cliff, Inco Ltd., Sudbury. Samples drawn from the feeds to the rougher and the first cleaner were tested in a portable continuous mini flotation cell. The use of the cavitation reactor improved the flotation kinetics on both samples. The effect on selectivity was mixed; it improved for the cleaner feed, but some deterioration was observed for the rougher feed. The test work, although limited, illustrates that the cavitation reactor offers the potential benefit of increasing circuit capacity while maintaining selectivity.

8.4.3 *Using cavitation to aerate natural waters*

The use of hydrodynamic cavitation has an important practical significance for the aeration of natural waters in rivers and reservoirs, since it can be used, for example, in fish farming, especially during winter. Litwinienko et al. (2005) proposed the construction of hydrodynamic cavitation water aerators in lakes. Figure 8.2 shows a schematic diagram of such an installation.

The main elements of the aeration installation are the hydrodynamic cavitation reactor (5), the separation chamber (7), and the aeration chamber (8). Water with a reduced air content is pumped (5) into the hydrodynamic cavitation reactor where a large number of cavitation bubbles ($10^{10}/m^3$) filled with air form, saturating the water and forming a water-air mixture. In the cavitating stream, intensive mass exchange processes occur and the water becomes enriched with oxygen, which is then directed into the aeration chamber (8) through chamber (1). The exit of the aeration chamber is attached to the air/water separation chamber (7) in which, thanks to buoyancy, the remaining air bubbles that are not used, rise and saturate the surface layer of water in the tank. The oxygen-enriched water is directed to a lower level in the aeration tank which promotes the aeration of the entire volume of water.

8.5 USING CAVITATION IN THE TREATMENT OF BALLAST WATER

Water was first used in the nineteenth century as ballast in ships with the appearance of steel hulls. Ballast water is necessary to ensure safety and the proper

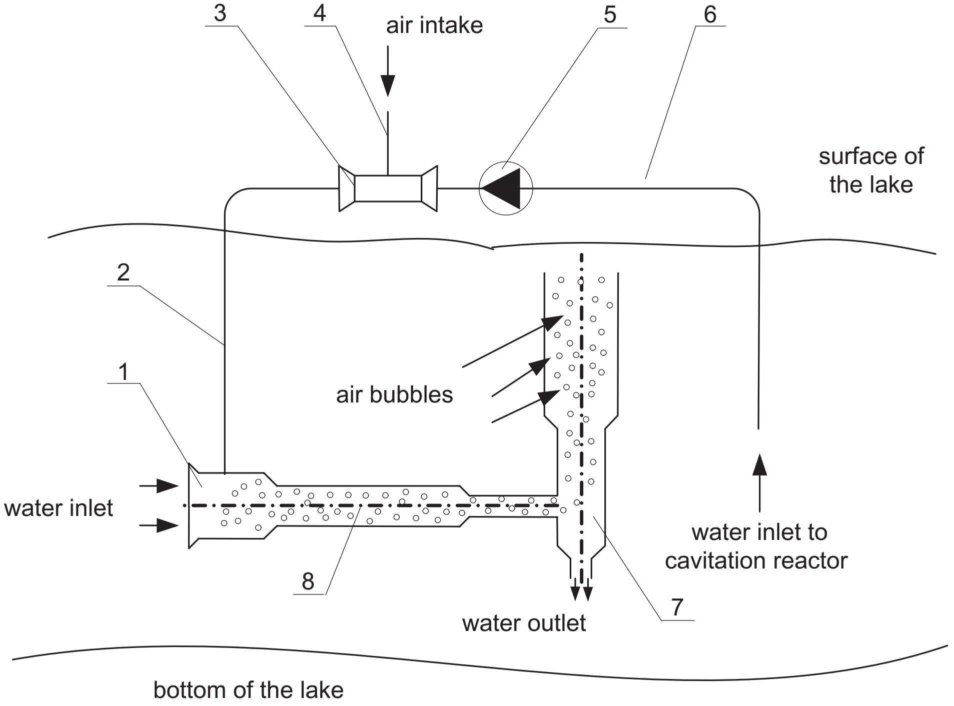

Figure 8.2. Apparatus for water aeration: 1 – water chamber, 2 – pressure pipeline, 3 – hydrodynamic cavitation reactor, 4 – air supply, 5 – pump, 6 – suction pipe, 7 – separation chamber, 8 – aeration chamber.

functioning of the modern fleet. Water is pumped into the ballast tanks to improve balance and stability of the cargo vessel, especially when unloaded, or when changing trim. Ballast waters are usually taken on during the unloading of the cargo vessel, and pumped out during loading. They can also be taken on whilst sailing, to compensate for the weight lost due to fuel and usable water consumption.

The ballast waters contain various microorganisms, and sometimes larger species of plants and animals. When the vessel discharges its ballast, these organisms are discharged as well and can cause an adverse effect on flora and fauna in that particular marine zone (disturbances in the homeostasis of that habitat, caused by the excessive proliferation of “newcomers”). Ballast waters can also be a source of microbiological contamination. In 1991 cholera bacteria was found in the ballast waters of ships that called at ports on the east coast of the United States.

The threat from invasive marine species is one of the four greatest threats to the world’s oceans (Kozłowski, 2009). Although this threat is not perceived as such, as in the case of petroleum products, the impact of invasive marine species is often much more dangerous to the marine environment, because of its irreversible effects. In many studies with respect to this example, hundreds of cases have been documented where ballast waters may have been the cause of the introduction of new organisms into the environment. If these organisms have the conditions to become invasive, it can seriously disrupt the indigenous ecological equilibrium.

Biological pollution is also caused by bacteria, viruses, fungi and higher organisms. Often the vessel's route causes the organisms to be transported into regions where they do not naturally exist, and they find themselves in conditions ideal for survival. In the absence of natural enemies the new organisms become harmful to the whole ecosystem, that region's economy, and also pose a threat to humans. While the effects of chemical pollution are immediately noticeable and appropriate preventive measures can be carried out, inasmuch the momentum of the biological pollution is invisible and the effects only appear after some time.

It is estimated that each year the worldwide fleet transports 2–3 billion tonnes of ballast water around the world, containing daily, on average, more than 3,000 species of plants and animals.

In order to effectively neutralise the ballast water, various methods are used:

- mechanical – filtration, microfiltration, hydrocyclones
- physical – UV radiation, ultrasound, hydrodynamic cavitation
- chemical – addition of chemicals, ozone, chlorine, chlorine dioxide, and others.

More commonly a combination of the above methods is used.

Ultrasound is a relatively new method of disinfection and has limited application in the treatment of ballast waters. A more beneficial effect can be achieved using hydrodynamic cavitation. The hydroxyl radicals created in the cavitating liquid environment are very effective in destroying plankton, algae, bacteria and viruses.

In recent years, hydrodynamic cavitation has become more widely used to treat the ballast waters, as it causes the destruction of microorganisms and the rupture of cell membranes. Thus it is very effective in destroying plankton, algae, bacteria and viruses.

Kato (2003) conducted experiments into the destruction of plankton in water taken from the University of Tokyo's campus lake, using a specially designed device, equipped with a cavitation nozzle (Figure 8.3.)

The hydrodynamic cavitation reactor has a cylinder with two nozzles of 0.12 mm diameter, which produce cavitation. The plunger pump produces a pressure of up to 150 MPa. Cavitation is generated in both nozzles.

The water taken from the lake contained large quantities of plankton such as Chlorophyta, Diatoms and Ciliata. The effect of cavitation, in terms of reducing the plankton's particle size, was tested at pressures of 100 and 150 MPa. Very high nozzle pressure produced a cavitating stream of more than 100 MPa, which fragmented the plankton into smaller particles of less than 50 μm.

The study confirmed that the cavitation nozzle is very effective in destroying plankton in water at an applied pressure of 150 MPa. However, the optimum device settings and its effectiveness were not been fully explored during the experiment.

The Japanese Maritime Safety Agency studied the effect of hydrodynamic cavitation for the elimination of plankton in ballast tanks. The project was launched in 1999 (Kato, 2005). Figure 8.4 shows a prototype device for implementing cavitation. The water flowing through the slit nozzle, consisting of a number of 100 mm long slits and a collision plate across the pipe's cross-sectional area, produces cavitation streams in two directions upon exit. The rate of water flow was 115 and 150 m^3/hr, which corresponds to water (liquid) speeds of 4.1 and 5.3 m/s.

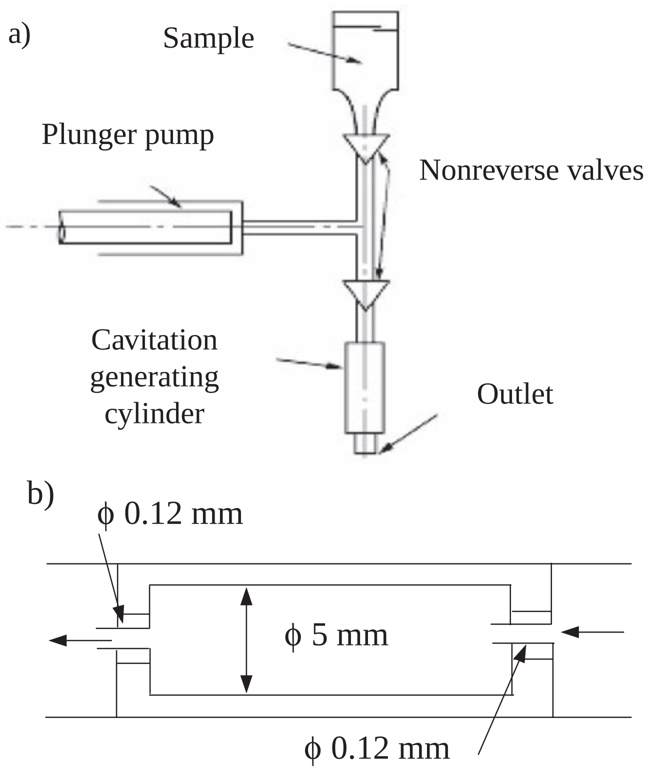

Figure 8.3. Experimental device: a) flow system, b) cavitation generating cylinder.

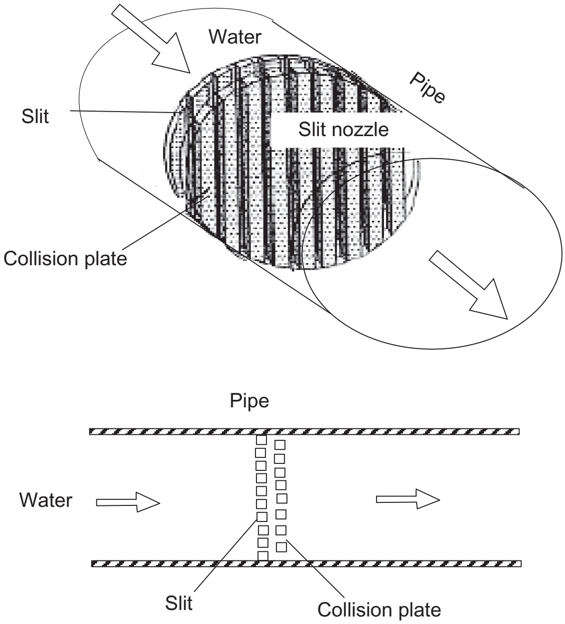

Figure 8.4. Schematic diagram of a prototype device to generate cavitation on board a vessel (Kato, 2005).

This process was applied to the degradation of phytoplankton and zooplankton in sea water from Imari Bay, on the island of Kyushu (Kato, 2002). The destruction of plankton increases when the flow rate increases.

Sawant et al. (2008) presented the results of studies into the disinfection of sea water using hydrodynamic cavitation. Under experienced conditions, over 80% of the zooplankton present in sea water was removed.

During high rates of cavitation liquid flow rapid vibrations occur, caused by bubble implosions in the surrounding fluid. Under these cavitation conditions, several effects can occur such as shock waves or turbulent shear stress, which are responsible for rupturing the zooplankton cells.

8.6 CAVITATION IN THE DISPOSAL OF PETROLEUM PRODUCTS

Oil spills from tankers have large implications for the oceanic environment. Mechanical removal of oil is the best solution to this problem. However, the removal of oil is often difficult for many reasons, including bad weather. The dispersion of oil is the next best solution and for this purpose chemicals are used. Substances which disperse oil can in turn cause more problems, since they are also environmentally harmful to some extent.

The use of cavitation appears to be a future method in the dispersion of oil. This method of disposal does not cause a negative impact on the environment.

Kato et al., (2006) present the possibility of using a high speed water jet for the dispersion of oil spilled at sea. Figure 8.5 shows the loop of the cavitation jet experiment.

A pump (Kaercher K-370+, Winnenden, Germany) generates high pressures of up to 7.5 MPa. The water is ejected from a nozzle into a water tank under atmospheric pressure, forming a cavitating jet. The maximum flow rate is 97 cm^3/s and the flow rate is regulated by a regulation valve. The excess water returns directly to the feed tank through the regulation valve.

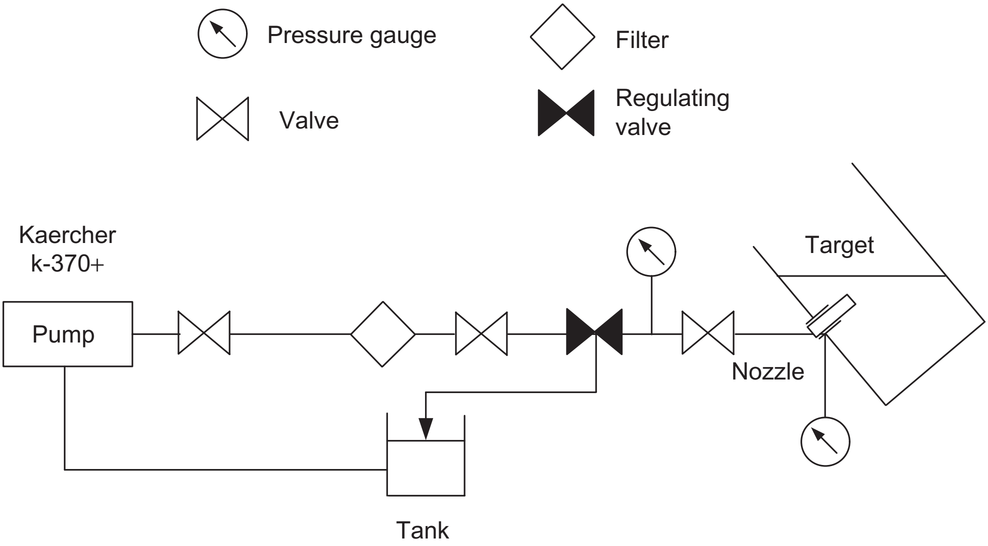

Figure 8.5. Schematic diagram of a cavitating jet loop experiment.

Figure 8.6 shows the setup of the submerged cavitating jet in the experimental tank. The cavitating jet was ejected upward at an angle of 45°, which was realized by inclining the tank. It is well known that strong mixing occurs when cavitation bubbles collapse at the interface of two fluids; therefore, the experimental setup was arranged to satisfy this condition. The inclined jet arrangement is robust for small water/oil surface elevations caused by the water jet ejection. The distance between the nozzle and the target was set at 20 mm throughout the experiment. The target was a 3 mm thick acrylic plate. The cavitation bubbles in the cavitating jet collapsed on the target placed at the water/oil interface. The target is essential in this arrangement, if there is no target, the cavitating water jet rises up into the air and does not disperse the oil. The target improves the oil dispersion but, it may be eroded after some time.

Figure 8.7 shows the setup of the in-air water jet which impinges vertically on the oil/water surface. The distance between the nozzle and the oil's surface was set at 20 mm. A 3 mm thick guide plate was set horizontally, 10 mm below the water's surface. The guide plate has a centrally located 5 mm diameter hole. The water jet hits the oil's surface and then passes through the hole, which draws in the oil layer. Hence the oil is dispersed effectively through the shearing force of the jet flow and the collapse of the cavitation bubbles when generated by the water jet.

Laboratory experiments showed that a high-speed water jet is very effective in dispersing heavy oil. When a high-speed water jet hits an oil layer on the sea's surface, the jet tears off the oil layer and following the collapse of the cavitation bubbles, causes the oil to disperse. The submerged cavitating jet is also effective in dispersing oil spills.

The dispersed oil droplets are usually much less than 50 mm in diameter, and are easily decomposed into CO_2 and H_2O by the action of sunlight or bacteria in the sea. Dispersants are usually used for dispersing oil spills, but there is concern about the possible side effects because they are chemical products. In contrast, the water jet is safe and clean, because only sea water is used. It is thus highly advantageous to use a high-speed water jet. It is important that the oil layer and the oil droplets come close to the high-speed water jet in order to realise a good dispersion of oil. Dispersion is better in sea water than in fresh water, probably because sea water contains many microorganisms that discharge surfactants.

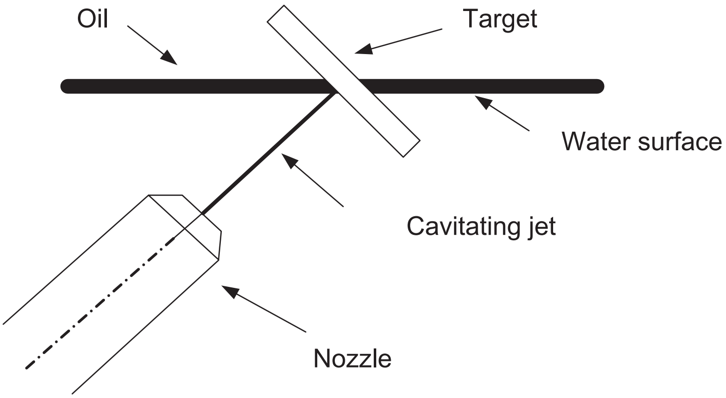

Figure 8.6. Submerged cavitating jet.

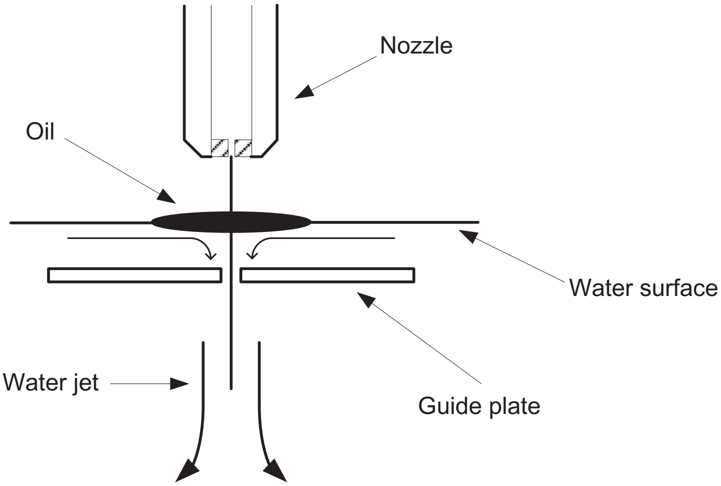

Figure 8.7. In-air water jet.

Figure 8.8 shows the schematic diagram for the treatment of wastewater containing oil products, using an aerated hydrodynamic cavitation reactor, as studied by Kolesnikow et al. (1998).

Aerated hydrodynamic cavitation reactors are devices contained within chambers where ultrasonic vibrations are the result of water flow. A pressure of not less than 0.3 MPa is required. The liquid flowing through the aerated hydrodynamic cavitation reactor chamber produces a partial vacuum which is conducive to the injection of additional air or liquid into the chamber through the suction nozzles. Inside the chambers there is a localised increase in the speed of liquid flow and changes in local pressures. At the exit from the cavitation nozzle a water/air cone forms, which breaks down into small bubbles which pass through a layer of turbulent liquid. The dispersed air, in bubble sizes of 0.4–0.7 µm, increases the effectiveness of the effluent treatment process.

The effectiveness of the process using the aerated hydrodynamic cavitation reactor was tested during wastewater treatment of petroleum products in factories producing soot. Wastewaters polluted with petroleum products were purified in five vertical flotation cells, the output of each being 28 m^3/hr. In order to improve their effectiveness aluminium sulphate was used as the coagulant.

The authors put inside each flotation cell three aerated hydrodynamic cavitation reactors, the output from each being 10 m^3/hr (see Figure 8.3). Table 8.1 summarises the comparative data for the wastewater flotation treatment using the two methods.

The use of hydrodynamic cavitation helped to greatly intensify the flotation process with a 6-fold increase in the removal effectiveness of solids, a 3.5 fold reduction in the COD value, and a 60-fold increase in the removal effectiveness of hydrocarbons.

The use of the aerated hydrodynamic cavitation technology can:

- intensify the flotation treatment of industrial effluent containing oil products.
- increase the saturation of water by gas (air, oxygen) and cavitation bubbles.
- significantly increase the contact surface between the phases.

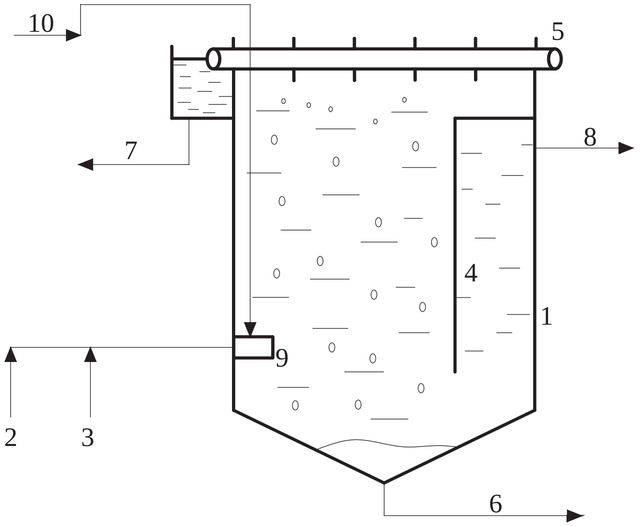

Figure 8.8. Schematic diagram for the treatment of wastewater using an aerated hydrodynamic cavitation reactor, 1 – flotation cell, 2 – supply sewage pump, 3 – pump, 4 – barrier, 5 – scraper, 6 – sedimentation discharge, 7 – petroleum products discharge, 8 – treated sludge discharge, 9 – aerated hydrodynamic cavitation reactor, 10 – air supply.

Table 8.1. Comparison of wastewater purification when separating off petroleum products by means of pressure flotation with and without the use of an aerated hydrodynamic cavitation reactor (Kolesnikow et al., 1998).

		Purification using pressure flotation	
Parameter	Raw sewage	Only	With an aerated hydrodynamic cavitation reactor
Temperature, °C	10–30	10–30	10–30
Colour	dark-grey	light-grey	light
Suspension, mg/dm^3	300	30–60	5–12
Dry weight, mg/dm^3	3500	1200	800
COD, mg O^2/dm^3	180	110	30
Hydrocarbons in a hexane extract, mg/dm^3	300	30–60	0.5–3

All of the above help to increase the removal of petroleum products from the effluent by up to 90%, and from suspensions by up to 85% in existing effluent treatment equipment.

8.7 SUMMARY

Based upon a review of the subject literature and our experiences, hydrodynamic cavitation appears to be promising for the neutralisation of petroleum products and other mixtures of liquid hydrocarbons which are currently entering the environment.

Processes involving hydrodynamic cavitation are becoming simpler and are influencing a reduction in energy consumption in effluent treatment.

It is important also to intensify the effects of cavitation. This can be achieved by combining cavitation with advanced oxidation processes, utilising oxidising agents such as ozone or hydrogen peroxide.

The possibilities of applying hydrodynamic cavitation and cavitation reactors discussed in this chapter are based upon specific examples. It should be emphasised, that the prospects for the implementation of technologies utilising hydrodynamic cavitation are much wider than presented here. However, in each particular case it is necessary to develop or select the most effective cavitation reactor design and carry out preliminary operational trials. This will allow for the optimal use of effects which accompany hydrodynamic cavitation and to obtain the required result in the most measurable way.

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CHAPTER 9

Application opportunities for hydrodynamic cavitation in environmental engineering technologies

Hydrodynamic cavitation appears to be a new, advanced technology for the degradation of complex compounds and an alternative to ultrasound-induced cavitation. The use of hydrodynamic cavitation in environmental engineering technologies allows processes to be greatly effective during water and effluent treatment. A technology which utilises the cavitating liquid environment can be considered as a non-waste technology and environmentally friendly due to the possibility of degradation of low biodegradable, hazardous and carcinogenic organic compounds, which are resistant to conventional disposal methods. Examples include pesticides, dyes, or high molecular organic compounds, which in the cavitating liquid environment become susceptible to biodegradation.

The examples which have been presented regarding hydrodynamic cavitation in environmental engineering suggest that this method is effective and less burdensome for the environment.

One of the opportunistic and constantly growing areas for the application of cavitation is water disinfection. Recently more widespread attempts have been observed at applying cavitation to the disinfection of municipal effluent, because in the cavitating liquid environment degradation also occurs in addition to disinfection, which is significant during the decomposition of organic compounds which cause disorders in the endocrine glands (endocrine disrupters), more commonly present in municipal effluent and leachate from municipal landfills.

Analysing the rich literature on the degradation of the various pollutants in water, effluents and leachate, one can conclude that hydrodynamic cavitation is becoming increasingly widespread in its use to assist the biological treatment processes. It is undoubtedly connected with the cost of generating hydroxyl radicals using AOP.

The examples presented here prove the purpose of undertaking the subject of applying hydrodynamic cavitation to water and effluent treatment processes.

Based upon a review of the subject literature and personal research an opportunity exists to reduce the energy demands of the degradation processes through the use of hydrodynamic cavitation. An important factor will also be the technological process simplification when neutralising petroleum products and other liquid hydrocarbon mixtures which are currently entering the environment. The real task is to develop an appropriate method involving hydrodynamic cavitation, where there is no necessity to use catalysts, and in addition which can be realised under normal temperature and pressure conditions. It would allow for a significant technological simplification of the process and reduce its energy consumption.

Overall, it can be said that hydrodynamic cavitation is a well-established technology on both the laboratory and pilot scales, but the combined effort of the engineers and physicists is required to effectively harness this technology on an industrial scale.

Summarising the research into the selected applications of hydrodynamic cavitation, in processes associated with the treatment of the different elements within the environment, it can be concluded that the use of cavitation is a promising solution. Undoubtedly, there are still many areas, and to date undiscovered ways of using it. Certainly in the coming years we will witness new discoveries and probe deeper with current research into possibilities of applying cavitation to intensify the processes used in environmental engineering.

Containing the state-of-the-art in hydrodynamic cavitation, the book consists of two parts. The first part presents the physical basis of cavitation and a systematic classification of various kinds of cavitation and their formation sources. Special attention is paid to a group of factors that promote cavitation formation in natural liquids. A general model of cavitation is formulated as well as a sub-model describing dynamics of the formation, development and collapse of cavitation bubbles. The sub-model also includes effects of cavitation bubble occurrence on the liquid in the direct vicinity of bubbles. Finally, part one also includes a thermodynamic hydrocavitation model of water containing cavitation nuclei (natural waters). The second part deals with the application of hydrodynamic cavitation effects to advanced oxidation of substances that pollute the natural environment. Results of laboratory experiments on the application of cavitation effects to decompose selected organic compounds which hardly undergo biodegradation are presented, as well as a concept of the cavitation phenomenon application on an industrial scale.

Application of Hydrodynamic Cavitation in Environmental Engineering will be useful to professionals dealing with the design and practical application of hydrocavitation reactors, and to academics in environmental engineering.

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