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Proiect POSDRU/159/1.5/S/132397 – Excelenţă în cercetare prin burse doctorale si postdoctorale – ExcelDOC

„Dunărea de Jos" University of Galaţi
Doctoral School of Egineering

DOCTORAL THESIS

ABSTRACT

Research on the use of sonic generators for the extraction of hazardous substances from wastewaters and technological liquids

Cercertări privind utilizarea generatoarelor sonice pentru extracţia substanţelor periculoase din ape şi lichide tehnologice uzate

PhD student,
Eng. Nicoleta MATEI (CIOBOTARU)

Scientific adviser,
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Series I 6: Mechanical Engineering No. 37

GALAŢI
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Keywords

- extraction of hazardous substances from wastewaters and technological liquids;
- ammonia wastewater;
- sulfide wastewater;
- sonic generators;
- ultrasonic treatment;
- sonic treatment;
- decontamination.

Contents

Introduction

The wastewaters, are natural waters whose quality has been adversely affected by matters and contaminants. The water bodies can be both naturally and artificially polluted. However, the status of "waste water" is a consequence of the natural sources use by the human factor. Of fundamental importance, water is employed in all existential segments, from the drinking water consumption by the more or less populated urban centers, to the feed in agriculture, livestock breeding, transports and all industrial processes. The purveyance to fulfill all these requirements can be made from any natural source, consisting of rivers, lakes, seas, oceans or groundwater. After use, the discharged water can be contaminated bacteriologically or by a number of organic or inorganic compounds based on nitrogen, sulfur, heavy metals, pesticides, etc. The wastewaters are known as effluents and the waters they flow into are called receptors. When a receptor water flows into another, they are referred as emissaries.

The industry development and the use of more and more toxic complexes, require the imple-mentation of effective treatment technologies so as the risk of water quality degradation, caused by the discharge of wastewaters and technological liquids, is not increased. The wastewater treatment technologies are useful both to ensure the necessary characteristics for the discharge into emissaries and to reuse them in order to protect natural water resources.

The pollutants covered by this study are ammonium and inorganic sulfides. The choice of this contaminants is based on their provenance from most contemporary techno-logical processes. Hence, the need for a constant monitoring of these hazardous substances and their contact with the environment is understood. The two compounds are specific indicators of sewage being responsible for decomposition processes, rotting, eutrophication and thus for the destruction of aquatic flora and fauna once entered in the surface waters. These pollutants can enter the aquatic environment in different ways, either directly in the case of industrial effluents or indirectly due to inefficient sewage treatment plants.

This doctoral thesis aims to approach a new field of science, namely the use of ultrasound in wastewater treatment processes. Classic mechanical filtering processes in the purification of surface and industrial water, have some inconveniences: low productivity, limited opportunities for retaining small particles or the frequent stop installations in order to be cleaned. Instead, ultrasonic energy may increase filtration rate, can proceed without the addition of chemical reagents and does not require many additional process steps, leading to the removal of many inconveniences. Also, conventional oxidation based on chemical and biological processes often proves to be insufficient in the removal of certain types of pollutants. Innovative water treatment represented by the use of ultrasound in both sonic and ultrasonic field is an advanced oxidation process, a technique of perspective that reduces pollutants in wastewater. Ultrasound can also be combined with other advanced oxidation processes.

This paper proposes the use of gas driven sonic generators for the elimination of ammonia or sulphide from wastewaters with high concentrations, technology that has not been shown in scientific papers published to date. Also, for determining the influence of the acoustic emitter type on the effectiveness of wastewater decontamination, the paper carried out a comparative study of two technologies based on the use of ultrasound.

Experiments were conducted to meet the requirements of national legislation on the loading degree of the sewage, permissible to be discharge into the public sewerage networks of settlements or to be evacuated in natural receptors.

The first chapter deals with the current state of the experimental achievements and the technological facilities widely used for the decontamination of wastewaters and technological liquids containing ammonia or sulfide. A critical analysis of the presented technologies was performed and their main advantages and disadvantages were highlighted. The studied technologies are stripping processes, ion-exchange sorption, membrane processes, biological methods or oxidative methods (chemical, electrochemical and advanced oxidation), which have been discussed both for ammonia water and sulphide wastewater.

Chapter 2 describes the action of ultrasound in liquids and the main acoustical parameters. Also, in this section the efficiency of ultrasonic technology obtained to date in the treatment of various effluents is presented. This efficiency is exposed depending on the main acoustical parameters responsible for the maximum effect on the cavitational events generation, namely frequency and ultrasonic intensity.

Chapter 3 describes the technological principles of the current acoustical emitters, mechanical and electromechanical, and some experimental achievements of the acoustical generators for the treatment of liquid media.

In Chapter 4, the two experimental systems underlying this research and their operating parameters (acoustic parameters and operating parameters) are presented. The equipments utilized in conducting the experiments and the research activities are described, as well as the technical specifications of each apparatus. At the same time, various techniques and treatment regimes are proposed as for the sonic or ultrasonic treatment of studied wastewaters to be optimized.

Chapter 5 refers to the materials and the methodology for determining the quality indicators of the studied wastewaters, and to the description of the specific characteristics of the analyzed wastewater types.

Experimental results regarding the treatment in ultrasonic field of industrial ammonia wastewaters and of the simulated sulfide wastewaters are described in Chapter 6 and Chapter 7, respectively. The effects of irradiation depending on the treatment time, on the operating mode of the electromechanical generator (continuous or intermittent), on the presence or absence of sample aeration, on the sample temperature, on the sample volume, and on initial concentration variations are described.

Chapters 8 and 9 describe the effects of the treatment applied in the sonic field for the ammonia wastewater and sulfide wastewater, respectively. Experimental determinations were performed according to the treatment time, the operational conditions of the gasodynamic generator (continuous or intermittent), the sample temperature, the sample volume, as well as for variations of the initial concentration. Finally, in Chapter 10, the overall conclusions are presented, original contributions and research perspectives.

Chapter 1

The current state of hazardous substances extraction processes from wastewaters and technological liquids

Wastewater treatment or purification is a complex process of retention and neutralization of the dissolved harmful substances, in colloidal or suspension form, present in urban and industrial wastewater, that are not accepted in the aquatic environment in which the treated wastewater is discharged and that allow restoring the physicochemical properties of water before use [7].

Treatment processes of industrial wastewaters can be conventional (similar to those for urban wastewater), namely physico-mechanical processes (primary treatment), physico-chemical and bio-chemical processes (secondary treatment) or advanced processes (tertiary treatment) [8]. Adopting a particular process for the purification of contaminated water depends on the nature of pollutants, the amount of water or utilized technological liquid and the maximum limits imposed on treated wastewater discharge into the environment.

1.1. Technologies and installations for ammonia water decontamination

Ammonia waters can result from various processes. In the metallurgical industry, the dry distillation of earth coal for coke production generate ammonia waters as a by-product, together with tar, coke oven gas and crude benzene [14]. The effluents from mines and rolling mills usually contain large amounts of ammonium ions and nitrates due to the use of blasting agents based on ammonium nitrate or to the use of ammonium sulfate based eluents from the ion exchangers used on the extraction of metals [18]. Another important environmental problem is the wastewater from oil refineries, which typically contain 20-80 mg/l ammonia, harmful for fish in water bodies where the effluent discharges [21]. In fisheries, there is a particular source, with elimination of ammonia, due to the metabolic processes of fish [22,23].

The main methods used to remove or break down ammonia or ammonia-nitrogen from wastewaters are stripping [15,25,26], membrane filtration [27], nitrification-denitrification [21,28,29], intermittent chlorination [30], ion exchange [22,31,32], electrolysis [23,33], ultrasonic irradiation [34-37].

1.1.1. Stripping and distillation of ammonia

Wastewater treatment by stripping is a viable solution if the volume of treated wastewater is relatively low and the concentration of ammonia in water is high.

In [40], a new technique for ammonia stripping based on the use of a rotating packed bed, at ambient temperature, was compared with the traditional stripping process used by Liao et al. [38] to remove ammonia from wastewater resulting from swine manure. To study

the efficiency of the rotating packed bed, two miniature stripping plants have been proposed, namely an experimental laboratory system and a pilot system. In Figure 1.3, the ammonia stripping experimental arrangement scheme in the rotating packed bed is given, wherein: 1 - Ammonia storage tank; 2 - Pump; 3 - Thermocouple; 4 - Rotating packed bed; 5 - Packed bed; 6 - Ion-selective electrode; 7 - Motor; 8 - Air flow meter; 9 - Air compressor; 10 - Neutralization tank. Manure wastewater containing 3021 mg/l ammonia, has reached a separation efficiency of 90% after 7 hours of recirculation, at an ambient temperature of 18-21°C [38]. On the other hand, the volume and the height of these miniature stripping systems, laboratory and pilot scale, were 38 and 14.6 times smaller respectively than the conventional stripping tower. Moreover, the continuous liquid flow of 5 l/min of the rotating packed bed systems is also larger than that of 0.845 l/min in the conventional stripping tower. The miniature rotating packed bed system showed a decontamination efficiency over 95%, for a more concentrated wastewater (5630 mg/l) and for a significantly reduced hydraulic retention time of the liquid [40].

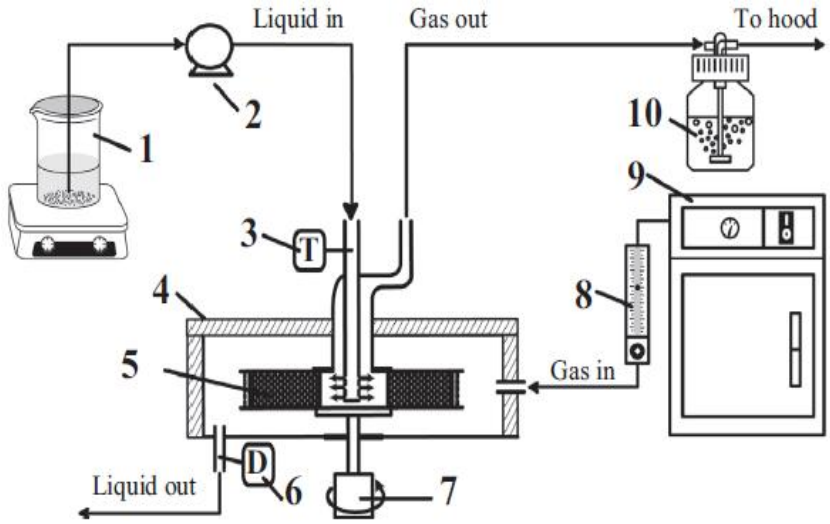

Fig. 1.3. Experimental apparatus sketch of ammonia stripping in a laboratory-scale rotating packed bed [40]

Although nowadays new enhanced techniques based on air stripping of ammonia from wastewater have been developed, tiyh better results and higher efficiency, it could be noted, for each presented process, the high treatment time, ranging between 4 and 14 hours. Also, despite decontamination yields up to 100%, additional treatment processes of the water discharged are oftenly necessary, to enable discharge into the public sewer systems or natural watercourses.

1.1.2. Membrane processes

The filtration process is a physical separation of particles by means of semi-permeable membranes. Problems encountered in using this method are the need for permanent replacement of membranes and their subsequent refurbishment or recycling due to the silting phenomenon. In [53], a diagram of a plant based on reverse osmosis for removal of ammonia from domestic water and from ammonia water prepared in the laboratory is shown. The concentrations of the treated water were low, between 3-4 mg/l and were reduced by

membrane processes by 99% in a solution containing ammonium ions complexed with iron ions.

At higher initial concentrations, ammonia removal efficiency is reduced due to the increased viscosity of the solution that affects the flow of the effluent and the mass transfer rate. Elimination systems of the ammonia deposited on the membrane after the cleaning processes is a further environmental problem [54].

1.1.3. Biological processes of nitrification-denitrification

Biological processes are based on the action of microorganisms which remove the nitrogen based compounds from water by using it as food. Nitrification is mainly applied for two types of wastewater [56]: domestic, where, depending on the emissary water, the formed nitrogen may be necessary to be removed; and industrial, in which, depending on the concentration of impurities containing nitrogen, nitrification must oftenly be followed by denitrification.

Chen et al. studied new biological processes, as partial nitrification and denitrification, for the decontamination of landfill wastewater. The experimental set-up is shown in Figure 1.12, where: 1 - Influent tank, 2 - Pump, 3 - Anoxic 1 (A1), 4 - Oxic 1 (O1), 5 - Oxic 2 (O2), 6 - Anoxic 2 (A2), 7 - Settler, 8 - Effluent, 9 - Mixer, 10 - Air pump, 11 - Airflow meter, 12 - DO and pH meter, 13 - pH meter, 14 - Internal recycling, 15 - Sludge recycle, 16 - Air diffuser, 17 - Waste sludge.

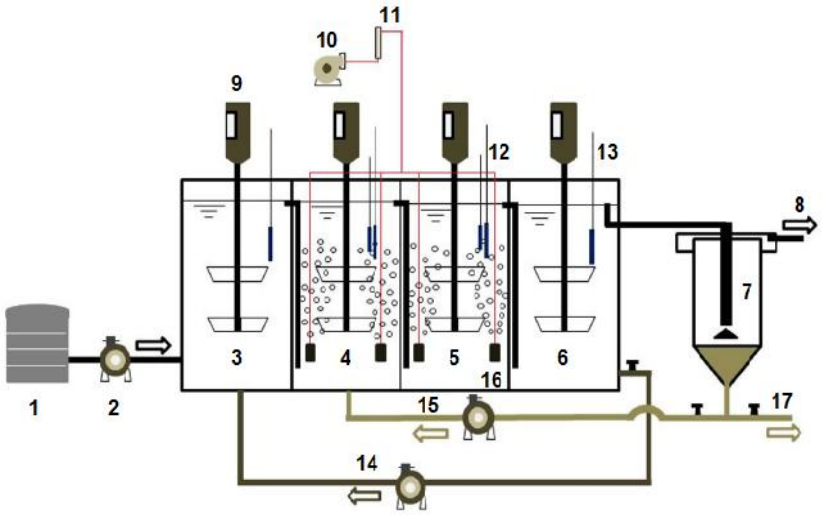

Fig. 1.12. The schematic of the AOOA process [63]

According to the authors, the conventional technology of nitrification and denitrification is not suitable for removing nitrogen from the landfill leachate due to the high concentration of ammonium and the low ratio of carbon - nitrogen (C/N) [63,64]. The initial ammonia concentration was around 1425 mg/l. Ammonia removal efficiency was of 95%, the level of nitrite accumulation of 90% and total nitrogen removal efficiency was of 66.4%. However, there must be noted the scale of the process, the large number of steps, the need for a strict control of the dissolved oxygen (0.1 -0.5 mg/l), of the temperature and pH, as well as the long time of the reactor functioning which was fed continuously for 188 days [63].

The method of denitrification is used, generally, to convert the nitrogen from ammonia to gaseous nitrogen which is harmless for the metabolism of the bacteria. The

main disadvantages of this process are the long reaction time required, denitrifying bacteria growth is slow and high concentration of ammonia inhibits the biological processes [62]. Removal of ammonia from wastewater by the conventional method of combined nitrification (aerobic) and denitrification (anaerobic) is a process that requires generates high costs and energy and generates large amounts of sludge [66]. In addition, nitrification is affected by a number of factors, such as pH, toxicity, presence of metals and non-ionized ammonia [59].

1.1.4. Sorption of ammonium ion by ion exchange

This method relies on the ability of some solid substances, low soluble, to absorb anions or cations from the solution and to give others instead. The eluate rich in ammonia can be removed, recovered by chemical absorption or destroyed by electrolysis with chlorine, which reacts with the ammonia to produce nitrogen gas [71].

In [23], a novel technique for ammonia removal from aqueous solutions through a hybrid cation exchanger was studied. However, the elimination of ammonia was achieved after 24 hours and the concentration of the ammonia water was low, ranging from 1-10 mg/l.

Sorption of ammonium ion by ion exchange is a simple and easy to implement process, but the ion exchange resins existing on the market have low adsorption capacity for ammonia and are expensive [62]. The major disadvantage of this process is the high cost of the chemical regeneration step and the need to eliminate the ammonium concentrate [31].

1.1.5. Chemical processes of ammonia oxidation

1.1.5.1. Ammonia removal by break-point chlorination

Water treatment through chlorination is a method used when the ammonia concentration is not very high, and it is usually applied for disinfection with potabilization purposes. The formation and the speciation of the chloramine types in a given solution depends on the pH, temperature and the amount of chlorine related to the concentration of ammonia [74]. In Figure 1.17, a theoretical break-point curve, referring to the treatment of wastewater containing ammonia is shown [71,76]: Zone 1 is associated with the reactions of chlorine with ammonia to form monocloramine; Zone 2 is associated with the increase of dicloramines and NH_3 disappearance; Zone 3 it is associated with the development of free chlorine after breakpoint.

Stoichiometrically, the quantitative ratio of 7.6:1 is needed for the oxidation of ammonia to nitrogen gas [71]. When using break-point chlorination, attention should be paid to the possible formation of excess acid (which some wastewaters do not neutralize) [71]. Also, another disadvantage of this process is the consequent need for removal of residual active chlorine.

1.1.5.2. The electrochemical oxidation of ammonia from water

Both ammonia (aq) and ammonium can be oxidized electrochemically, directly or indirectly. Indirect oxidation is more rapid, efficient and cost effective than direct oxidation and takes place in the presence of chloride ion in high concentration (over 300 mg/l) [74,79,80].

On the processes of ammonia elimination by electro-oxidation, the main disadvantage is the addition of various chemical reagents [23] and the high consumption of

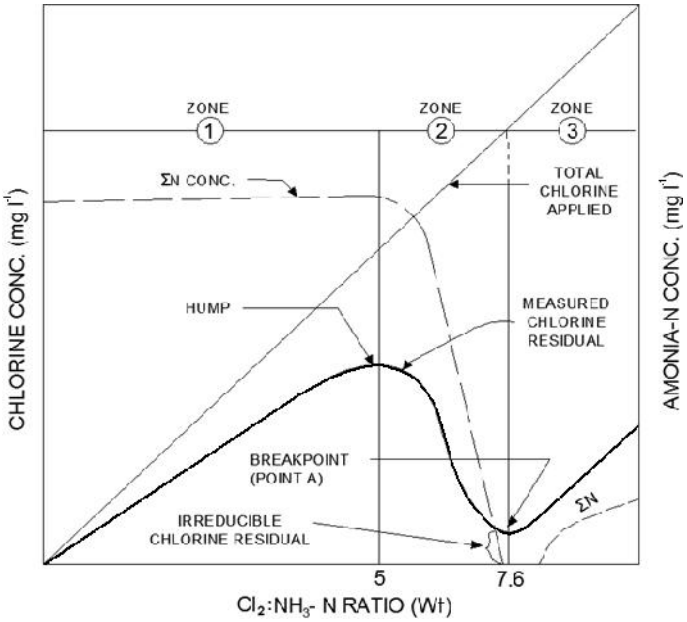

Fig. 1.17. Theoretical curve of break-point chlorination, for ammonia water treatment [71,76]

electricity that is lost through heat generation by Joule effect, which ultimately leads to degradation and changes in the water quality.

1.1.5.3. Ultrasonic irradiation of ammonia water

Ultrasonic irradiation is a new advanced oxidation process with promising results in reducing the levels of contaminants in wastewater [81] and is based on the phenomenon of cavitation. Sonochemical processes occur in the vicinity of the ultrasonic transducer, where acoustic cavitation is high [84] therefore industrially sonochemical reactors lose efficiency compared to laboratory scale reactors [85].

1.2. Technologies and installations for sulfide wastewater decontamination

The importance of sulfide monitoring in the environmental samples is recognized, as it is a toxic anion, harmful and corrosive even at low concentration [86]. The sulfur compounds are among the major contaminants in the oil industry [87]. Most polluted liquids from coke plants contain ammonia, phenol, cyanide and sulfide, generated from ammonia distillers, where the sweat accumulate in the gas coolers [91]. Another source of contamination by sulfides are the pulp and paper manufacturing processes [92]. Textile and leather industry consumes large amounts of water and generates complex effluent streams, which contain a wide variety of contaminants [96]. Also, sulfur compounds such as hydrogen sulfide, mercaptans and organic sulfides are a representative group of compounds with unbearable smell, often emitted from sewage wastewater [95].

When this type of wastewater is discharged into the environment, much of the dissolved oxygen is consumed by sulfur compounds, mainly sulfides, which can generate direct harmful effects on aquatic life, depending on temperature, pH and the content of dissolved oxygen [91]. A primary concern is given by the acceleration of corrosion caused by

hydrogen sulfide, which can substantially reduce the lifetime of the concrete components and of the routing systems of wastewater, thus having profound economic effects [103,104].

In liquid medium, the sulphides are generally present in three forms, H_2S, HS^- and S^{2-}, which are in equilibrium in water [105]. The presence in the water of the three forms of sulfide is dependent on pH, as shown in Figure 1.20. The compound with the highest volatility, H_2S, is met at pH values below 6 units. Bisulphite ion (HS^-) may be present in the range of 3-9 pH units and at alkaline values (pH > 9) it is converted to the sulfide ion (S^{2-}).

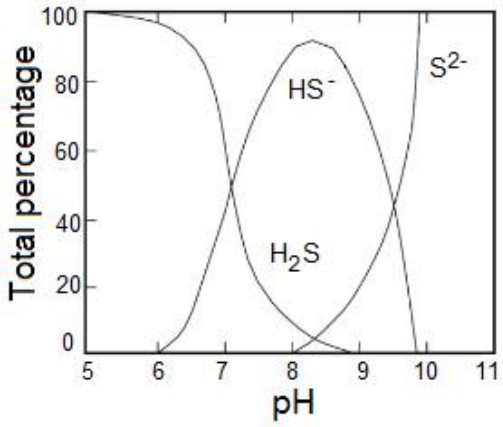

Fig. 1.20. Diagram of sulfur species distribution according to the pH [105]

1.2.1. Techniques of aeration and air stripping of sulfide from wastewater

Aeration-based technique is suitable for water contaminated with sulfide in low concentrations (up to 4 mg/l) [107]. The process may be applied only in acidic medium in which the form of the sulfides occurs with the high volatility [108].

Generally, aeration and air stripping generate the growth of microbe colonies during the treatment, which can lead to fouling of process unit and an increase in the turbidity of the effluent [114]. Packed columns need to be accompanied by odor control systems, which are expensive and can be problematic in operational terms [100]. Other disadvantages of this method [101] can be: low solubility of oxygen in water, which produce a local effect of the method and the need for multiple injection points; high energy requirement and maintenance.

1.2.2. Reduction of sulfide content of wastewater by filtration processes

Filtration is usually used as a subsequent stage of aeration, stripping and oxidation techniques [115] and can perform well in certain clinical conditions [116].

The presence of turbidity in the raw water can affect the efficiency of the technologies based on oxidation and filtration [117]. When exposed to oxidizing agents (oxygen, chlorine, etc.), precipitation of sulfides as deposits abutting the filter material can occur, which prevent the passage of water supply. This creates the transition of a significant quantity of precipitants in the treated water and thus the need for a high rate of replacement of the membranes, which leads to reduced efficiency of the system [119].

1.2.3. Sorption of sulfide ions by ion exchange

Ion exchange method requires a reduced contact time and can remove sulfides entirely independent of pH, when applied to wastewater or groundwater with a concentration that do not exceed 2-3 mg/l [109,110,121].

The main disadvantages of this method are the formation of high concentrations of sulfate, which can interfere with the removal of the target anion, and the generation of a stream of residual salt [110,122,123]. Regeneration of the ion exchangers aimed at the removal of hydrogen sulfide can be done with a sodium chloride solution, and treatment will result in a greater amount of chloride in the treated water [113].

1.2.4. Elimination of sulfides from wastewater by biological method

In biological processes, gaseous H_2S is solubilized in aqueous solution, where it is oxidized by microorganisms in the non volatile compounds, such as elemental sulfur and sulfate [124,125]. An anaerobic baffled stacking microbial cell was constructed by Liu et al. to remove sulfides from wastewater [129]. Microbial fuel cells are devices that can oxidize organic materials and can generate electricity using bacteria as catalysts. For initial concentration of 60 mg/l sulfide and 800 mg/l Chemical Oxygen Demand (COD), for hydraulic retention time of 24 hours, the removal efficiencies were of 70% and 54.6% for sulfide or COD, as shown in Figure 1.23.

Dissolved sulfides can affect biological processes in wastewater treatment plants [101,130]. Anaerobic wastewater treatment provides good results, but sulfide formation in reactors restrict its application by inhibiting anaerobic digestion [131]. In addition, microorganisms can exfoliate the surface of the treatment basins and cause turbidity downstream of the storage facilities [100].

1.2.5. Sulphide oxidation processes

1.2.5.1. Neutralization of sulfides from wastewater by chemical oxidation

Sulphide oxidation techniques can be achieved by means of various oxidizing reagents, such as oxygen [133,134], hydrogen peroxide [135-138], ozone [139-141], potassium permanganate [116,142,143], chloride [144,145], iron salts [101,146-148], etc. It is important to note that oxidation based technique is used in general, in the case of water sanitation systems containing sulfide, in the case of water having relatively low concentrations [101,134], or in combination with other techniques for treating effluents with higher concetrations [138,139]. Among the disadvantages of the oxidation techniques, the production of turbidity or the appearance of incomplete oxidation by-products may be mentioned [100].

1.2.5.2. Ultrasonic irradiation of sulfide wastewater

This advanced oxidation technique currently has a small area of use in terms of sulfide wastewater treatment. Mahamuni et al. [138] investigated the effect of ultrasonic technique on the elimination of sulfides from water. The process was optimized by the addition of hydrogen peroxide in the presence of certain catalysts. The results were promising, but the singular effect of free OH radicals generated during sonolysis, did not have a very high efficiency of sulfide removal from water. This may be because the research was conducted

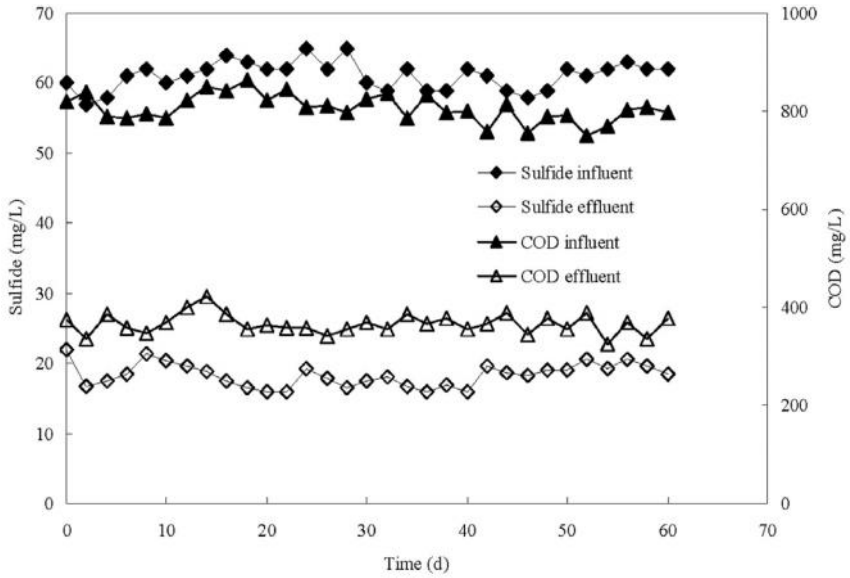

Fig. 1.23. The variations of sulfide and COD versus time, in the influent and enfluent, by anaerobic baffled stacking microbial cell treatment [129]

on an organic sulfide, namely methyl phenyl sulfide, which has the property of being relatively unreactive [138].

1.3. Conclusions

The literature review on the existing technologies and methods for the decontamination of industrial wastewaters, namely waters containing ammonia and waters containing sulfides, led to the following conclusions:

- The main disadvantage of the installations currently used to decontaminate water by ammonia stripping process is the high consumption of thermal energy required for the process technology and the need for complex technological lines which involve a variety of processes. Another problem of ammonia stripping is the strict control of pH which involves high costs, because it requires the addition of raw materials (lime or caustic) for processing the ammonium hydroxide ions to ammonia in state vapors;
- The biological processes of nitrification-denitrification give good results particularly on ammonia removal from some domestic or industrial wastewaters where concentrations are lower. High concentrations of ammonia inhibits the biological processes for nitrification-denitrification processes. In addition, the required reaction time is long, and the growth of the denitrifying bacteria is slow;
- In the case of chlorination, subsequent steps are necessary to remove excess chlorine, because the process consists in the permanent adding of chlorine to the water, for the complete oxidation of ammonia;
- When using the filtration methods, problems encountered consist in the need of permanent replacement of the membranes and their subsequent recycling due to the toxic substances deposited during the process, which is a further environmental problem.

- The ion exchange methods, based on reversible chemical reactions, are not very complex, but existing ion-exchangers have low absorption capacity for ammonium and involve high costs.
- Concerning the ammonia elimination processes by electro-oxidation, the main disadvantage is the addition of various chemical reagents and the high consumption of electricity that is lost by Joule heat production, which ultimately lead to degradation and changing water quality.
- Studied scientific papers, which were based on the reduction and ammonia by ultrasound, discloses the use of high frequencies and an increased treatment time. The analysis of only very small volumes of sample in laboratory scale It is also noted.
- Aeration-based technique is indicated for water contaminated with sulfide in low concentrations. The process may be applied only in an acidic medium in which the form of the sulfides occurs with the increased volatility.
- In general, the aeration and air stripping of the wastewaters contaminated with sulfides produce the growth of microbe colonies during the treatment, which can lead to the fouling of the process unit and an increase in the turbidity of the effluent.
- Filtration is usually used as a later stage of aeration, stripping or oxidation techniques. When exposed to oxidizing agents (oxygen, chlorine, etc.) precipitation can take place as sulfide deposits abutting the filter material, thus prevent ing the passage of water supply. This creates the transition of a significant quantity of precipitants in the treated water and the need for a high rate of of the membranes replacement, which leads to reduced efficiency of the system.
- The sorption of sulfides from wastewater by ion exchange can lead to the formation of high concentrations of sulfate, which may interfere with the elimination of the target anion. The efficiency of sulfide removal is variable and the resins may be contaminated due to the growth of sulfur bacteria.
- Dissolved sulfides can affect the biological processes from wastewater treatment plants. Anaerobic wastewater treatment provides good results, but sulfide formation in reactors restrict its application by inhibiting anaerobic digestion. Other disadvantages may include strict control of temperature and pH, and the long duration of the process.
- The dosage of chlorine to remove sulfides is performed by the addition of a quantity of up to 10 times higher than the concentration of hydrogen sulfide. Therefore, additional techniques are required to remove the excess of chlorine.
- Ultrasonic irradiation has only a limited area of use in terms of sulfide wastewater treatment.

Chapter 2

Acoustic waves action on liquids

Sonic and ultrasonic waves propagation in the reaction medium is based on a series of acoustic parameters or measures. These sonochemical parameters are defining on the degree of pollutants removal from wastewaters. Some of these parameters, with particular relevance to this study, are further exposed.

2.1. Velocity of acoustic waves propagation

The propagation of acoustic waves in liquids, when oscillations occur adiabaticly, is done with the velocity expressed depending on the adiabatic compressibility, the pressure and the density of the liquid in which the acoustic wave propagation is done [152].

2.2. Acoustic energy attenuation

When an acoustic wave propagates into a viscous fluid, its attenuation and dispersion occur in the propagation medium [153]. The attenuation of the acoustic wave, α_s, in Neper/m, can be calculated by:

$$\alpha_s = \sqrt{\frac{\omega\rho}{2\eta}} \tag{2.3}$$

In addition to the viscosity, the appearance of the heat conduction phenomenon is also important, thich result from the heat transfer between the expansion and compression regions [155].

2.3. Specific acoustic impedance

This measure is defined by the ratio of the acoustic sound pressure, p, and the particle velocity along the propagation direction, ν, and represents the resistance of the irradiated environment [151]:

$$Z_s = \frac{p}{\nu} \tag{2.5}$$

Acoustic impedance depends on the specific characteristics of the propagation environment.

2.4. Acoustic cavitation

When ultrasound is introduced into a liquid medium, oscillating regions are created by cycles of compression and expansion [158-160]. The alternation of these cycles generates the appearance of cavities in the liquid in the form of micro bubbles, which increase their volume and implode by absorbing the ultrasonic waves [161]. Schematic representation of a cavitational bubble growth and collapse in a liquid irradiated with ultrasound, is shown in Figure 2.1.

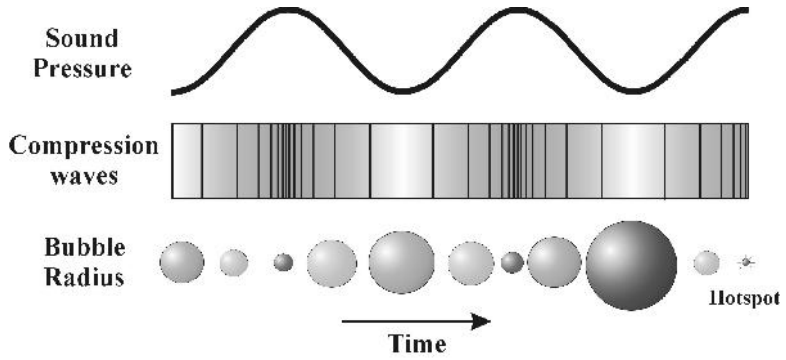

Fig. 2.1. Schematic representation of bubble growth and collapse in a liquid irradiated with ultrasound and the resulting hot-spot [81,162]

The collapse of the microbubbles in the irradiated liquid is called acoustic cavitation and is one of the main oxidation processes [1]. The cavitation effects are both physical (shock waves, microjets, turbulence, shear forces) [163] and chemical, by the appearance of highly reactive free radicals [149,164]. Acoustic cavitation can generate extreme conditions of high temperature and pressure locally, that underlie the theory of hot-spot [167].

Ultrasonic cavitation is a physico-chemical phenomenon whose performance depends on certain parameters [170]. Some of these parameters are described below.

2.4.1. Ultrasonic intensity

The intensity of an ultrasound beam in one point is the amount of energy which passes transversely through a unit area per unit time, at a certain moment [171].

The experimental results presented show that a higher ultrasonic intensity results into an increased concentration of hydroxyl radicals and of mass transfer, which leads to an increased degradation of pollutants [180,181].

2.4.2. Ultrasonic frequency

Acoustic frequency levels and areas of application are shown schematically in Figure 2.7. The effect of the pollutants removal by the appearance of alternative cycles of compression and rarefaction may be due to sound waves in the range of 16 kHz - 100 MHz, respectively in both the sonic and ultrasonic field [150,186].

According to Fuchs et al. (2005), the number of cavitational bubbles produced increases with increasing frequency. A low frequency will produce fewer implosions of the cavitational bubbles, but with higher energy, while a higher frequency will produce more implosion of the cavitational bubbles, but with less power [2].

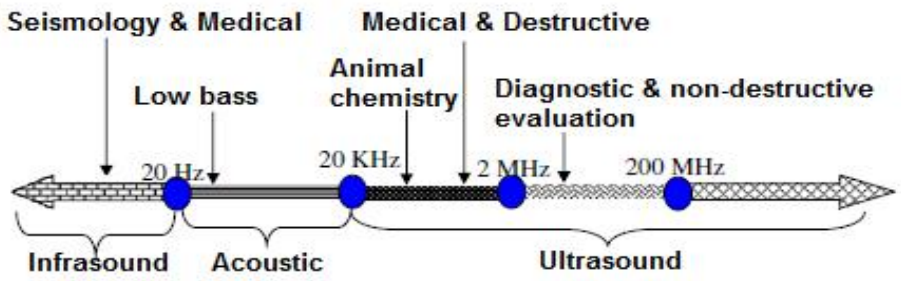

Fig. 2.7. Diagram of sound and ultrasound range [184,187]

2.4.3. The temperature and the physical properties of the treated solution

The thermal impact of the cavitational bubbles continuous implosions in the media subjected to the sonolysis, depends on its physical properties such as viscosity and vapor pressure [209,210], surface tension, dissolved gases and the temperature of the sample.

According to several authors, the temperature increase of the ultrasonically treated liquid medium, leads to an increase in the vapor pressure and in the viscosity and to a reduction of the surface tension [212-214]. With increasing vapor pressure of the liquid, the vapor content of the acoustic cavities increases and has a drop of energy released during the cavitational collapse [212]. On the other hand, by reducing the viscosity and/or surface tension, the threshold intensity required to cause cavitation [213,214] reduces and makes the effect of increasing temperature to be favorable.

2.5. Conclusions

The study regarding the action of the acoustic waves on liquids, has led to the following conclusions:

- There were determined the parameters (or acoustic measures) by whichthe sonic and ultrasonic wave propagation in the liquid reaction medium is achieved, these parameters being defining on the pollutants removal efficiency from wastewaters.
- It was determined the velocity of the acoustic waves propagation during the ultrasound irradiation, the phenomenon of acoustic energy attenuation and the acoustic specific impedance (the resistance of the irradiated medium).
- Cavitation is one of the main oxidation processes being defined as the phenomenon in which a large amount of energy is released by microseconds, through the formation of micro bubbles and cavities, that increase their volume and implode.
- There were determined the products generated by the water sonolysis, which are involved in side reactions of reduction or oxidation of the dissolved gases present in the treated liquid.
- There were determined the reaction zones in the process of cavitation for a liquid medium irradiation, ie hot-spot area (cavitation bubble), the gas-liquid interface and the liquid in the vicinity of the interface.
- Cavitation is initiated by the excitation of the pre-existing micro bubbles or other inhomogeneities in the liquid, such as particulate matter or gas nuclei.
- The intensity of an ultrasound beam in a point is the amount of energy which passes transversely through a unit area per unit time at a certain moment; however, energy efficiency is given by the actual energy available for generating the cavitational events.
- If the acoustic power supply remains constant, a reduced frequency will produce fewer implosions of the cavitational bubbles, but with higher energy, while a higher frequency will produce more implosions of the cavitational bubbles, but with less energy.
- The very high ultrasonic frequencies reduce the cavitational effect, as the negative pressure in the rarefaction cycle is insufficient by duration and/or intensity to initiate cavitation; compression cycle occurs faster than the time required for microbubbles to implode.

Chapter 3

Types of sound and ultrasound transmitters and their use

The categories of the sound and ultrasound emitters [215], according to the principle underlying the generation of acoustic waves, are:

- mechanical emitters, where the energy to produce the vibrations is mechanical;
- electromechanical emitters, where the energy to produce the vibrations is electrical. These emitters are based on different types of electromechanical transducers: piezoelectric, magnetostrictive and electromagnetic.

3.1. Mechanical acoutic generators

The mechanical emitters (or generators) can be of different types and constructive forms. The most powerful mechanical emitters are the Hartmann acoustic generators, which are also called gasodynamic sonic generators [172]. To intensify the technological processes, they use the shock waves occurring in unsteady flows from supersonic jets of gas [226].

Figure 3.2 shows the structure of the jet in the emptying fase of the resonance chamber, where: 1 - nozzle; 2 - central rod; 3 - resonance chamber; y1, y2 - pressure jumps. As a result of the main jet collision with the pulsating jet generated by the resonator, the inclined pressure jump y1 occurs, which propagates along the jet. In the first phase of resonance chamber emptying, a second pressure jump y2 also occurs, but with lower intensity [228].

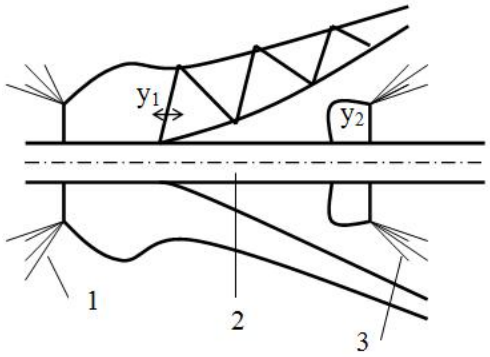

Fig. 3.2. The structure of the air jet stem generator [228]

The air flow sent through the nozzle of the mechanical generator generates the additional effect of aeration/bubbling, or oxygen diffusion into the water, in addition to the effect of the ultrasonic waves development. Gasodynamic sonic generator has proved to be a solution in water purification technology from aquaculture [232,233], for the decontamination of some industrial wastewaters [234] as well as in some food applications [235,236].

3.2. Piezoelectric ultrasound generators

On the ultrasonic transducers based on inverse piezoelectric effect, the electrical energy is converted into mechanical energy in the form of a piezoelectric crystal oscillation [81]. This mechanical energy is converted into acoustic energy in the form of ultrasonic waves progressing through a liquid medium [157]. Schematic representation of this type of transducer is shown in Figure 3.5, where: 1 - the clamping screw of the transmitter; 2, 5 - block of metal (e.g., aluminum, iron, copper); 3, 4 - piezoelectric ceramic plates (cylindrical, annular).

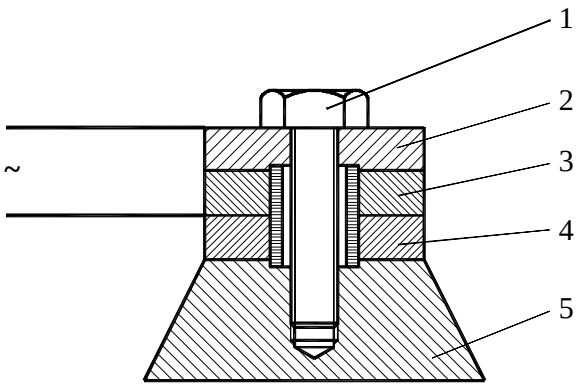

Fig. 3.5. Construction of sandwich-type ceramic piezoelectric transducer [240]

A pilot scale representation of the equipment based on acoustic cavitation due to the reverse piezoelectric effect is given in Figure 3.6. In recent years, there are used for different treatment processes, the piezoelectric systems represented by the ultrasonic bath and the ultrasonic probe. While the treatment container vessel is immersed within the ultrasonic bath, the ultrasonic probe is immersed directly into the sample container. An important difference between the two acoustic systems, is that the ultrasound probe can deliver a much higher intensity than the ultrasonic bath (up to 100 times higher), which makes each system suitable for a different set of applications [171]. According Gogate et al. (2004) the devices with larger dissipation area have higher energy efficiency at similar levels of energy input provided. Also, the use of equipments based on multiple frequencies (multi-transducers) has been reported to be more beneficial in comparison with a single frequency-based equipment [150]. The literature describes many achievements of the experimental piezoelectric transducers. However, it is noted the prevalent usage of this method on the experimental scale and less on the industrial scale [242].

Matouq et al. used a piezoelectric ultrasonic transmitter, in order to remove the pesticides from a simulated wastewater. The experiment managed to remove the contaminant in a proportion of 70%, for an initial concentration of 1200 mg/l [243]. The studied acoustic wave frequency was of 1.7 MHz and the average treatment timpe for sample volumes of 40-60 ml, was of 300 seconds. Young studied the decomposition of mono-chloro-phenols in [244] by acoustic power of 550 W and acoustic frequency of 20 kHz. After 6 hours of treatment, more than 80% of the mono-chloro-phenols were decomposed in an aqueous solution at a pH value of 3 units.

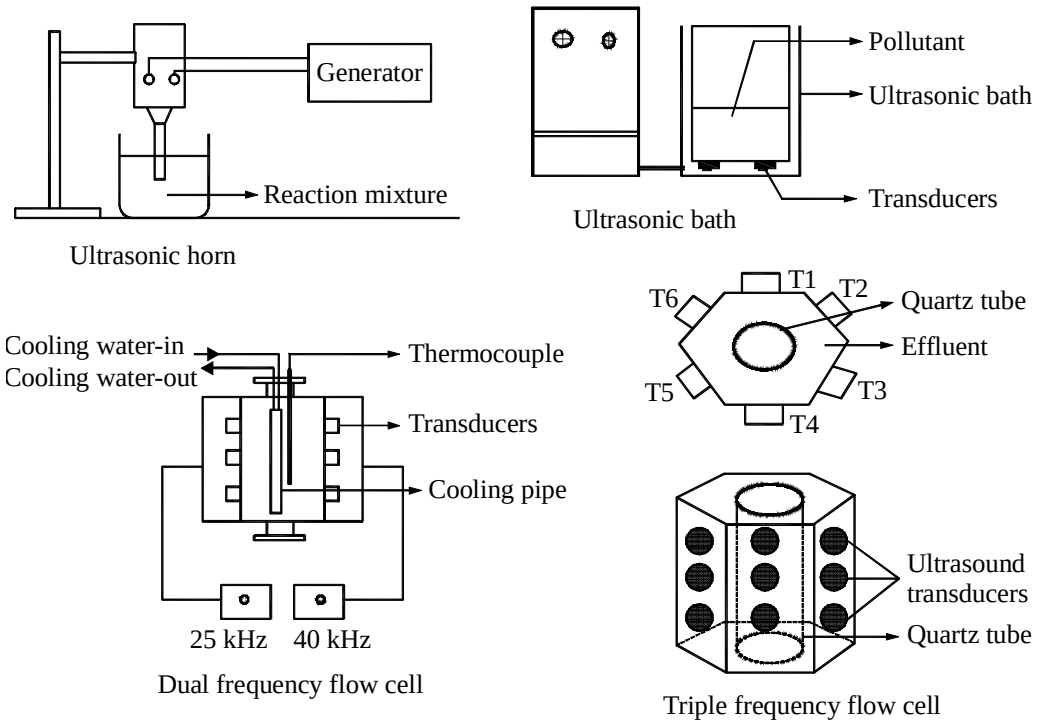

Fig. 3.6. Schematic representation of the equipments based on acoustic cavitations [150]

3.3. Magnetostrictive ultrasound generators

Operation of the magnetostrictive generator is based on the fact that some ferromagnetic substances change size at magnetization. If these substances are disposed in an alternating magnetic field, they will start to oscillate, in which case they can become sources of ultrasound [151]. Figure 3.8 shows the cross section of a prototypical Terfenol-D magnetostrictive transducer, in which the generated strains and forces are sufficiently large to prove advantageous in transducer design [247].

Magnetostrictive transducers are inherently more rugged [249] and better suited for industrial use [221]. The highest reasonable frequency achievable in a magnetostrictive transducer is around 30 kHz [250]. Magnetostrictive systems rely on the double conversion of electrical to magnetic energy and then from magnetic to mechanical to produce the sound wave.

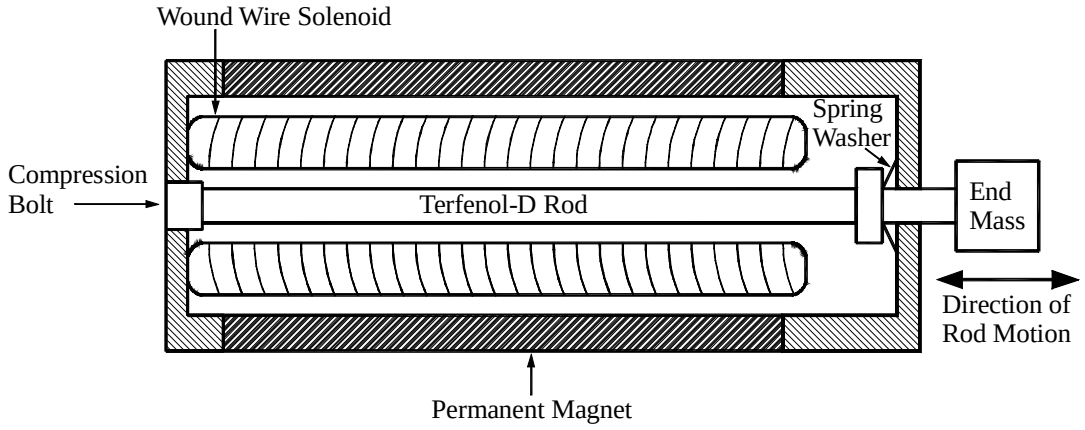

Fig. 3.8. Cross section of a prototypical Terfenol-D magnetostrictive transducer [247]

Magnetic systems are usually less than 50% efficient due to the energy lost in heating of the coils and the effects of magnetic hysteresis. Additionally, the generators, even if well tuned, are generally no more than 70% efficient [251]. Thoma et al. used a magnetostrictive system to degrade both benzene and toluene in a continuous stirred tank reactor [221]. They obtained good decontamination results by the use of 22 liters reaction vessel consisting of opposing diaphragm plates operating at 16 kHz and 20 kHz [221].

3.4. Conclusions

The study of the different types of sound and ultrasound emitters and their use, revealed:

- The operational possibilities of the main types of acoustic emitters were determined, namely mechanical and electromechanical emitters.
- Mechanical transducers typically use air as the working medium for the production of both low-frequency ultrasound and bubbling.
- The most powerful mechanical acoustic generators are the Hartmann-type, which are also called air jet or gasodynamic generators. Their operation depends on the proper adjustment of the air pressure supply transmitted through the nozzle, and on the distance between the nozzle and the resonator.
- Ultrasonic transducers based on reverse piezoelectric effect, convert the electrical energy into mechanical energy in the form of oscillation of the piezoelectric crystal.
- Pilot scale equipments based on acoustic cavitation due to the reverse piezoelectric effect are represented by the ultrasonic probe system, the ultrasonic bath system and the multiple frequency ultrasonic cells.
- Magnetostrictive transducers use the ferromagnetic property of a material to transform the energy of a magnetic field into mechanical energy.
- Magnetostrictive systems are based on a double conversion from magnetic energy into electrical energy and then into mechanical energy, having an efficiency below 50%.
- All the constructive forms of the acoustic emitters have promising results, but due to the wide range of frequencies and acoustic powers, the inverse piezoelectric effect based, are most used.
- Despite the type of transducer, the ultrasonic technology is generally used on experimental – scale, magnetostrictive generators being the most suitable for the use at industrial level.

Chapter 4

The experimental installations realized and utilized for the treatment of wastewaters and technological liquids

Within this thesis, two distinct experimental installations were designed and developed, basen on sonic or ultrasonic technology respectively, to treat industrial wastewater contaminated with ammonia or sulfide. The two categories of plants are distinguished by the energy used to produce acoustic waves.

The experimental installation operated by the sonic air jet generator uses the mechanical energy to produce acoustic vibrations. The supersonic jet of gas is transmitted by the mechanical generator, loses its stability and emits shock waves of high frequency (unsteady), after the interaction with a resonant cavity [254].

The experimental installation operated by the ultrasonic generator uses electrical energy, converted into electro-mechanical energy, in the form of oscillation of the piezoelectric crystal [157]. This energy becomes ultrasonic energy and generates stationary acoustic waves, in no resonance regime [151].

4.1. The experimental installation with mechanical sonic generator

4.1.1. The installation scheme

The study of the sonic treatment was conducted by the experimental installation shown in Figure 4.1 (1 - compressor, 2 - compressor manometer, 3 - pressure regulator, 4, 6 - valves, 5 - air filter, 7 - control manometer, 8 - vessel containing the wastewater sample to undergo treatment, 9 - mechanical sonic generator, 10 - electric hotplate, 11 - work table).

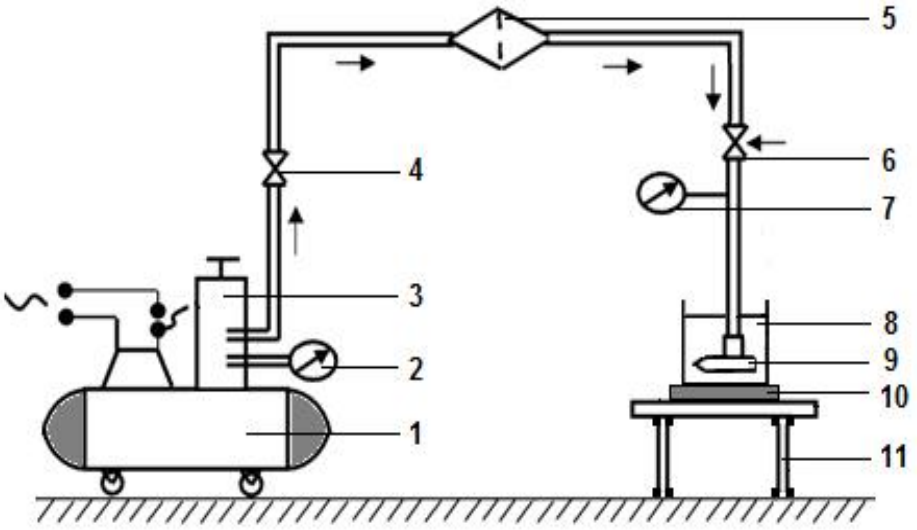

Fig. 4.1. The schematic experimental set-up by mechanical sonic generator

The working gas, namely the compressed air generated by the compressor 1, enters in the installation under the needed pressure for the generator to function, when the valve 4 is opened. The woring gas is adjusted using the pneumatic reducer 2 up to the necessary pressure indicated by the manometer 3. The sonic generator supply is made by the air filtered with the filter 5 and the exact adjustment of the gas pressure entering into the sonic generator is made using the intake valve 6. The compressed air supply the gasodynamic generator 9 located in the glass vessel 8, containing the wastewater sample, which is positioned on the worktable 11.

The compressor utilized to produce compressed air

The pressure of the compressed air supplying the experimental plant equipped with the mechanical sonic generator, determines the acoustic parameters control, namely acoustic intensity and frequency. These parameters are the main responsible for the maximum effect of acoustic cavitation during irradiation [170]. Also, by means of the compressed air, the aeration of the wastewaters subjected to treatment occurs, by the phenomenon of bubbling.

Laboratory electric hotplate

This device has been used as a source of heating the sample so as the regime of eliminating the pollutants with increasing the temperature to be determined. The device is equipped with 3-stage operation, which varies depending on the upper limit attainable of the temperature.

4.1.2. The experimental mechanical sonic generator

The air jet sonic generators are mechanical devices with no moving parts, that generate pressure waves with sonic and ultrasonic low frequency (10 to 30 kHz). It has been estimated that the Hartmann gasodynamic stem generator is best suited to support the bubbling processes for the studied wastewaters.

Simultaneous processing by acoustic waves and bubbling of the technological liquids represents a scientific novelty in industrial wastewater treatment. The method for calculating this type of generator, proposed by Prof. Dr. Eng. Balan George [231] allows sizing the geometrical parameters depending on predetermined values of the air flow rate, frequency and work pressure operating the generator.

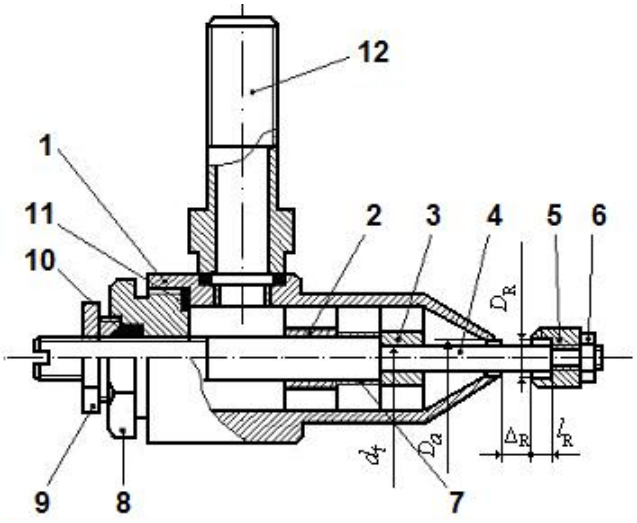

Fig. 4.5. Design scheme of the mechanical sonic generator

According to the method [226], the gasodynamic generator was calculated and designed, as shown in Figure 4.5, where: 1 - nozzle; 2, 3 - stand-cross; 4 - stem; 5 - resonator; 6 - resonator bolt nut; 7 - socket; 8 - screwed cap; 9 - check nut; 10 - sealing; 11 - sealing ring; 12 - air fitting; D_a - nozzle diameter; d_t - stem diameter; Δ_R - distance between nozzle and resonator; D_R - resonator diameter; l_R - resonator depth. The compressed gas passed through nozzle 1 reaches the resonator 5 fixed on the stem 4, which is installed within the nozzle of the generator (Fig. 4.5). Stem 4 provides control of the distance between the nozzle and the resonator, Δ_R, so as the frequency of acoustic oscillations to be modified. The supersonic jet of gas from the nozzle loses its stability after interaction with the cavity of the resonator and emits high frequency shock waves [254,256].

4.1.2.1. Acoustic parameters of the gasodynamic sonic generator

Operation and adjustment of the mechanical air jet generator is made according to certain geometric and gasodynamic parameters [172]. The basic gasodynamic parameters of the sonic generator are those that determine the flow regime in the generator [257]: sound intensity, Mach number (which determines the output section of the nozzle) and the unisobar character of the flow.

The main geometric parameters of the mechanical air jet generator, which determines acoustic characteristics, as shown in Figure 4.8 (1 - nozzle, 2 - resonator, 3 - stem; 4 - the first nucleus of the jet, 5 - the acoustic oscillations of the generator, φ_a - nozzle edge angle, ψ_R - resonator edge angle), have been studied in [172,226,232,255,258], and are represented by: nozzle diameter D_a; stem diameter d_t; resonator diameter D_R; resonator depth l_R; noozle to resonator distance Δ_R.

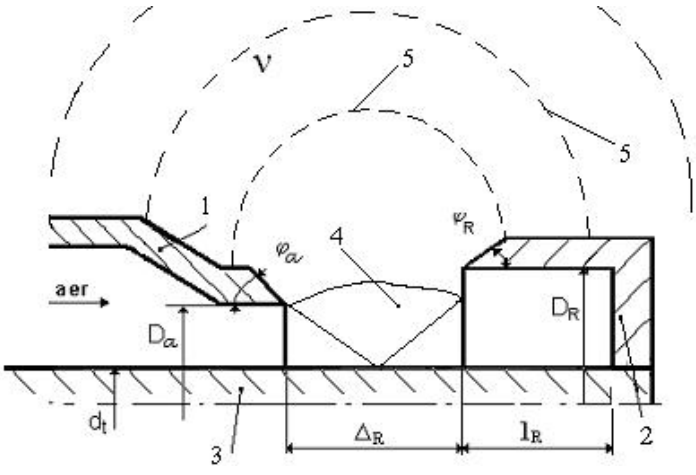

Fig. 4.8. The oscillations generation in the sonic generator [231]

4.1.2.2. Acoustic measurements of the gasodynamic sonic generator

The acoustic parameters represented by the frequency and the acoustic intensity level were determined by using the Solo-Metravib 01dB device, France. The acoustic intensity level and the frequency have been determined according to the air pressure suplying the generator. The gasodynamic experimental generator was located at a distance of 2 meters above the

ground level and at distances in the range of 3 ÷ 6 meters from the walls, in a soundproof space.

Figure 4.11 shows the change in sound intensity levels at different distances between the nozzle and the resonator, according to the air pressure supply of the gasodynamic generator. For the nozzle-resonator distance Δ_R = 1.2 mm the gasodynamic stem generator emits sound field with the highest values of acoustic intensity level and frequency for the air supply pressure of 0.05 MPa (sound intensity level - 102.4 dB and frequency - 18.25 KHz) and air supply pressure of 0.1 MPa (sound intensity level - 107.1 dB and frequency - 19.16 KHz).

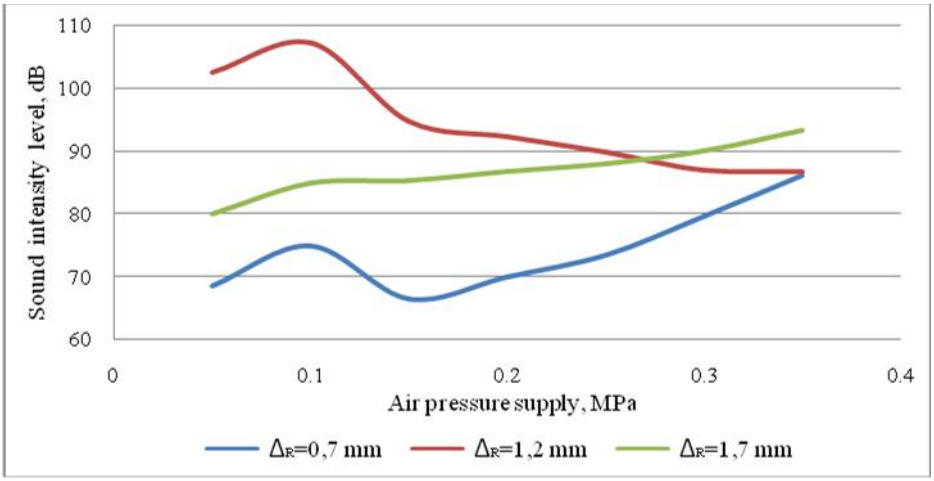

Fig. 4.11. The overall intensity level of the air jet generator for various distances between the nozzle and the resonator (Δ_R = 0.7 ÷ 1.7 mm), depending on the supply air pressure [255]

4.1.2.3. The heating operation applied to the gasodynamic sonic generator

Unlike the ultrasonic piezoelectric generator, of which the sample heating is inherent during the treatment, for the mechanical sonic generator, the treatment has an opposite effect of sample cooling, depending on the pressure of the supply air coming from the compressor, as a result of the supply air extent and its bubbling through the liquid sample.

However, analyzes of ultrasonic treatments have shown a beneficial effect of increased temperature on the decontamination regime. Thus, the influence of heating in sonic treatments to be observed, different volumes of the studied samples were heated by means of an electric laboratory hotplate.

1. The temperature evolution for the air pressure supply of 0.05 MPa

- For the sample volume of 500 ml, the heating is made to 62°C, in the case of continuous sonic treatment, during the first 50 minutes, value that will remain constant. Inthe case of the intermittent operation, the sample heating is slightly increased, by about 2-3°C compared to the continuous treatment regime.
- By reducing the sample volume to 300 ml, a faster increase in temperature was recorded (Fig. 4.15). In this case, the limit was of 62°C (continuously) and 65°C (intermittently).
- In the case of 100 ml volume, the time required to heat the wastewater sample to the limit value is reduced to 30 minutes. After this period, the temperature is stabilized at values of 72°C and 75°C, for continuous and intermittent operation, respectively.

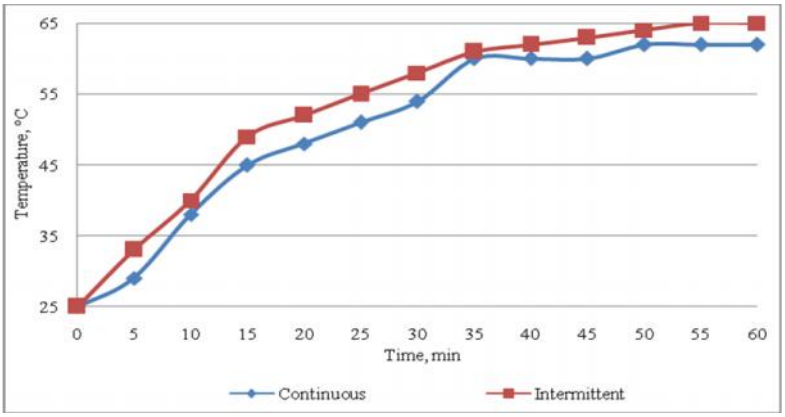

Fig. 4.15. The temperature dynamics in continuous and intermittent operation, for supply air pressure of 0.05 MPa and sonic treatment applied to 300 ml of wastewater

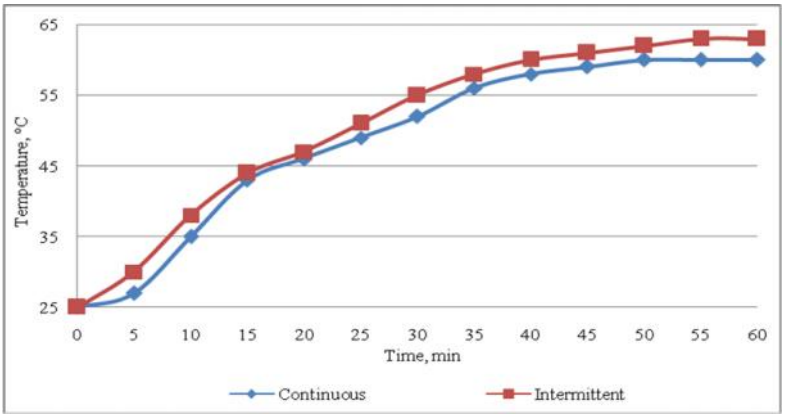

Fig. 4.18. The temperature dynamics in continuous and intermittent operation, for supply air pressure of 0.1 MPa and sonic treatment applied to 300 ml of wastewater

2. The temperature evolution for the air pressure supply of 0.1 MPa

- For the 500 ml sample volume, the sample heating was performed up to 60°C and 62°C, for continuous or intermittent treatment.
- For the volume of 300 ml, the heating is effected up to 60°C at the continuous treatment, after 50 minutes, and up to 63°C for intermittent operation processing, after 60 minutes of sonic treatment (Fig. 4.18).
- In case of 100 ml sample volume, after 30 minutes, the temperature riches 70°C for the continuous treatment and 73°C for intermittent operation.

4.2. The experimental installation with piezoelectric ultrasonic generator

4.2.1. The installation scheme

The schematic representation of the ultrasonic set-up for the treatment of wastewater originated from industrial processes, containing ammonia or sulfide, was done in Figure 4.20 (1 - electronic generator, 2 - electromechanical transducer, 3 - ultrasonic probe ; 4 - vessel containing wastewater sample, 5 - cooling water coil, 6, 7 - hoses for cooling water inlet-outlet; 8 - thermometer; 9 - aeration pump; 10 - air stone). The electric energy

produced by the electronic generator 1 is converted to mechanical energy in the form of oscillation of the piezoelectric material from the electromechanical transducer 2.

This mechanical energy is converted into acoustic energy in the form of ultrasonic waves transmitted through the probe 3 to the water sample from the vessel 4. Ultrasonic waves cause oscillations of the distances between the liquid molecules from the original position by cycles of compression and rarefaction.

The heating effect of the irradiated sample is eliminated by applying the cooling water coil 5, provided with the hose 6 fed to the current water source, respectively with the outlet hose 7. The temperature of the ammonia water was continuously monitored by the thermometer 8, immersed in the sample. To create the bubbling effect, namely the additional diffusion of oxygen into the liquid, the aeration pump 9 was used, provided with the air stone 10, with the role of a fine spraying of bubbles.

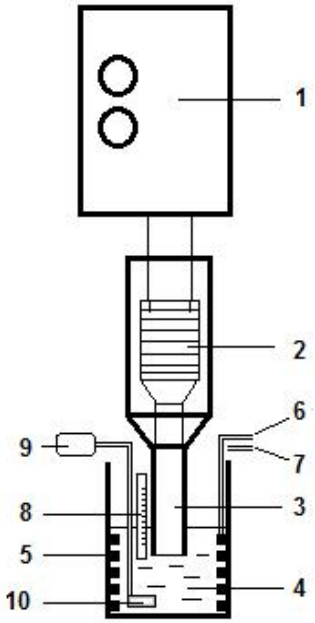

Fig. 4.20. The pilot scheme of the set-up with piezoelectric ultrasonic generator

The practical arrangement of the experimental set-up with piezoelectric ultrasonic generator, during the treatment of industrial wastewater, is shown in Figure 4.21, where: 1 - stand; 2 - electric generator; 3 - mounting bracket; 4 - worktable; 5 - vessel containing the wastewater; 6 - thermometer; 7 - copper coil; 8 - supply/drain hoses for the cooling water; 9 - air stone of the aeration pump.

4.2.2. The utilized piezoelectric ultrasonic generator

In this doctoral thesis, the ultrasonic probe system with electromechanical transducer based on the inverse piezoelectric effect was used.

To generate ultrasound, the transducer uses electrical excitation that is transferred to the environment to be treated through the probes (also called sonotrodes). The working frequency of the generator is of 30 kHz. The amplitude used in the industrial wastewater treatment experiments was the maximum amplitude working with each of the utilized ultrasonic probes. In Table 4.5, the technical characteristics of the two utilized probes are listed.

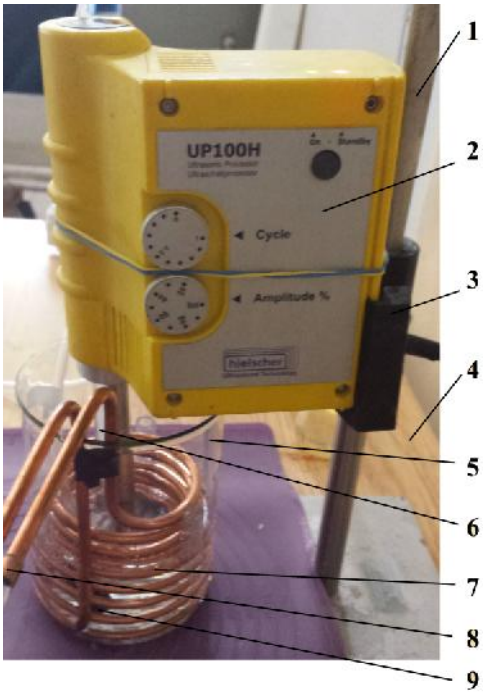

Fig. 4.21. The experimental installation with
piezoelectric ultrasonic generator, during treatment

Table 4.5. Characteristics of the ultrasonic probes used in conducting the experiments

Probe type	Maximum depth of immersion (mm)	Probe diameter (mm)	Maximum amplitude (μm)	Ultrasonic intensity (W/cm^2)
MS 3, Microtip 3	30	3	180	460
MS 10, Microtip 10	30	10	70	90

The cooling water coil

The coil for cooling water circulation in the vessel, was used for the role of ultrasound in the decontamination of wastewater from industrial processes to be strictly observed, without the additional heating effect that occurs during treatment.

The aeration pump

The aeration or oxygenation of the sample by the additional bubbling was carried out by means of an aquarium pump. The processes of oxygenation and stirring thus generated, stimulate the cavitational phenomena occurring at ultrasonic irradiation.

4.3. The thermic effect of the ultrasonic treatment

So as the influence of temperature on the elimination rate of the studied pollutants to be observed, the effect of heating due to the thermal energy emitted by the acoustic probes during irradiation was evaluated.

1. The thermal effect for the ultrasonic intensity of 460 W/cm^2 (probe MS 3)

- For the sample volume of 500 ml, the sample heating to 30°C in continuous operation without aeration can be observed, after 60 minutes. In the presence of aeration, the maximum of 29°C was recorded in same time interval. For intermittent operation, the sample heating is very low, the temperature being increased by only 1°C and 1.5°C from baseline without aeration and with aeration respectively.
- For the sample volume of 300 ml water, the temperature rises up to the maximum constant value of 34ºC, after 50 minutes (Fig. 4.29). In the presence of additional aeration, the sample temperature reaches a maximum of 33ºC, after 55 minutes. For the irradiation on intermittent operation, the sample temperature reaches 28ºC after 45 minutes, without aeration, or 27ºC, after 50 minutes, with aeration.
- The sample volume of 100 ml was analyzed for four different types of vessels. Constructive dimensions of the utilized containers in relation to the height of the sample volume of 100 ml, are given in Table 4.7. Variations in the heating mode depending on the shape of the reaction vessel, respectively depending on the diameter and the height occupied by the irradiated solution could be noted. Thus, after 60 minutes of ultrasonic treatment, the temperature reaches values of 40ºC, 37ºC, 39ºC, 35ºC, for the #1, #2, #3, #4 vessels respectively.

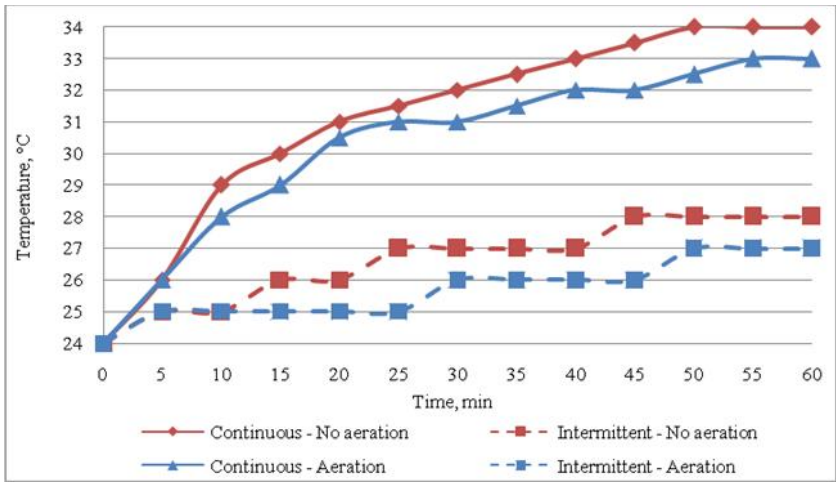

Fig. 4.29. The temperature dynamics in continuous and intermittent operation, for the intensity of 460 W/cm^2 and sample volume of 300 ml

Table 4.7. The sample height in the vessel for the volume of 100 ml

Utilized vessel	Diameter of the vessel, mm	Total heigh of the vessel, mm	The sample height in the vessel for the volume of 100 ml, mm
#1	45	67	67
#2	65	90	29
#3	60	120	43
#4	100	137	22

- Measurements were also taken for the wastewater sample of 50 ml. In this case, a new height of the liquid in the container is registered, the values being displayed in relation to the size of the vessels, in Table 4.8. The recorded limits of the temperature rise are 42ºC (#1), 40ºC (#2), 42ºC (#3).

Table 4.8. The sample height in the vessel for the volume of 50 ml

Utilized vessel	Diameter of the vessel, mm	Total heigh of the vessel, mm	The sample height in the vessel for the volume of 50 ml, mm
#1	45	67	34
#2	65	90	15
#3	60	120	22

2. The thermal effect for the ultrasonic intensity of 90 W/cm^2 (probe MS 10)

- For the sample volume of 500 ml, the temperature reaches 60°C within 60 minutes of continuous treatment, in a slightly faster regime when aeration is applied. In the case of pulsed ultrasound application, the sample heating is similar with or without aeration, reaching 46ºC after 60 minutes.
- The irradiation of the volume of 300 ml at ultrasonic intensity of 90 W/cm^2, produces a temperature rise to a maximum value of 60ºC starting the 60th minute, for continuous treatment. Intermittent ultrasonic irradiation generates a constant maximum value of 46ºC, after 50 minutes without aeration, and after 55 minutes with aeration (Fig. 4.33).
- For the volume of 100 ml, at the ultrasonic intensity of 90 W/cm^2, continuously and in the presence of aeration, the temperature reaches 72ºC in the first 20 minutes of treatment, in vessel #1. Concerning vessel #3, the same maxium value is reached, but after 40 minutes of treatment. The containers with increased diameters, have constant values of 65°C (40 minutes) and 62ºC (60 minutes), namely vessels #2 and #4 respectively.
- For the most reduced sample volume, the sample heating is realised to 80°C after 20 minutes in container #1 and after 40 minutes in container #3. The maximum value was obtained after 20 minutes of 72ºC in vessel #2.

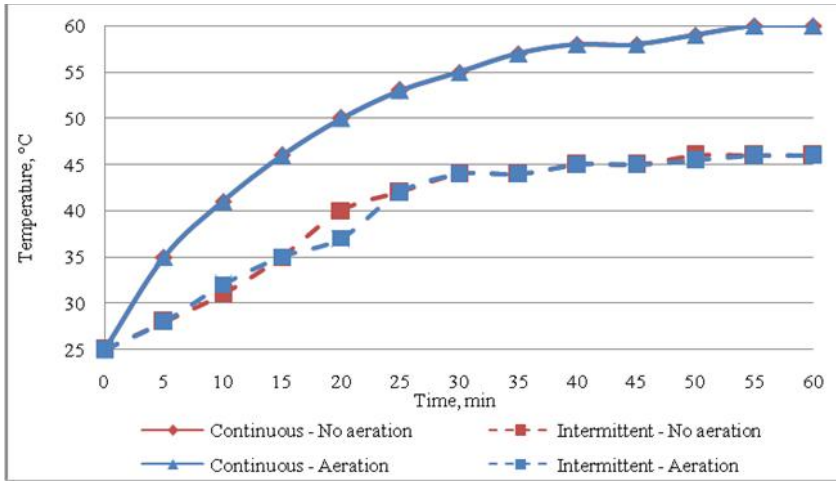

Fig. 4.33. The temperature dynamics in continuous and intermittent operation, for the intensity of 90 W/cm^2 and sample volume of 300 ml

4.4. Conclusions

In the stage of setting the sonic or ultrasonic treatment technologies for the decontamination of ammonia and sulfide industrial wastewaters, the following were achieved:

- Design and implementation of the two categories of installations, which are distinguished by the energy used to produce acoustic waves.
- Design of the experimental set-up with gasodynamic sonic generator for the treatment of ammonia or sulfide industrial wastewater.
- Establishment and study of the optimum parameters of the mechanical sonic generator, depending on the supply air pressure, namely the pressure of 0.05 MPa (acoustic intensity level of 102.4 dB and frequency of 18.25 KHz) and the pressure of 0.1 MPa (acoustic intensity level 107.1 dB and frequency of 19.16 kHz).
- Establishment of the heating methodology of the ammonia or sulfides wastewater, during sonic treatment, so as the effect of the temperature increase to be determined similarly to the heating effect during ultrasonic irradiation.
- Design of the experimental set-up with piezoelectric ultrasonic generator for the treatment of industrial wastewater with ammonia or sulfide.
- Study of the technical characteristics and the operating regime of the ultrasonic piezoelectric generator.
- Determination of the ultrasonic generator intensity effect, on the temperature evolution of the studied wastewaters.
- Establishment of the research methodology regarding the effect of the acoustic power density, the effect of additional aeration, the effect of operating regime of the piezoelectric generator (continuous or intermittent), the effect of varying the wastewater sample volume, the effect of the system geometry and the effect of varying the initial concentration of the studied wastewaters, on the decontamination efficiency.

Chapter 5

The treatment methodology of some wastewaters

5.1. The research methodology for ammonia wastewater treatment

5.1.1. Ammonia water features

In this thesis, the source of the studied ammonia water is the ion exchangers industry. After washing the ammonia gas, ammonia water results as wastewater. The physico-chemical properties of the ammonia water at the time of discharge from the generating industrial process, are shown in Table 5.1.

Appropriate dilutions were made to the initial concentrations of ammonia of 72.8 mg/l and 145.6 mg/l, which ware subsequently subjected to the sonic/ultrasonic analysis.

5.1.2. Determination of ammonia concentration

The ammonia content was determined by the colorimetric method with Nessler's reagent [270]. Sensitivity of the reaction is very high, so that the ammonia can be detected even in very low concentrations. In Figure 5.2, the sonic or ultrasonic ammonia water treated samples, during the ammonia content determination are presented.

Table 5.1. The physico-chemical properties of the ammonia water at the time of evacuation from the industrial process

No.	Ammonia water parameters	Units	Analysis method	Value	Uncertainty value	Observations
1	pH	upH	Instrumental	11,81	-	T=20,9°C
2	Volatile ammonia	g/l	Titrimetrically	76,075	-	
3	Density	g/cm^3	Gravimetric	0,961	-	

Fig.5.2. Volumetric flasks with sonic/ultrasonic treated water samples, during the determination of the ammonia content by the spectrophotometer

5.1.2.1. The apparatus used for the determination of ammonia

The ammonia content was determined using the spectrophotometer UV/VIS M330B, represented in Figure 5.3. The spectrophotometer has the technical specifications listed in Table 5.2. With this appliance, the extinctions of the treated water samples were read.

The readings were performed at 420 nm wavelength. By using the read extinctions, the ammonia concentration was calculated from the calibration curve.

Fig. 5.3. The utilized spectrophotometer for the ammonia content determination

Table 5.2. Technical specifications of the UV/VIS spectrophotometer

Spectrophotometer UV/VIS	**Technical specifications**
Wavelength level	190÷900 nm
Wavelength accuracy	± 1nm
Zero drift	< 0,003 pe oră
Photometric accuracy	> 1%
Field of extinctions	0÷999
Field of absorbance	0÷200%
Dimensions	520 x 340 x 190 mm
Weight	18 kg

5.1.2.2. Calibration of the spectrophotometer

There were prepared 6 standard samples of 0, 5 10, 15, 20 and 25 ml working solution, represented by the ammonium chloride (NH_4Cl). The working solution used in drawing the calibration curve, contains 5 µg NH_4^+ at 1 ml, therefore the concentration of standards were of 0, 25, 50, 75, 100 and 125 µg at 50 ml, according to Table 5.3.

Table 5.3. The standard scale for the colorimetric determination of ammonium

Standard samples, ml	**0**	**5**	**10**	**15**	**20**	**25**
Standard solutions, µg NH_4^+/ 50 ml	0	25	50	75	100	125
Extinction standard samples	0,200	0,450	0,625	0,872	0,981	1,094

The standards extinctions are read with the spectrophotometer at 420 nm wavelength. By using the obtained values, the calibration curve was drawn through the points, by linear regression (Fig. 5.4), with the equation: $y = 135{,}5 \cdot x - 32{,}89$, having a correlation coefficient R = 0.988433, and an error of 0.011567. Thus, it has been estimated that the most suitable for the calibration curve of the device is the linear regression. The calibration curve was then used to calculate the concentrations of ammonia in the treated water.

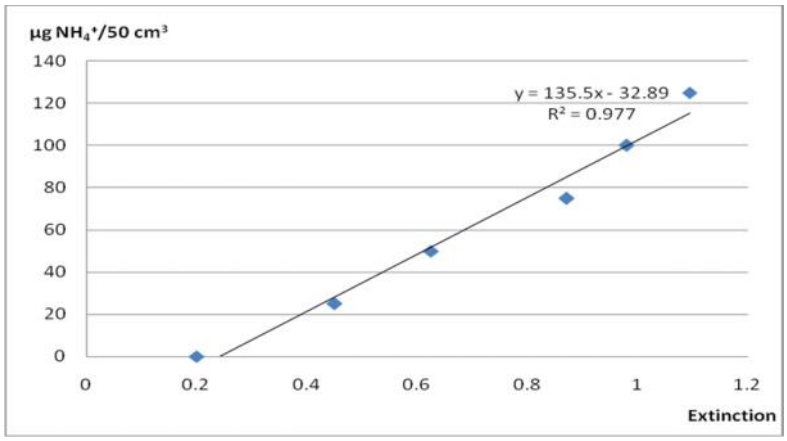

Fig. 5.4. The calibration curve for ammonia (NH_4^+) of the spectrophotometer

5.2. The research methodology for sulfide wastewater treatment

5.2.1. Sulfide wastewater features

Experiments have been conducted on a wastewater containing sulfides simulated in the laboratory. The sulfide wastewater was simulated similarly with the contaminated wastewater originated from industrial processes, by the method presented in [86]: A stock solution of sulfide of 1 g/l was prepared by dissolving sodium sulfide in water, namely 3,0769 g $Na_2S \cdot 9H_2O$ (Merck, Germany). The standardization was performed by the iodometric method [269].

a. b. c.

Fig. 5.5. Aspects from the laboratory on the sulfide (S^{2-}) content determination of sonic/ultrasonic treated samples

Appropriate dilutions were made to obtain the final concentrations of working solutions, of 75 mg/l and 120 mg/l.

5.2.2. Determination of sulfide concentration

The sulfide content was determined by the titrimetric (volumetric) method [272]. The principle of this method consists in the determination of the excess iodine of a titrated solution of iodine, after the reaction of iodine with hydrogen sulfide and the sulfides present in the water. The presence of the S^{2-} ion is distinguished by the appearance of a white precipitate, according to Figure 5.5 a. If after a period of 20 minutes, while the reaction is carried out, the sample remains discolored, a known volume of iodine solution is added until the color of the sample becomes yellow (Fig. 5.5 b). The excess of iodine was titrated with sodium thiosulfate solution ($Na_2S_2O_3$) 0.025 N in the presence of starch as indicator, until the color changed from blue to colorless sample (Fig. 5.5 c).

5.3. Determination of pH value

Determination of pH was achieved by the electrometric method [272]. This method is based on measuring the electromotive force of an electrochemical cell made up of the water sample, a glass electrode and a reference electrode.

Measurements were made using a laboratory pH meter shown in Figure 5.6, before and after the sonic/ultrasonic treatment. The reading of the pH value was carried out with the concomitant reading of the sample temperature. Technical characteristics of the utilized pH meter are shown in Table 5.4.

Fig. 5.6. Inolab 720 device used in the determination of pH

Table 5.4. Technical specifications of the utilized pH meter

Inolab 720 pH-meter	**Technical specifications**
Levels of pH measuring	-2 ÷ +16
Levels of temperature measuring	-5 ÷ 105 (^{0}C)
pH accuracy	± 0,01
Temperature accuracy	± 0,1 (^{o}C)
Conductivity	0÷1999 µS/cm or 0÷500 mS/cm
Dimensions	230 x 210 x 70 mm
Weight	~ 0,850 kg

5.4. The methodology of sonic/ultrasonic treatment of the residual wastewaters

For the effectiveness of the sonic/ultrasonic treatment to be determined, the sample volume was varied for the two types of residual water. The analyzes were carried out on four sample volumes, namely 500 ml, 300 ml, 100 ml and 50 ml. Also, the influence of the system geometry has been monitored. For this purpose, for the volumes of 100 ml and 50 ml were, four different vessels were utilized.

The sampling in order to read the concentration of pollutants in the treated wastewater sample, was conducted from the the bottom of the vessel, in the immediate vicinity of the utilized sonotrode, where the effect is greatest and cavitation activity is higher [84].

Depending on the contaminant concentration of the studied wastewaters, which were calculated by the methods disclosed, the removal efficiency E was determined, defined by the equation [36]:

$$E\,(\%) = \frac{|C_i - C_f|}{|C_i|} \cdot 100 \tag{5.11}$$

where: C_i - initial contaminant concentration (mg/l), C_f - final contaminant concentration determined after the sonic/ultrasonic treatment (mg/l).

5.5. Conclusions

In the stage regarding the methodology for determining the physico-chemical properties of the wastewaters containing ammonia or sulphide, there were achieved the following:

- The necessary materials and the working methodology for determining the studied parameters in the sonic/ultrasonic treated ammonia wastewater were established.
- After the appropriate dilutions, the initial concentrations of the ammonia water originated from industrial processes which have been subjected to experimental tests have been determined, namely the initial concentrations of 72.8 mg/l and 145.6 mg/l respectively.
- The equipment required to measure the content of ammonia in the studied wastewater was prepared and calibrated.
- The equipment required to measure the pH value of the ammonia water, was prepared and calibrated.
- After the appropriate dilutions, the initial concentrations of the sulfide wastewater simulated in the laboratory which have been subjected to experimental tests have been determined, namely the initial concentrations of 75 mg/l and 120 mg/l respectively.
- The methodology for determining the concentration of sulfide in the wastewater subjected to sonic and ultrasonic treatment, was established.
- It was established the methodology for sampling the treated wastewater from the vessel, in order to analyze the levels of contaminants after the sonic/ultrasonic treatments or to determine the effectiveness of decontamination of the studied methods.

Chapter 6

Experimental results of ammonia water treatment by ultrasonic technology

6.1. The dynamics of pH values during the ultrasonic treatment of ammonia water

The initial pH value was of 10.17 for the original concentration of 72.8 mg/l and of 11.43 for the initial concentration of 145.6 mg/l. The initial values of the pH are reduced during the irradiation because the formed free radicals (especially hydrogen), affect the initial pH of the solution [273,274].

The minimum values of pH, recorded after 120 minutes of irradiation of 90 W/cm^2, were between 8.79 and 7.74, for the initial concentration of 72.8 mg/l and between 10.12 and 8.81, for the initial concentration of 145.6 mg/l, respectively for the sample volumes of 500 to 50 ml.

At elevated pH values, the dominant form of the present ammonia can evaporate in the cavitation bubble and can decompose pyrolitically [82,166]. The best of ammonia-nitrogen removal efficiency can be achieved for values of pH between 8.2 and 11 [82].

6.2. The effect of ultrasonic intensity, on the decontamination efficiency of ammonia water, in the presence of sample heating

6.2.1. The effect of treatment time and the optimum time intervals establishment

In order the optimal range for reading the ammonium concentration to be determined, sampling of the treated water was carried out at 1 minute, 5 minutes and 10 minutes. Ammonia concentration readings at the intervals of 1 to 5 minutes did not reveal fluctuations or a significant degree of decontamination. Initialisation of the decontamination process is observed in the first 10 minutes of irradiation. Regarding the duration of the ultrasonic treatment, it may be adjusted depending on the treatment type and regime.

6.2.2. The effect of treatment regime and the optimum regime establishment

The dynamics of the values depending on the treatment regime, is shown in Figure 6.7 for the ultrasonic intensity of 90 W/cm^2, and 460 W/cm^2 respectively. On the ultrasonic intensity of 90 W/cm^2, continuously, irradiated wastewater falls within allowable limits for discharge directly into natural waterways after 115 minutes [3]. The results for intermittent (pulsed) treatment regime, shows a lower efficiency of decontamination compared to the continuous treatment regime.

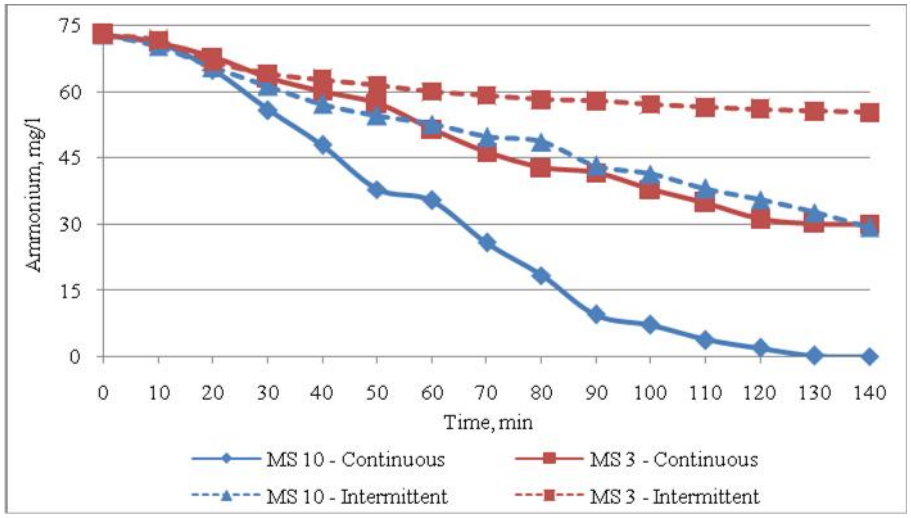

Fig. 6.7. The variation of the ammonia concentration, depending on the ultrasonic intensity and the operating mode

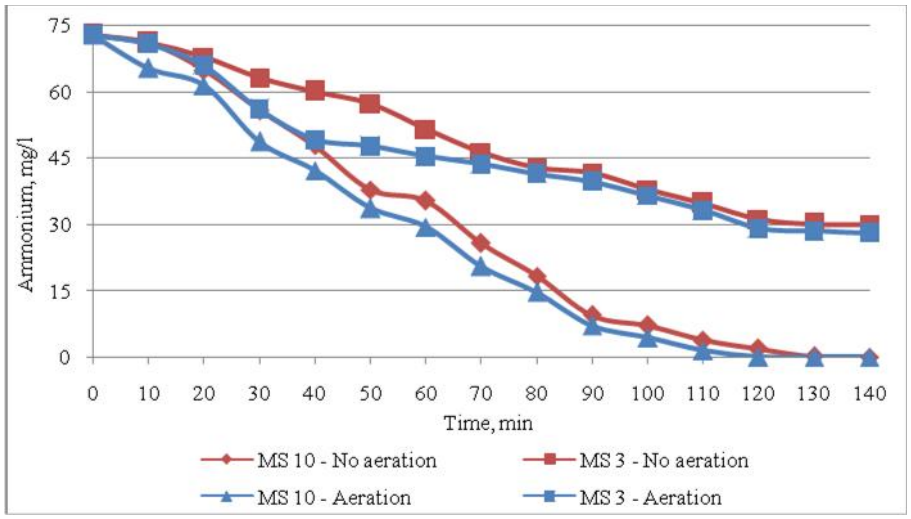

Fig. 6.8. The variation of the ammonia concentration, in continuous mode, depending on the ultrasonic intensity and the aeration regime

The treatment by the MS 10 probe, in the intermittent mode, generates a decrease in the concentration to 29.17 mg/l in the 140th minute of treatment, value falling within the allowable limits for the discharge into the sewage systems. The decontamination effectiveness in this case is of 59.97%.

6.2.3. The effect of additional aeration

With the introduction of additional aeration by means of the aeration pump, it is desirable to create the bubbling effect, in order to create similar conditions with the treatment conducted by the air jet generator, in the sonic field. As shown in Figure 6.8, in the presence of sample aeration, the MS 3 probe yields intervals in which decontamination is faster than without aeration, but only up to the allowable limit for the discharge into the public sewerage networks (30 mg/l) that was reached after 120 minutes. The treatment of the ammonia water

sample by the ultrasonic probe MS 10, in the presence of aeration, generates full decontamination of the sample after 120 minutes.

When the ultrasonic irradiation is combined with aeration, the latter increases the concentration of cavitation bubbles in solution, increasing energy efficiency and accelerating ultrasonic cavitation and pyrolysis [166]. However, the use of aeration creates uniform mixing conditions of the solution and makes the use of mechanical agitation unnecessary [245]. The application of aeration leads to facilitating the removal of ammonia [278]. The effect consists in increasing the area of interface between air and water, resulting in the removal of the ammonia-nitrogen in the form of free ammonia [166].

The obtained results show that the ammonia degradation rate is increased in the initial stages of the treatment, when the solution is saturated with the gas fed by means of aeration. As the sample degassing process occurs, the system becomes more stable, resulting in a lower level of response and linear variations during operation [276].

6.3. The effect of ultrasonic intensity, on the decontamination efficiency of ammonia water, in the abscence of sample heating

6.3.1. The effect of treatment time and the optimum time intervals establishment

When using the water cooling coil, constant values of the ammonia content after treatment intervals of 70-90 minutes, are noted. Thus, the duration of the treatment in the presence of the cooling water has been established within this period.

6.3.2. The effect of treatment regime and the optimum regime establishment

For the acoustic power density of 460 W/cm2 (MS 3 probe), the results obtained for a constant temperature of the sample are shown in Figure 6.10. Decontamination is done gradually within 90 minutes of irradiation, with the efficiency of 12.09%. The tests were repeated in the intermittent regime, at constant temperature. The level of of ammonia removal is greatly reduced, by 2.60%, after 90 minutes. Regarding the MS 10 probe, the concentration of 55.58 mg/l (efficiency increase by only 2.87%) is reached, after 90 minutes. This result may be due to the possible occurrence of the phenomenon of ammonia reabsorption. A possible explanation would be the solubility of ammonia, which recombines with the wastewater poorer in ammonia, so with greater potential for absorption.

6.3.3. The effect of additional aeration

In Figure 6.11 the effects of additional aeration on the ammonia wastewater sample, at a constant temperature, in continuous mode, are exposed. The ammonia removal efficiency by probe MS 3 is increased as a function of time, reaching the value of 15.26%, or 61.69 mg/l, after 90 minutes of irradiation. The treatment conducted continuously by the probe MS 10, makes the degree of removal to be increased using the additional aeration. In this case, the ammonia extraction is done constantly within 50 minutes of treatment, the concentration being decreased by 26.82% from baseline.

The maintenance of a constant temperature by using the cooling water coil allows observing the more favorable effect of aeration compared with the treatment without introducing the additional air.

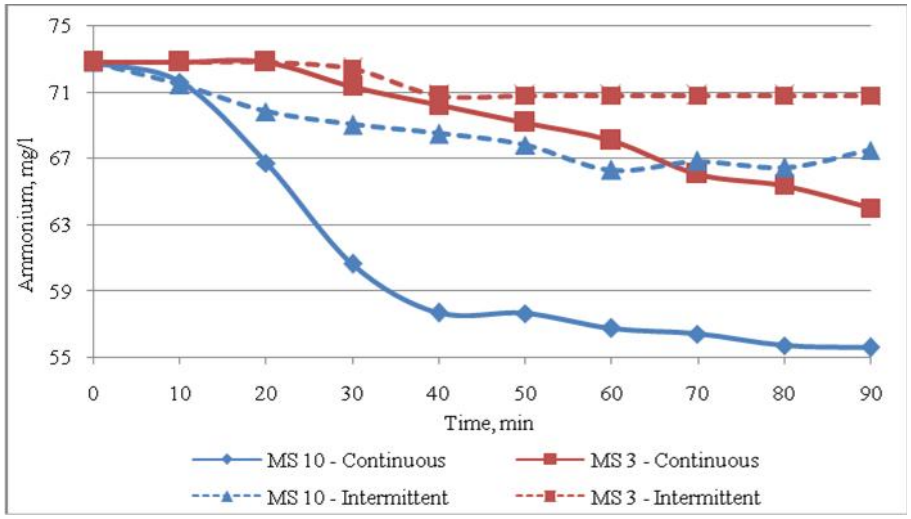

Fig. 6.10. The variation of the ammonia concentration without heating, depending on the ultrasonic intensity and the operating mode

This is due to the dependency of the diffused oxygen into the water by aeration, to the water temperature, since the amount of oxygen accumulated in the sample increases with decreasing temperature [285].

6.4. The effect of temperature and the establishment of the optimum ammonia water treatment regime

Figures 6.13 and 6.14 give the ammonia elimination values, in continuous regime, without aeration and with aeration respectively, with and without heating.

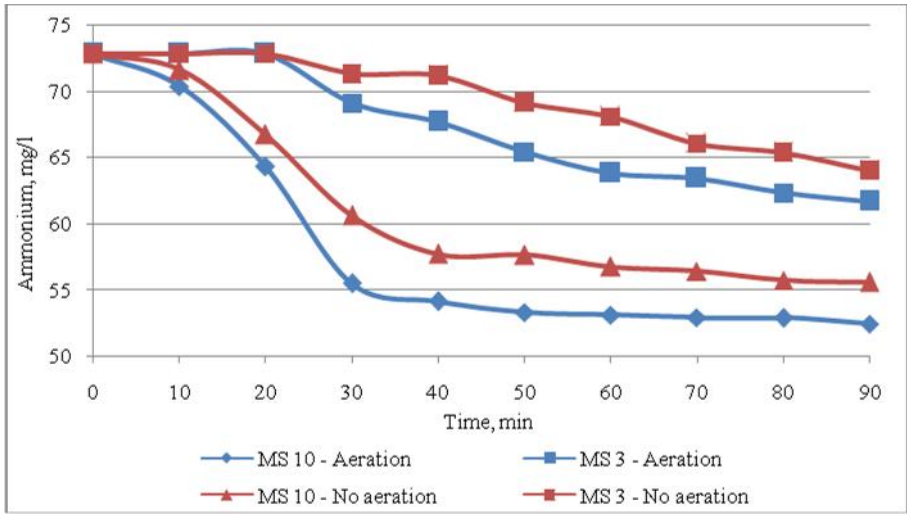

Fig. 6.11. The variation of the ammonia concentration, in continuous mode, without heating, depending on the ultrasonic intensity and the aeration regime

The temperature rise generates a reduction in the acoustic cavitation threshold, which means that liquids cavitate at lower intensities [286]. By increasing the temperature the rate of chemical reaction increases due to the increased rate of collision between molecules [138]. Also, in addition to the inherent volatility of the compound, increasing the temperature will increase the volatility of the compound [287].

Plesset found that the maximum value of the decline rate of cavitation bubbles in distilled water takes place at temperatures between 40°C and 50°C. It also showed that cavitation events are lesser affected at higher temperatures due to the increase in vapor pressure. At the same time, increased damage at lower temperatures has a less obvious interpretation and may be due to increased chemical activity with increasing temperature [262]. Considering the favorable impact of sample heating on reducing the concentration of hazardous substance in the studied wastewater, subsequent determinations were made without applying the cooling water coil.

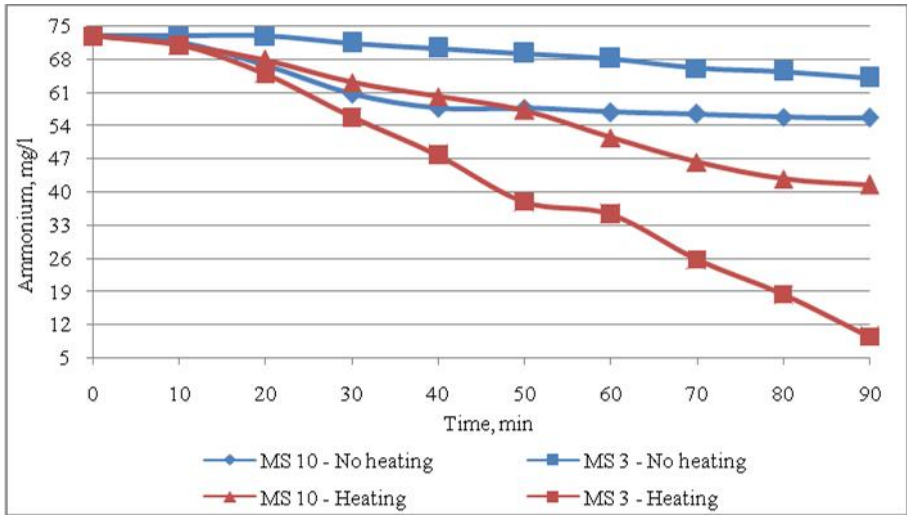

Fig. 6.13. The variation of the ammonia concentration, in continuous mode, without aeration, depending on the sample heating regime

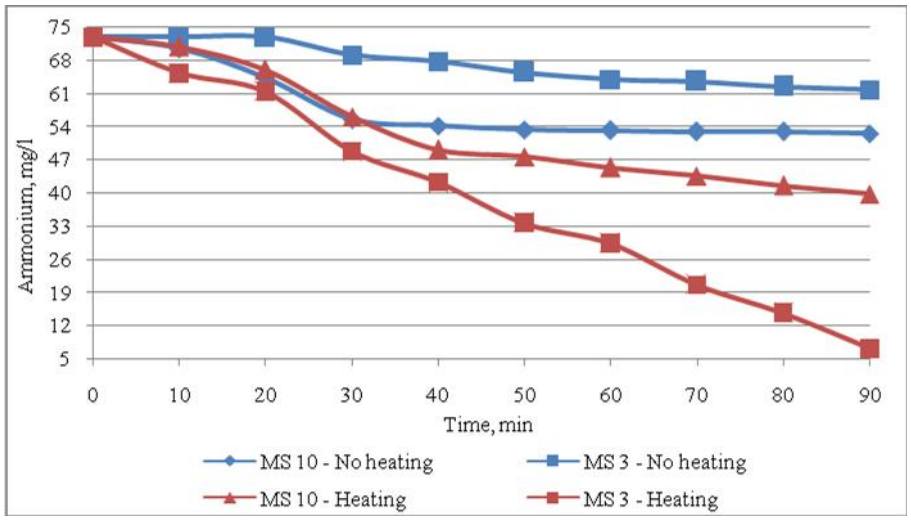

Fig. 6.14. The variation of the ammonia concentration, in continuous mode, with aeration, depending on the sample heating regime

6.5. The effect of the sample volume

6.5.1. The ammonia water sample volume of 500 ml

For this volume, the higher acoustic power density generated by the MS 3 probe, produces

an increase in the decontamination efficiency by using aeration, to the value of 26.52%, compared to the treatment without aeration, with 19.10% efficiency in between 30-80 minutes. Subsequently, the extraction rate is reduced significantly when the treatment is carried out strictly under the effect of ultrasound and more pronounced when the effect of sample aeration is acting additionally. In the case of the lower acoustic power density, generated by the MS 10 probe, the ammonia extraction process occurs from the first 10 minutes. Decontamination is done to the final concentration of 24.16 mg/l, in the presence of aeration. The obtained values are within the limits permitted for the discharge into the public sewerage networks [3], after 90 minutes, under the influence of additional aeration.

The higher energy efficiency observed for the ultrasonic probe with higher irradiation surface and lower ultrasonic intensity (MS 10), is due to a more uniform energy dissipation [288]. Regardless the acoustic power density (the power input into the system per unit volume of the ultrasonic irradiated effluent), ther input power into the system is higher when is done thtough larger areas of irradiation [150].

6.5.2. The ammonia water sample volume of 100 ml

By reducing the space occupied by the irradiated liquid, a better propagation of the acoustic waves into the sample is generated. The result obtained in the presence of aeration and heating lies in the total elimination of ammonium, after 60 minutes of ultrasonic treatment. The higher ultrasonic intensity, corresponding to the MS 3 probe, generates a reduction in the ammonia concentration up to 15.57 mg/l without aeration and 12,135 mg/l with aeration. The comparative decontamination efficiency for the studied sample volumes of ammonia water, namely 500 ml, 300 ml and 100 ml, is exposed in the Figures 6.21 and 6.22 for the ultrasonic intensity of 460 W/cm^2 and 90 W/cm^2.

In all the given conditions, the removal degree is increased by reducing the volume of ammonia water, treated with ultrasound. Furthermore, smaller volumes involve higher temperatures with high effect on the removal process. It is noteworthy that the better removal rates are recorded by the use of MS 10 probe, irrespective of the volume treated, which shows that the effect of temperature is higher than the ultrasonic intensity effect.

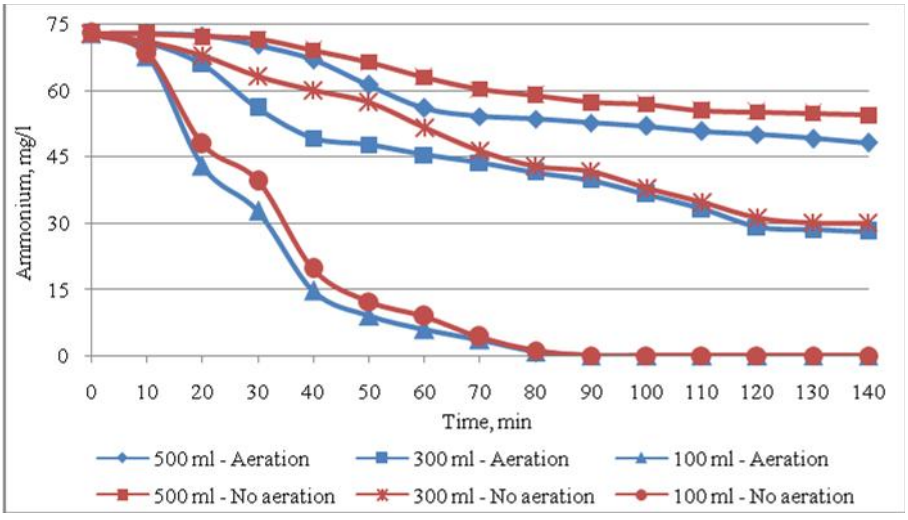

Fig. 6.21. The variation of the ammonia concentration, in continuous mode, depending on the aeration regime and the sample volume, for the ultrasonic intensity of 460 W/cm^2

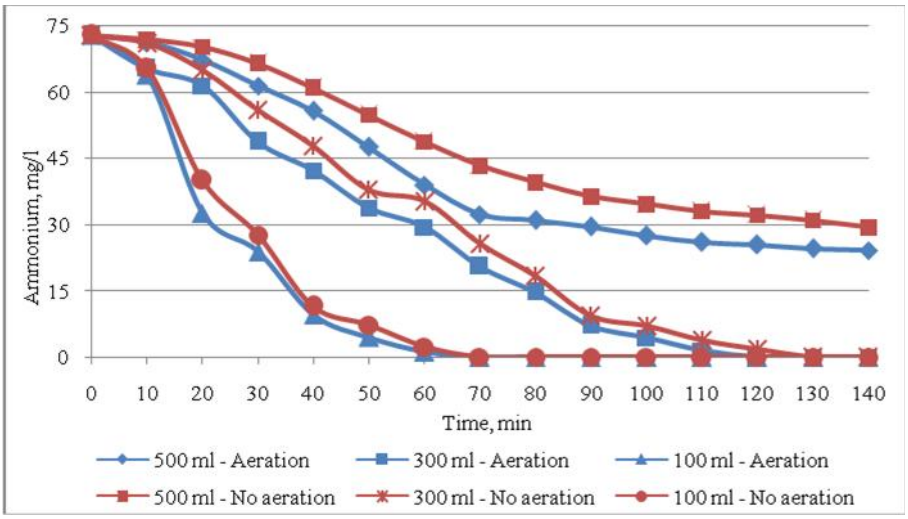

Fig. 6.22. The variation of the ammonia concentration, in continuous mode, depending on the aeration regime and the sample volume, for the ultrasonic intensity of 90 W/cm^2

6.6. The effect of the diameter and of the liquid height in the vessel

The propagation of the sound wave into the liquid, results in the movement of the fluid molecules. This movement occurs in the direction of the sound wave propagation outside the transducer, depending on the pressure gradient which is called the acoustic streaming. The behavior of the acoustic streaming depends on the physico-chemical properties of the liquid, on the operating parameters, such as acoustic power dissipation and frequency of irradiation, and on the geometrical parameters, such as the size and geometry of the reactor [289]. The carried out analyzes showed an increased efficiency of decontamination with decreasing the sample volume of the ammonia wastewater. However, for a complete picture of the ultrasonic irradiation effect, it is necessary to also determine the influence of the working vessel geometry on the pollutant removal rate.

The design of the reactor in terms of the relationship between the diameter of the immersed transducer and the diameter of the reactor, the height of the liquid and the position of the transducer, play an important role in determining the distribution of the cavitation activity and therefore, in determining the effectiveness of the sonochemical reactors for a particular application [212]. For this purpose, the measurements were performed on the sample volumes of 100 ml and 50 ml, in the vessels #1, #2, #3 and #4.

6.6.1. The ammonia water sample volume of 100 ml

The constructive form of the 4 utilized containers are of special influence on the ammonia water decontamination. On the other hand, the various temperatures recorded for the treatment of the same liquid volume, act distinctly on the removal process based on ultrasonic technology.

The main feature of the vessel #1, represented by the lowest diameter, generates the uniform transmission of the acoustic waves into the liquid, without the need for a supplementary period of time, in order the sample layers next to the vessel wall to mix with those neighboring the acoustic probe [36]. This is the case of the vessel #4, characterized by

a large diameter in relation to the liquid height in the vessel. For the ultrasonic intensity of 90 W/cm^2, the complete decontamination of the sample required smaller intervals of treatment, compared to the ultrasonic intensity of 460 W/cm^2. Thus, after 60 minutes, the pollutant removal efficiency was of 100% for the vessels #1, #2, #3 and of 98.46% for the vessel #4 (Fig. 6.24). Also, the immersion degree of the transducer, as well as the liquid height in the vessel, influence the degree of reflection of the sound waves incident from the liquid mass and from the walls of the vessels [290].

Another issue that caused differences on the decontamination regime can be represented by the free area above the mass of liquid in each container. Increasing the height of the liquid free surface causes the vapor concentration above the sample and, therefore, increases the vapor pressure of the liquid. With increasing the vapor pressure of the liquid, the vapor content of the acoustic cavities increases, which imply a drop of the energy released during the cavitational collapse [212]. This may be related especially with the containers #4 and #2, that have a superior free surface above the liquid compared to the height occupied by the liquid.

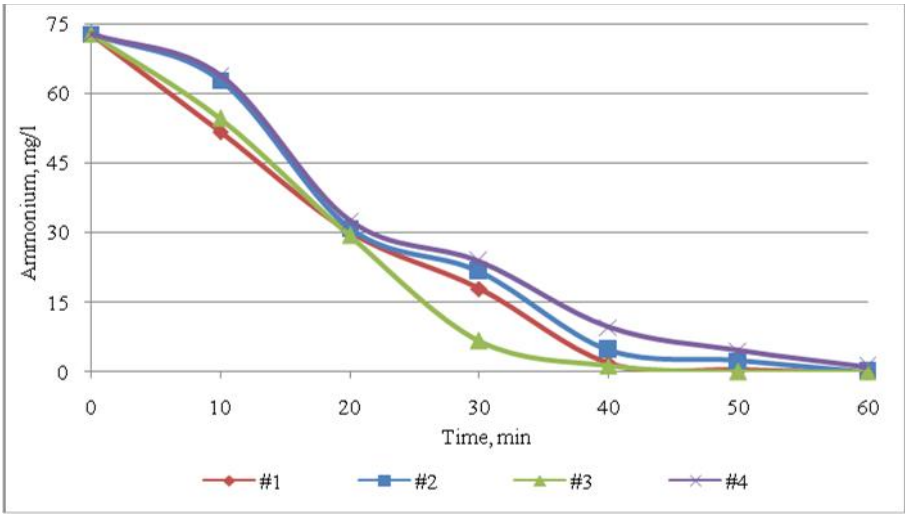

Fig. 6.24. The variation of the ammonia concentration, depending on the reactor geometry, in continuous mode with aeration, for the sample volume of 100 ml and intensity of 90 W/cm^2

Instead, for the vessel #1 such a free zone is missing, because the liquid volume occupies the whole height of the vessel. In this case, the vapor pressure is lower, which means that the cavitation threshold and the cavitational intensity are increased, as well as the speed of the chemical reaction [279].

6.6.2. The ammonia water sample volume of 50 ml

For a clear image of the effect of the reactor geometry and of the ultrasonic irradiated liquid mass, the 50 ml volume of residual ammonia water was also analyzed. The ultrasonic treatment at the intensity of 460 W/cm^2 requires a total of 60 minutes for the decontamination of a 50 ml volume of ammonia wastewater.

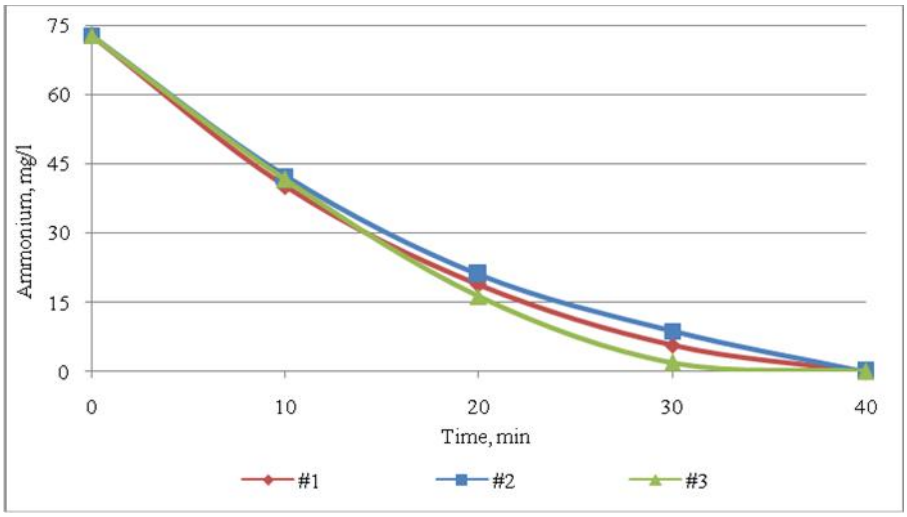

Fig. 6.26. The variation of the ammonia concentration, depending on the reactor geometry, in continuous mode with aeration, for the sample volume of 50 ml and intensity of 90 W/cm^2

The effect of the ultrasonic treatment performed for the acoustic power density of 90 W/cm^2 on the volume of 50 ml, achieves the maximum efficiency of the decontamination, in 40 minutes, for each of the three studied reaction vessels (Fig. 6.26). In this case, the sample temperature increases to a maximum of 80°C in the first 20 minutes, for the vessel #1, and after 40 minutes for the vessel #3. The container #2 records a temperature limit, after 20 minutes of ultrasonic treatment, not exceeding 72°C.

6.7. The effect of the initial concentration

6.7.1. The effect of ultrasonic intensity depending on aeration

The results obtained for the initial concentration of 145.6 mg/l, show that the efficiency is higher for the ultrasonic intensity of 90 W/cm2 (probe MS 10), in the presence of aeration, in a manner analogous to the results obtained for the initial concentration of 72.8 mg/l. However, the ammonia water decontamination occurs constantly, irrespective of the aeration regime or the applied ultrasonic intensity.

Notwithstanding, certain time intervals should be noted when the aeration is applied, namely the interval of 40 - 90 minutes for the MS 10 probe and the interval of 50 - 80 minutes for the MS 3 probe, in which the removal process is more pronounced. These periods of treatment correspond to the intervals around which temperature increases to the limit values, for both sonotrodes. Therewith, these ranges characterized by accelerated reduction in the ammonia concentration, correspond to the more favorable effect of the sample aeration/bubbling which implies the multiplication of the cavitational events. After these time intervals, the elevated temperature and the persistence of the aeration influence, lead to the degassing of the ammonia water sample and to the attenuation of the reaction rates.

The effectiveness of the decontamination versus the initial concentration is given comparatively in the Figures 6.28 and 6.29.

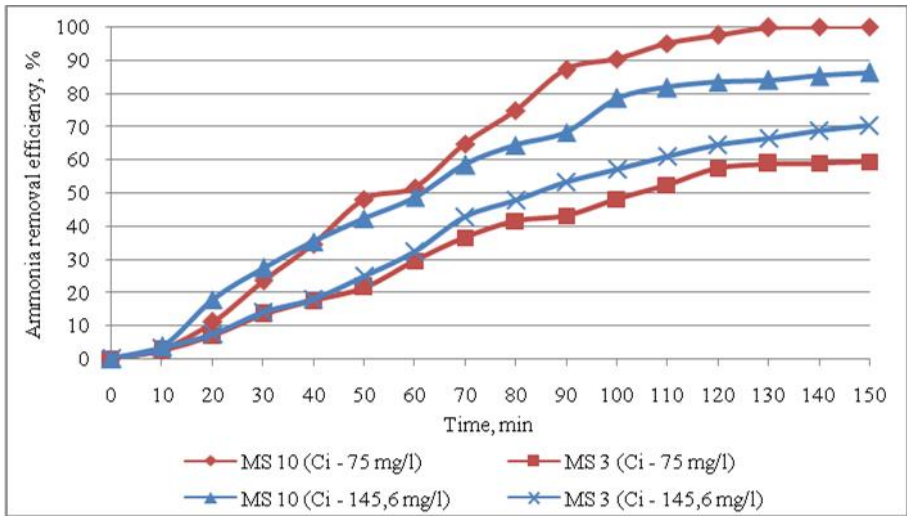

Fig. 6.28. The ammonia removal efficiency, depending on the ultrasonic intensity and the initial concentration, without aeration

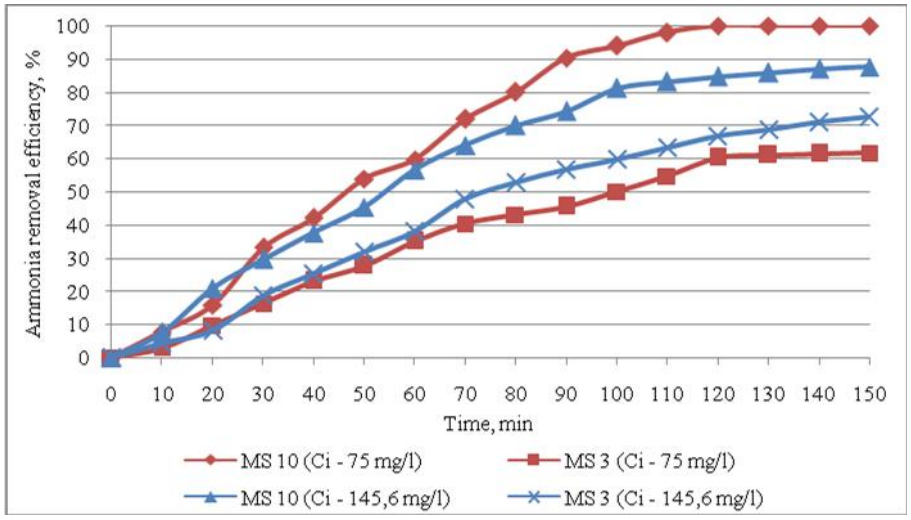

Fig. 6.29. The ammonia removal efficiency, depending on the ultrasonic intensity and the initial concentration, with aeration

The greater removal efficiency observed at the higher initial concentration can be explained by the intense micro-mixing generated by ultrasound and cavitation, which leads to increased interaction of the pollutants with the hydroxyl radicals [82,291].

6.7.2. The effect of the sample volume

Similarly to the results obtained for the lower initial concentration, the ammonia concentration decreased with decreasing the sample volume. Results are improved by the presence of aeration in all conditions, mainly in a specific range located in the first half of the analysis (which vary depending on the amount of wastewater), followed by the phenomenon of degassing.

For the MS 10 probe higher decontamination rates were obtained at the end of the experiment, for all the three volumes of the sample, i.e. 79.36% for the volume of 500 ml, 87.65% for the volume of 300 ml and 100% for the volume of 100 ml (Fig. 6.31).

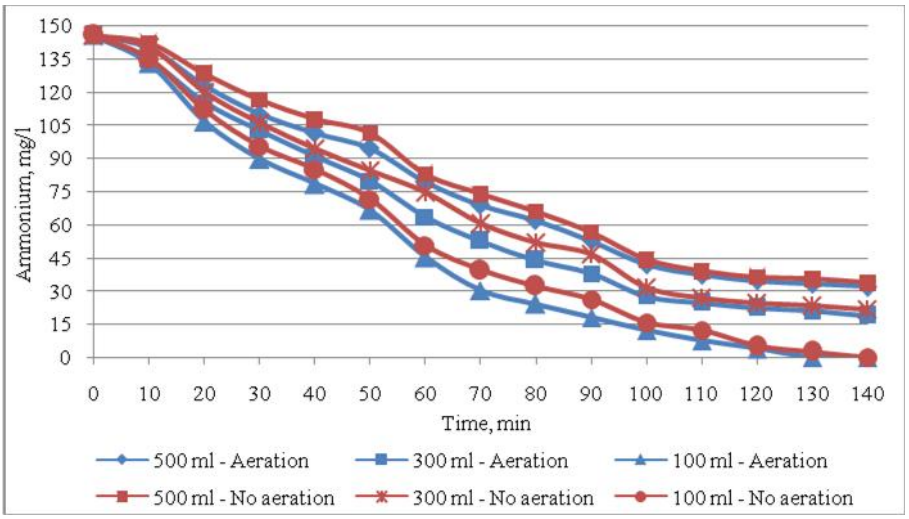

Fig. 6.31. The variation of the ammonia concentration, in continuous mode, depending on the aeration regime and the sample volume, for the ultrasonic intensity of 90 W/cm^2 (C_i=145,6 mg/l)

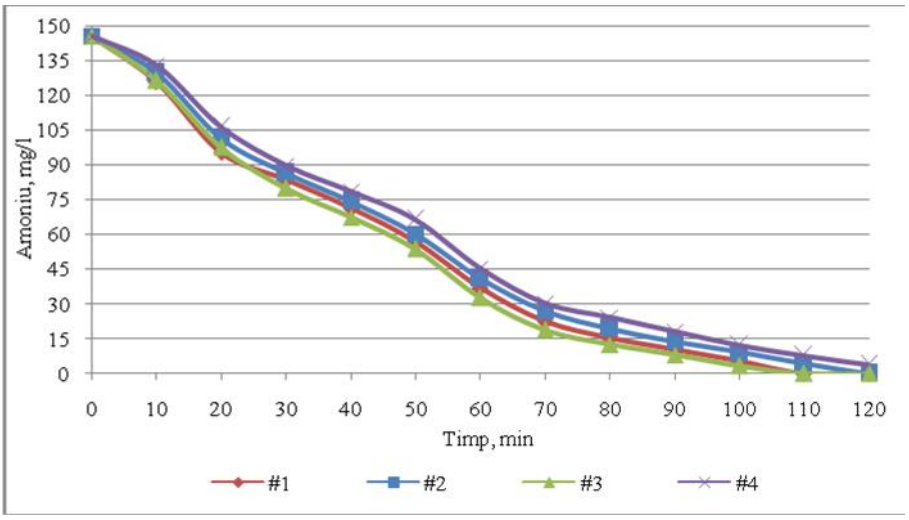

Fig. 6.33. The variation of the ammonia concentration, depending on the reactor geometry, in continuous mode with aeration, for the sample volume of 100 ml and ultrasonic intensity of 90 W/cm^2 (C_i=145,6 mg/l)

6.7.3. The effect of the diameter and of the liquid height in the vessel

Elimination is done constantly for all the working vessels. Similar to the treatment applied to the wastewater with lower initial concentration, the decontamination efficiency increases by reducing the diameter of the vessel. The difference that is observed as compared to the treatment applied to the residual water with lower initial concentration is the amount of time required to remove ammonia, which is much longer.

At the initial concentration of 72.8 mg/l, for the complete elimination of ammonia, 60 minutes were required for the probe MS 10 and 90 minutes for probe MS 3. Instead, for the initial concentration of 145.6 mg/l, the treatment duration required an extension up to 110

minutes for the probe MS 10 (Fig. 6.33), in which case the decontamination was complete for the vessels #3 and #1 and 120 minutes for the vessels #2. The vessel #4 showed a final concentration of 3.89 mg/l (97.32%) after the same interval of time, of 120 minutes.

According to the obtained results, it can be considered that at the base of the ammonia removal mechanism through ultrasound technology, is the process of pyrolysis. Ammonia molecules are displaced after the thermal decomposition, due to the immediate rise of the temperature and the pressure inside the cavitation bubbles, being transformed into nitrogen molecules and hydrogen molecules [166,201,275].

6.8. Conclusions

The stage of the experimental research realization and the interpretation of the obtained results, for the treatment of the ammonia wastewater originated from industrial processes by ultrasonic technology, revealed the following conclusions:

- Wastewater treated continuously, by the ultrasonic intensity of 90 W/cm^2 with aeration, falls within allowable limits for direct discharge into natural watercourses [3], after two hours of ultrasonic irradiation, for a sample volume of 300 ml.
- When the treatment is of intermittent operation, at the ultrasonic intensity of 90 W/cm^2 with aeration, decontamination is realized up to the limit for discharge into the sewege system (30 mg/l), after 80 minutes.
- For the treatments carried out in the presence of the cooling water (at a constant temperature), for the ultrasonic intensity of 460 W/cm^2, the best results are obtained at additional aeration, in which case the ammonium concentration decreases over the course of 90 minutes up to 15.26% in continuous operation and only up to 5.89% in intermittent operation.
- The results obtained for the intermittent treatment regime show a lower decontamination efficiency compared to the continuous regime. One possible explanation could be the interruption of the cavitational events developed during the ultrasonic irradiation into the ammonia water, through the breaks involved by the pulsed operation mode. This creates the need for a longer period of time necessary for the intermittent irradiation, to obtain an efficiency comparable to that recorded in continuous operation.
- When the ultrasonic irradiation is combined with aeration, the latter increases the concentration of cavitation bubbles into the solution, increasing the energy efficiency and accelerating the ultrasonic cavitation and the pyrolysis.
- The reaction rate is much greater when the system is saturated with gas, due to the availability for cavitation of the nuclei respresented by the bubbles of gas, but it decreases with the occurrence of the effect of degassing.
- Increasing the temperature the rate of the chemical reaction also increases due to the higher rates of collision between the molecules. The ammonia removal efficiency increased by reducing the diameter of the vessel holding the irradiated solution, regardless the studied liquid height in the vessel.

- The treatments conducted for changes in the sample volume, showed an increase of the decontamination efficiency in the presence of reducing the amount of wastewater under study. This result can be attributed both to the more pronounced heating of the irradiated solution that is involved by the lower volumes and to a more compact space occupied by the liquid that provides a better propagation of the acoustic waves.
- The design of the reactor in terms of the relationship between the diameter of the immersed transducer and the diameter of the reactor, the height of the liquid and the position of the transducer, play an important role in determining the distribution of the cavitation activity and therefore, in determining the effectiveness of the sonochemical reactors for a particular application.
- The treatment conducted at the ultrasonic intensity of 90 W/cm^2 through the probe MS 10 generates to the volume of 100 ml the integral decontamination in the presence of aeration, over a period of 50 minutes, for the vessel #3 (characterized by reduced diameter, reduced height of the liquid in the vessel), within 60 minutes for the vessel #1 (reduced diameter, the utmost height of liquid in the vessel) and #2 (enlarged diameter, smaller height of the liquid in the vessel compared to vessel #1), and after 70 minutes for the vessel #4 (the larger diameter, the lowest height of the liquid in the vessel).
- The differences on the decontamination regime also depend on the free area above the liquid mass occupied by each container. The increase in the height of the free surface of the liquid causes the vapor concentration above the sample and, therefore, increases the vapor pressure of the liquid. With increasing the vapor pressure of the liquid the vapor content of acoustic cavities increases and a drop of the energy released during the collapse of cavitation is registered.
- The sonolysis of the ammonia water of twice as high concentration, for the reference sample volume of 300 ml, in the presence of aeration, has an efficiency of 72.63% for the decontamination by MS 3 probe and of 87.65% for MS 10 probe.
- Increasing the initial concentration of pollutant in water, leads to increased availability of the pollutants for oxidation reactions, in the presence of active oxidizing species.
- In the case of the ammonia water with higher initial concentration, regardless the intensity of irradiation, there are certain time intervals ranging between 40 - 90 minutes, in which the removal process is more pronounced, not only because of the temperature rise to the limit values, for both sonotrodes, but also because of the sample aeration which implies the multiplication of the cavitational events. After these time intervals, the elevated temperature and the persistence of the aeration influence, lead to the degassing of the ammonia water sample and to the attenuation of the reaction rates.

Chapter 7

Experimental results of sulfide wastewater treatment by ultrasonic technology

7.1. The dynamics of pH values during the ultrasonic treatment of sulfide wastewater

The effect of the ultrasonic treatment on the pH of the sulfide wastewater simulated in the laboratory, has been studied for the two solutions, for which the initial pH value was of 11.20 for the initial concentration of 75 mg/l and of 11.90 for the initial concentration of 120 mg/l.

It has been found that the pH value decreases proportionally with increasing the treatment time and with the reduction of the sample volume, for the both initial concentrations. It can be considered that a moderately lower pH value can be one of the causes of the higher sulfides removal degree, which was recorded with increasing treatment time.

7.2. The effect of ultrasonic intensity, on the decontamination efficiency of sulfide wastewater, in the presence of sample heating

7.2.1. The effect of the treatment time and the optimum time intervals establishment

The initial concentration of sulfides from the studied residual wastewater has not changed in the intervals of 0-10 minute and even 0-20 minutes of irradiation in different operating modes for different conditions. This can be observed both for the ultrasonic intensity of 460 W/cm^2, and the intensity of 90 W/cm^2.

As regards the duration of the ultrasonic treatment, this may differ depending on the evolution of the removal degree for the sulfides present in the wastewater.

7.2.2. The effect of treatment regime and the optimum regime establishment

According to Figure 7.4, the effect of ultrasound on the decontamination process is significantly reduced in pulsed mode of operation, regardless of the ultrasonic intensity applied. However, there is a higher efficiency in the case of MS 10 probe, by which the sulfides are removed to a concentration of 67.9 mg/l, after 90 minutes.

7.2.3. The effect of additional aeration

Singular aeration may be applied to the decontamination of the sulfide wastewaters, but only for initial concentrations that do not exceed 4 mg/l [107,113]. The presence of aeration determines improved efficiency of sulfide removal for both studied acoustic power densities and for both operating modes, namely continuous and intermittent (Fig. 7.6).

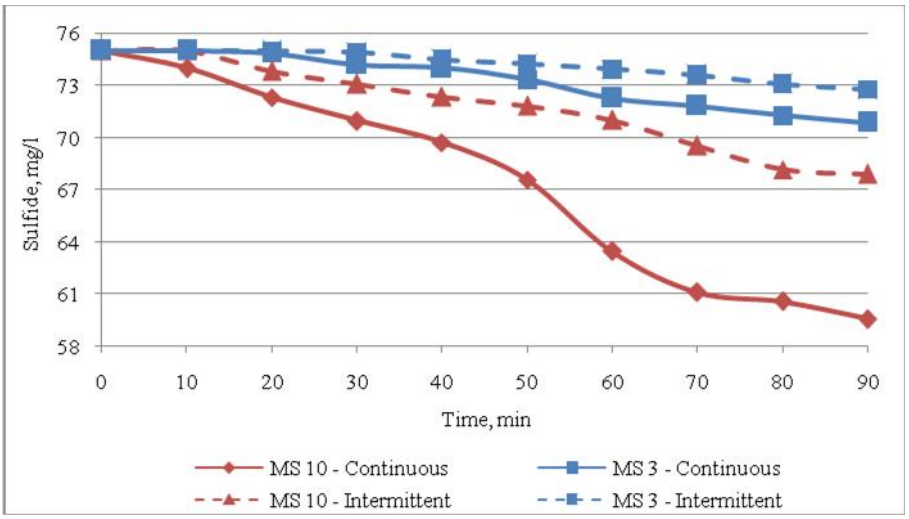

Fig. 7.4. The variation of the sulfide concentration, depending on the ultrasonic intensity and the operating mode

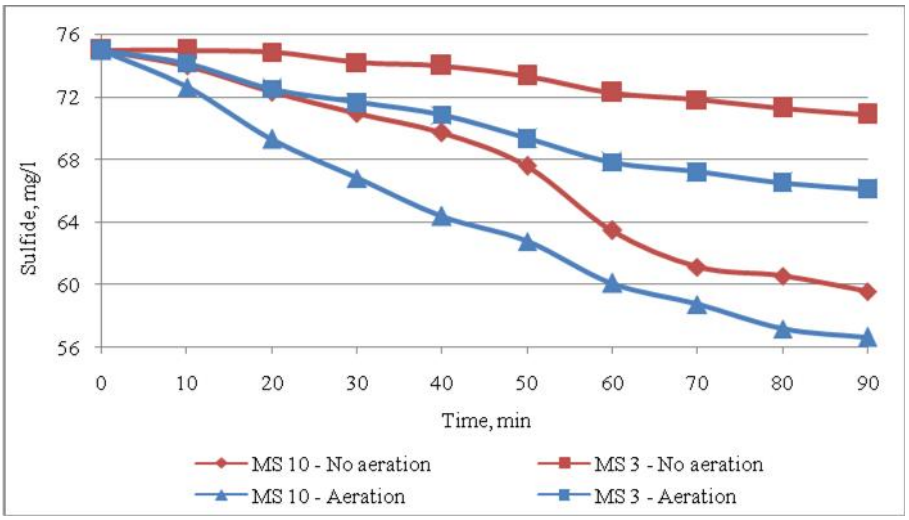

Fig. 7.6. The variation of the sulfide concentration, in continuous mode, depending on the ultrasonic intensity and the aeration regime

7.3. The effect of ultrasonic intensity, on the decontamination efficiency of sulfide wastewater, in the abscence of sample heating

7.3.1. The effect of treatment time and the optimum time intervals establishment

The ultrasonic effect without the additional effect of sample heating, generates a significantly reduced reaction rate. Concentrations were determined at 10 minutes intervals.

7.3.2. The effect of treatment regime and the optimum regime establishment

The effectiveness of the sulfide decontamination at a constant temperature depending on the operating mode, is shown in Figure 7.8. For the continuous irradiation, decontamination

occurs even in the absence of sample heating, but with lower efficiency, of 10.84% by MS 10 probe, and of 3.57% by MS 3 probe. The lower energy intake, which woulf further contribute to the generation of cavitation and achieving the desired chemical modification, makes the intermittent operation to determine an even lower decontamination effect, up to the concentration of 73.94 mg/l and 70.27 mg/l respectively.

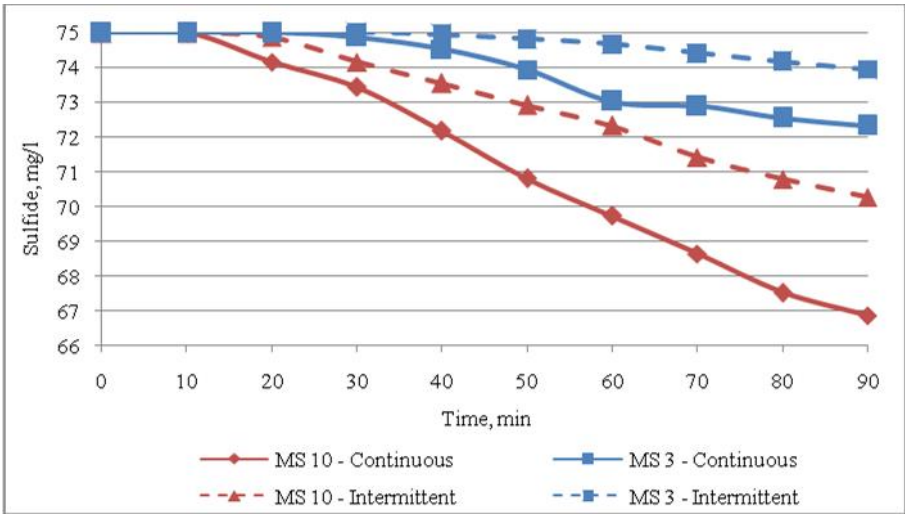

Fig. 7.8. The variation of the sulfide concentration without heating, depending on the ultrasonic intensity and the operating mode

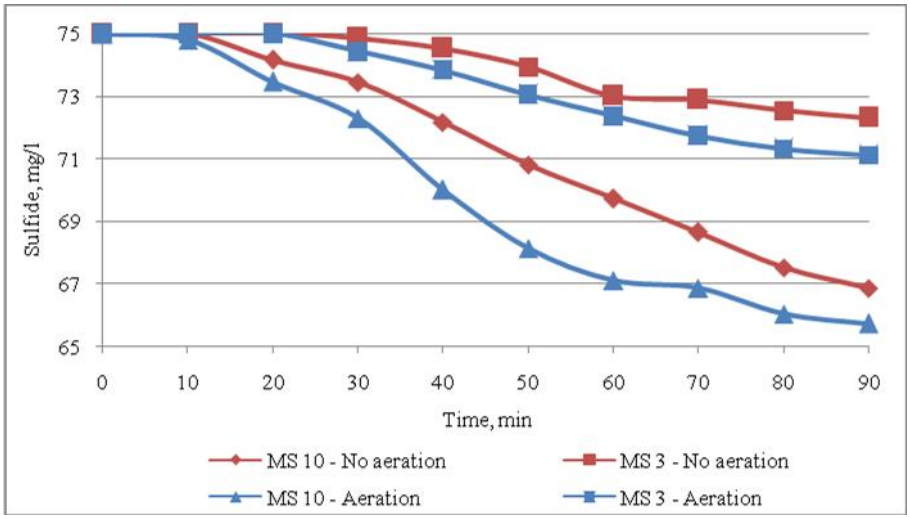

Fig. 7.9. The variation of the sulfide concentration, in continuous mode, without heating, depending on the ultrasonic intensity and the aeration regime

7.3.3. The effect of additional aeration

The additional contribution of the supply air, participates on the oxidation of the present sulfides by the produced oxygenation (Fig. 7.9). The presence of aeration enhances the sulfide wastewater decontamination degree even at a constant temperature, the removal efficiency increasing by 1.6% for the MS 3 acoustic probe and by 1.506% for the MS 10 acoustic probe, compared to the treatment without aeration.

7.4. The effect of temperature and the establishment of the optimum sulfide wastewater treatment regime

The fraction of energy dissipated as heat is also used for the chemical reaction to perform. Although it is usually marginal, it is very important to generate the desired effects, indicating that the total energy dissipated into the medium as heat occurs when the operation is performed in a closed circuit [260].

Figures 7.11 and 7.12 give the ammonia elimination values in continuous mode, without aeration and with aeration respectively, with and without heating. The elimination or the oxidation under high temperature conditions also has been shown to be effective for a variety of sulfides, in paper [136], where the best results have been obtained at temperatures up to 60°C.

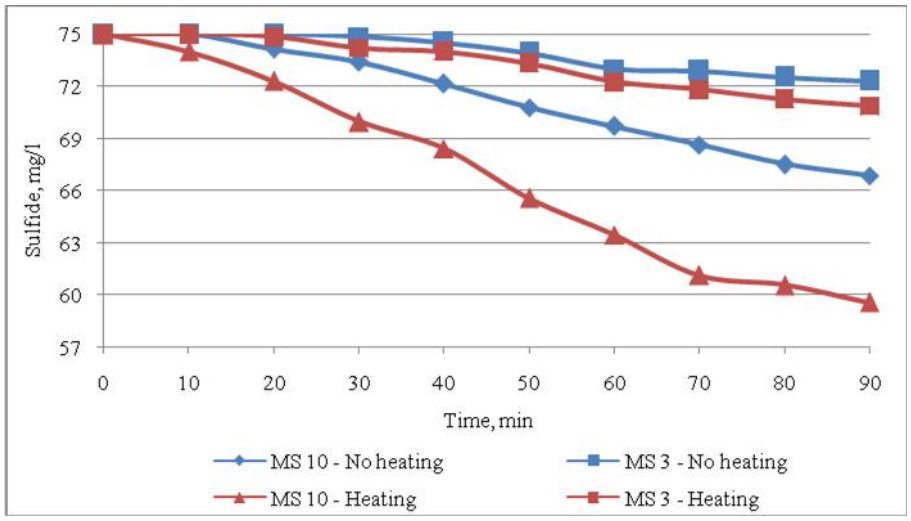

Fig. 7.11. The variation of the sulfide concentration, in continuous mode, without aeration, depending on the sample heating regime

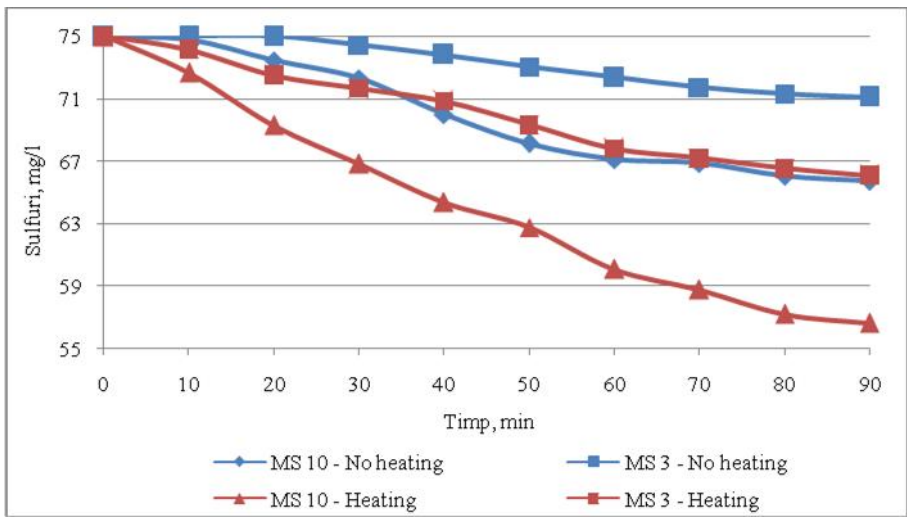

Fig. 7.12. The variation of the sulfide concentration, in continuous mode, with aeration, depending on the sample heating regime

7.5. The effect of the sample volume

7.5.1. The sulfide wastewater sample volume of 500 ml

For the ultrasonic intensity of 460 W/cm^2, there is an elimination of the sulfide content of only 0.10%, if aeration is applied, in the first 30 minutes. The large sample volume in relation to the concentrated energy dissipation, that is characteristic to MS 3 probe, generates a very low level of decontamination. The ultrasonic intensity of 90 W/cm^2 starts the oxidation of the present sulfides in the first 10 minutes of treatment, irrespective of the aeration. The energy dissipated as heat generates a temperature rise produced by the MS 10 probe, during the first 60 minutes, in the range of 23-60°C. At the end of the 90 minutes allocated to this analysis, the efficiency is of 18.34%.

7.5.2. The sulfide wastewater sample volume of 100 ml

The following values were obtained on the removal of sulfide content, by aeration:
- at the acoustic power density of 460 W/cm^2 (MS 3), the concentration decreased by 31.09%;
- at the acoustic power density of 90 W/cm^2 (MS 10), the concentration decreased by 47.74%.

The temperature generated by the probe MS 10 when treating the wastewater in this recipient, recorded an increase to 62°C after 60 minutes of treatment. Instead, for the probe MS 3, the treated liquid temperature reaches 35°C within 60 minutes of treatment. In all circumstances, the removal degree by ultrasonic treatment increases by reducing the volume of sulfide wastewater, not only due to the more uniform dissipation of the acoustic energy but also due to the heating effect, which increases with decreasing the volume of liquid (Figures 7.19 and 7.20).

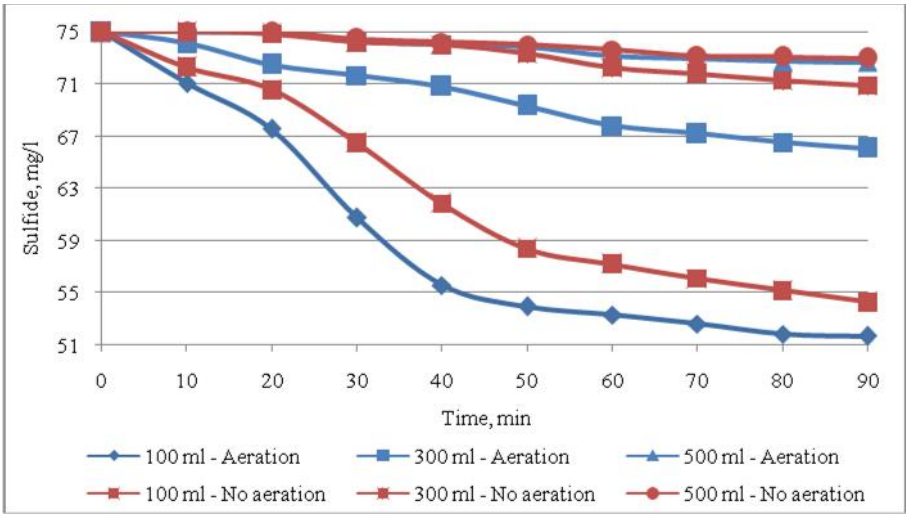

Fig. 7.19. The variation of the sulfide concentration, in continuous mode, depending on the aeration regime and the sample volume, for the ultrasonic intensity of 460 W/cm^2

7.6. The effect of the diameter and of the liquid height in the vessel

7.6.1. The sulfide wastewater sample volume of 100 ml

The comparative analysis of the decontamination effectiveness of sulfide wastewater has been made on the vessels #1, #2, #3 and #4. The constructive form of the four utilized

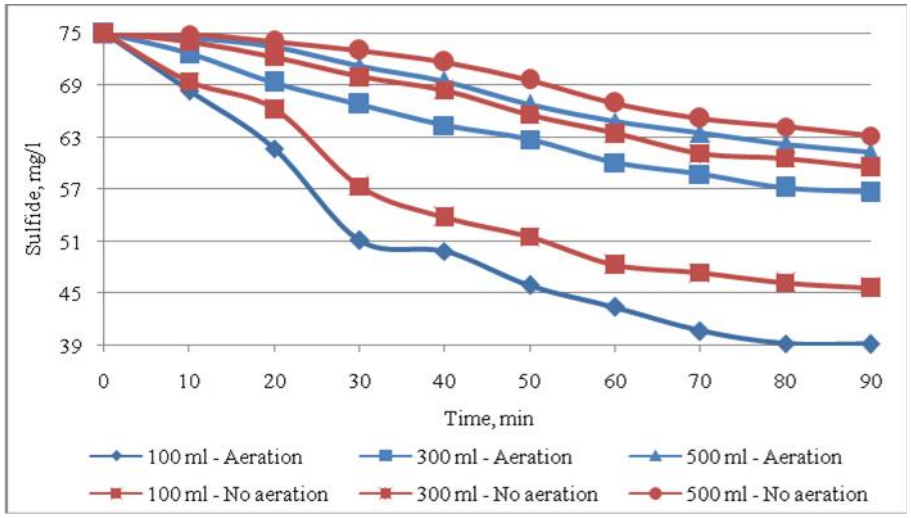

Fig. 7.20. The variation of the sulfide concentration, in continuous mode, depending on the aeration regime and the sample volume, for the ultrasonic intensity of 90 W/cm^2

vessels, significantly influences the removal regime of sulfides. Both studied acoustic intensities generate a higher degree of decontamination in the vessel #1. After 90 minutes of irradiation the pollutant is removed with a reaction rate of 55.28% (MS 10) and 35.45% (MS 3) for the initial concentration of 75 mg/l.

7.6.2. The sulfide wastewater sample volume of 50 ml

In the case of 460 W/cm^2 intensity, the ultrasonic treatment in vessel #1 shows a decline of 79.41% from baseline. In the case of vessel #2, the concentration decreases by 69.92%, and by 74.76% in the vessel #3.

Regarding the lowest volume of the sample studied, the results for the treatment by the intensity of 90 W/cm^2, are represented by a decrease of 85.24% after 90 minutes of treatment, for the vessel #1.

7.7. The effect of the initial concentration

7.7.1. The effect of ultrasonic intensity depending on aeration

In the case of applying the ultrasonic treatment to the wastewater of 120 mg/l initial concentration, after 90 minutes the sulfide content values reached a concentration of 71.38 mg/l, for the intensity of 90 W/cm^2 and of 104.84 mg/l, for the intensity of 460 W/cm^2. The sulfide removal efficiencies depending on the initial concentration of the wastewater, are presented in Figures 7.26 and 7.27 for the conditions of treatment in the absence or in the presence of aeration.

7.7.2. The effect of the sample volume

Under the additional effect of bubbling, the values obtained after 90 minutes of treatment were of 3.88% - 500 ml, 12.63% - 300 ml and 100 ml - 32.26%, for the ultrasonic intensity of 460 W/cm^2. At the ultrasonic intensity of 90 W/cm^2, the final concentrations of 28.50% - 500 ml, 40.51% - 300 ml and 47.14% - 100 ml, were achieved.

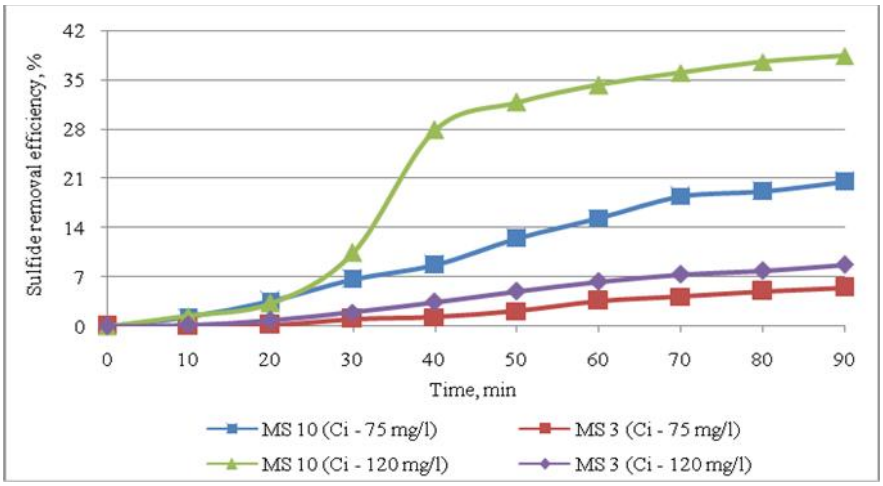

Fig. 7.26. The sulfide removal efficiency, depending on the ultrasonic intensity and the initial concentration, without aeration

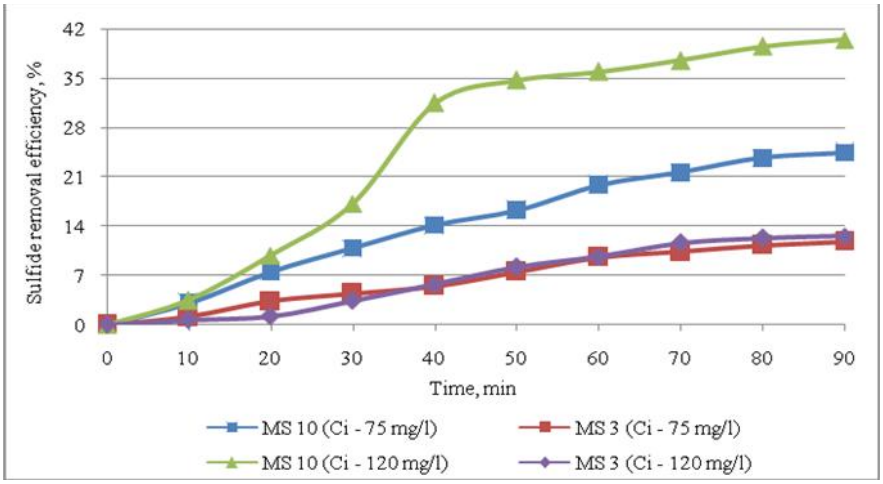

Fig. 7.27. The sulfide removal efficiency, depending on the ultrasonic intensity and the initial concentration, with aeration

7.7.3. The effect of the diameter and of the liquid height in the vessel

Both studied acoustic intensities generate a higher decontamination on the vessel #1. After 90 minutes of treatment, the pollutant is removed at a rate of 56.32% (MS 10) and 35.75% (MS 3), for the initial concentration of 120 mg/l.

The removal regime is similar to that obtained from the less concentrated solution, namely it is increased by raising the temperature of the sample, which is made different depending on the used reaction vessel. The results also have been improved by reducing the diameter of the working vessel, regardless studied heights of the liquid in the vessel.

7.8. Conclusions

In the phase of the experimental research realization and of the results interpretation for the treatment of the sulfides wastewaters contaminated syntheticallly, similar to those from industrial processes, the following conclusions resulted:

- The ultrasonic treatment performed in the continuous operation mode by the intensity of 460 W/cm^2 (through the MS probe 3), on the reference sample volume of 300 ml, do not lead to changes in the initial sulfide concentration in the first 20 minutes of irradiation. After 90 minutes, the decontamination efficiency is of 5.48%.
- As regards the ultrasonic intensity of 90 W/cm^2 (by the probe MS 10), the sulfide removal process begins after the first 10 minutes of treatment, recording a decontamination efficiency of 20.56%, after 90 minutes of treatment.
- The higher efficiency of the probe MS 10 is due to the pressure of the cavitation bubbles collapse, which is proving to be higher in lower operating intensities, due to the energy dissipation through a larger cross section.
- In order to compare chemical yield of the intermittent regime to that observed in a continuous irradiation equipment, a longer irradiation time must be applied, for the solution to be exposed to the same amount of acoustic energy.
- In the continuous operation mode, the sulfide removal capacity increases by 8.37% for the probe MS 3 and by 3.89% for the probe MS 10, when aeration is applied.
- At the continuous irradiation, decontamination occurs even in the absence of sample heating (at ambient temperature of 25°C), but with lower efficiency, of 10.84% with the probe MS 10 and 3.57% with the probe MS 3.
- The geometry of the reaction vessel significantly influences the sulfides removal regime. In addition, the differences of the temperatures recorded in handling the same volume of fluid into several containers, act distinctly in the elimination process based on the ultrasonic technology.
- On the vessels with a larger diameter (#2 and #4), the cavitational mixing is made more difficult because it requires a certain time to achieve the mix of the solution layers that are closer to the vessel wall with those from the region closest to the ultrasonic waves.
- The ultrasonic experiments on the sulfides wastewater of 75 mg/l initial concentration, have not achieved the degree of elimination to allow the direct discharge (up to the concentration of 1 mg/l [3]), but the results have been promising considering the absence of the use of organic solvents, catalysts or different chemical reagents.
- The decontamination efficiency of the sulfide wastewater of 120 mg/l initial concentration, is higher because the high concentration on the interface zone of the bubble raises the partial pressure of the pollutant. This leads to greater evaporation and further restraining of the pollutant in the cavitation bubble, that will suffer a pyrolytic decomposition when the extreme conditions are reached during the transitional bubble collapse.

Chapter 8

Experimental results of ammonia water treatment by sonic technology

8.1. The dynamics of pH values during the sonic treatment of ammonia water

During the sonic treatment of the ammonia wastewater originating from industrial processes, the pH values were reduced proportionally with increasing the treatment time, with increasing the air pressure supply of the sonic generator and with the reduction of the sample volume. It was found that the sonic treatment causes a more accelerated reduction in the pH values compared to the ultrasonic treatment, a result that can be attributed to the more intense oxygenation of the samples due to the air that produces the wastewater bubbling.

8.2. The effect of the generator air supply pressure on the efficiency of ammonia wastewater decontamination

8.2.1. The effect of treatment time and the optimum time intervals establishment

In order the treatment time needed to perform the sonic treatments on the ammonia wastewater to be determined, there were conducted several preliminary experiments. Initially, it was considered the time interval of 0-60 seconds, which proved to be enough for the sonic activation of the water containing ammonia from aquaculture and pisciculture [229].

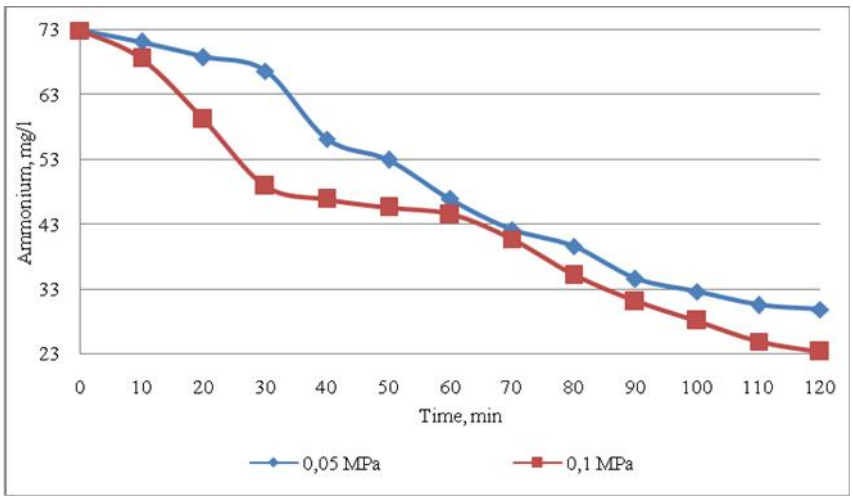

Fig. 8.6. The variation of the ammonia concentration, depending on the air pressure supply, at 10 minutes interval

Figure 8.6 presents the evolution of the concentration of ammonia for 10 minutes readings. Testing period was set for the time of registration of similar values for at least three consecutive readings, but within 120 minutes. Introducing air with a higher pressure in the wastewater, creates a more intense aeration of the sample, which ultimately lead to a higher rate of removal. The effectiveness of decontamination at the end of the experiment, indicates an amount of 59% (29.84 mg/l) at a pressure of 0.05 MPa, respectively 68% (23.29 mg/l) at a pressure of 0.1 MPa.

8.2.2. The effect of treatment regime and the optimum regime establishment

Similarly to the study conducted on the piezoelectric generator, it has been also intended determining the influence of the successive pauses in the treatment, in the form of the intermittent treatment regime. Intermittent operating mode was achieved by stopping or re-supply the sonic generator with compressed air by manual operation in intervals of 5/5 seconds of the compressed air supply valve.

The comparative results for the two treatment regimens, continuous and intermittent, are given in Figure 8.7, for the sample volume of 300 ml. According to the chart, the decontamination efficiency achieved with the pulsed mode of operation is significantly reduced. However, the reaction proceeds linearly with visualapproximation or without notable variation of the ammonia content, up to the final values of 56.72 mg/l in the case of the 0.05 MPa pressure, and 50.46 mg/l in the case of 0.1 MPa pressure.

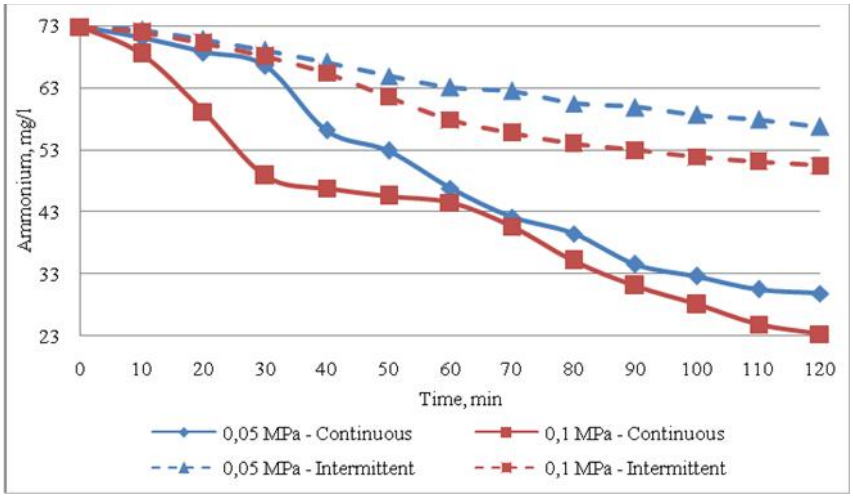

Fig. 8.7. The variation of the ammonia concentration, depending on the air supply pressure and the operating mode

8.3. The effect of the generator air supply pressure on the efficiency of ammonia wastewater decontamination, in the presence of sample heating

In order the effect of temperature to be observed for the sonic treatments, conducted by the air jet generator, the sample was heated artificially, by the means of a laboratory hotplate. The evolution of the sample temperature in these circumstances is presented in Chapter 4.3. The container containing the sample of ammonia water under study, was placed over the

laboratory electric hotplate, during the operation of the pilot plant based on the sonic technology, as shown in Figure 8.8 (where: 1 - compressor, 2 - system of air supply, 3 - vessel with ammonia water, 4 - sonic gasodynamic generator, 5 - laboratory electric hotplate, 6 - pH-meter). The temperature and the pH of the ammonia wastewater were determined for each reading of the ammonia concentration by a thermometer, and a pH meter respectively.

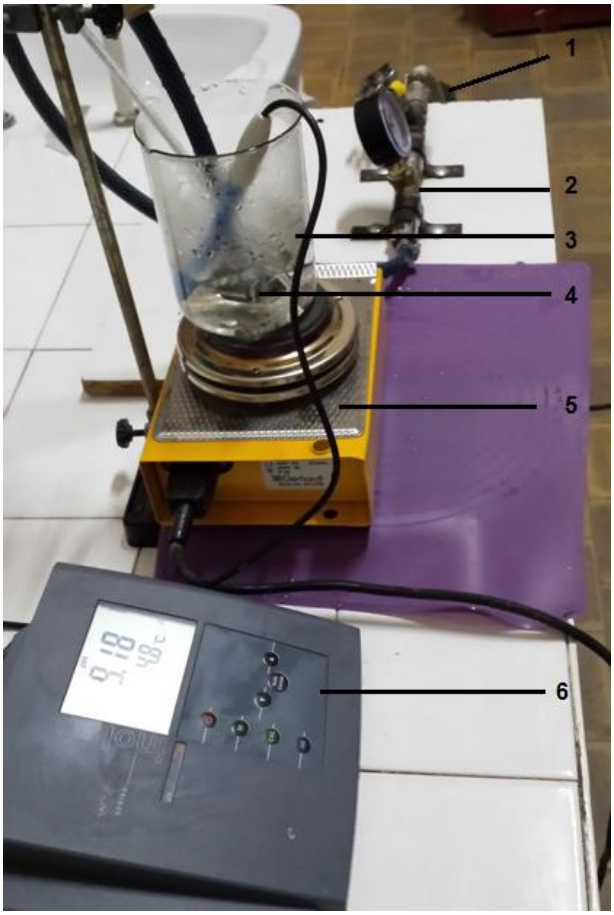

Fig. 8.8. The experimental installation with mechanical sonic generator during treatment of the ammonia waters in the presence of heating

8.3.1. The effect of treatment time and the optimum time intervals establishment

When using the hotplate, provided for the heating of the sonic treated sample, the experiment for the determination of the optimum treatment time was performed on the same sample volume of 300 ml.

The ammonia concentration readings were performed also at 10 minutes intervals, and the duration of the experiments was determined so as the values at consecutive readings to stabilize.

8.3.2. The effect of treatment regime and the optimum regime establishment

The comparative results obtained with and without the application of heating to the sonic treatment, continuously and intermittently, are shown in Figure 8.11 and 8.12 respectively. These graphs relate to the treatment of a volume of 300 ml ammonia water and points of the

dynamic of the concentrations for the same treatment time irrespective of the heating regime. The complete elimination of ammonia is reached after 40 minutes of sonication, respectively at 58°C sample temperature.

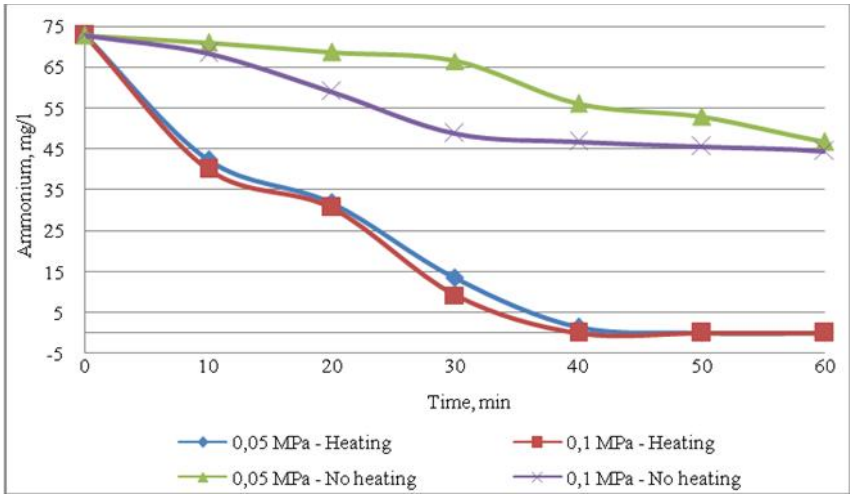

Fig. 8.11. The variation of the ammonia concentration, in continuous mode, depending on the sample heating regime

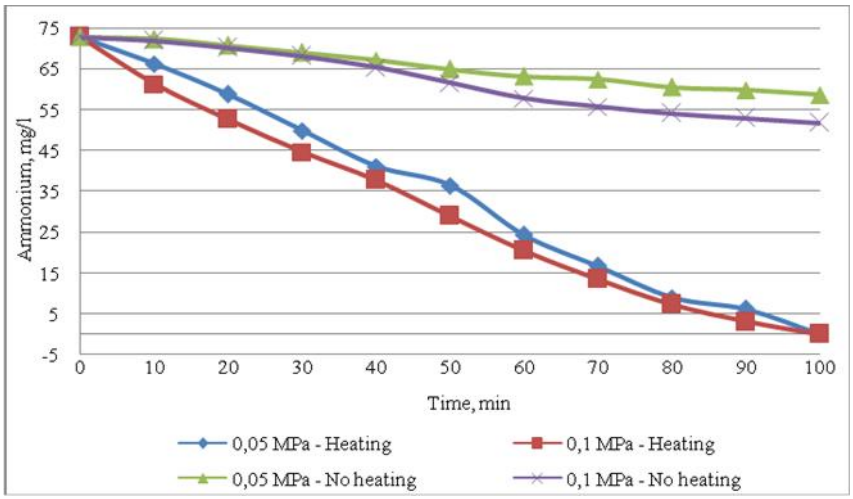

Fig. 8.12. The variation of the ammonia concentration, in intermittent mode, depending on the sample heating regime

The reduction the supply air pressure of the generator at a level of 0.05 MPa, generates a reduction in the rate of reaction. The ammonia removal is complete after 50 minutes, at which time the sample temperature is of 62°C.

8.4. The effect of the sample volume

The influence of the amount of ammonia wastewater subjected to the sonic treatment was studied. The results obtained by treating the sample volume of 300 ml were analyzed in comparison with those made from the sonolysis of the volumes of 500 ml and 100 ml.

8.4.1. The ammonia water sample volume of 500 ml

The character of the ammonia removal for a volume of 500 ml is irregular, which indicates the phenomenon of reabsorption depending on the treatment time. This phenomenon may be due to the fact that some of the ammonia dislocated only rises to the upper layers of the sample. The maximum efficiency of decontamination is reached after 90 minutes of sonic treatment, regardless the supply pressure.

When applying the sonic treatment in the presence of heating, a time interval of 60 minutes is necessary for the total removal of the pollutant, when the supply pressure of the air jet generator is of 0.1 MPa.

8.4.2. The ammonia water sample volume of 100 ml

For the sample volume of 100 ml, regardless of the utilized air supply pressure, the decontamination is made constantly, after 120 minutes values of 18,193 mg/l for 0.05 MPa and 14,535 mg/l for 0.1 MPa being achieved.

Regarding the dynamics of the ammonia concentration values for the three studied sample volumes, 500 ml, 300 ml and 100 ml is given comparatively for the pressures of 0.05 MPa and 0.1 MPa, when sonication is applied simultaneously with heating, the sample decontamination up to the allowed limits for discharge into the public networks [3] is done in very short time for the both supply pressures. The time intervals, specific for each analyzed volume of wastewater, correspond to the moment when temperature reaches similar values, between 46-48°C, which can be considered the optimum heating interval of the sample.

8.5. The effect of the initial concentration

8.5.1. The effect of the generator air supply pressure, depending on sample heating

In the Figures 8.20 and 8.21 are exposed the decontamination efficiencies, comparatively for the two studied initial concentrations, for singular sonic treatment or for sonic treatment with heating. It can be seen from both graphs that the rate of ammonia degradation, as well as

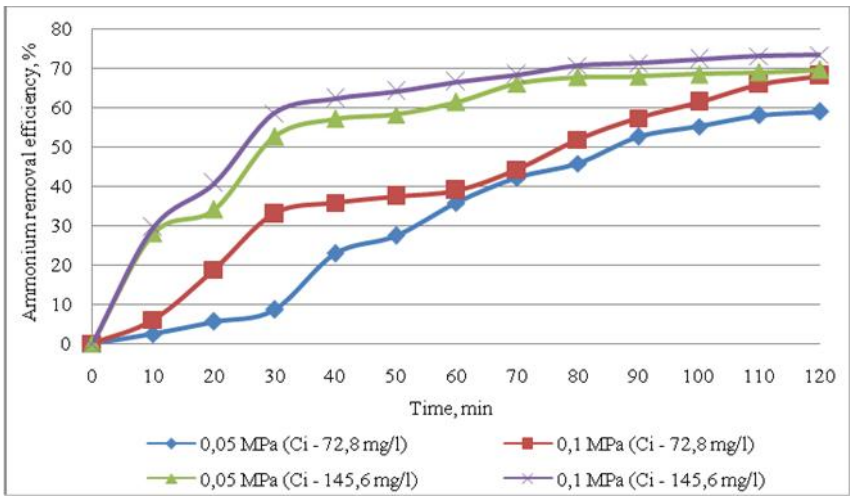

Fig. 8.20. The ammonia removal efficiency, without heating, depending on the air supply pressure and the initial concentration

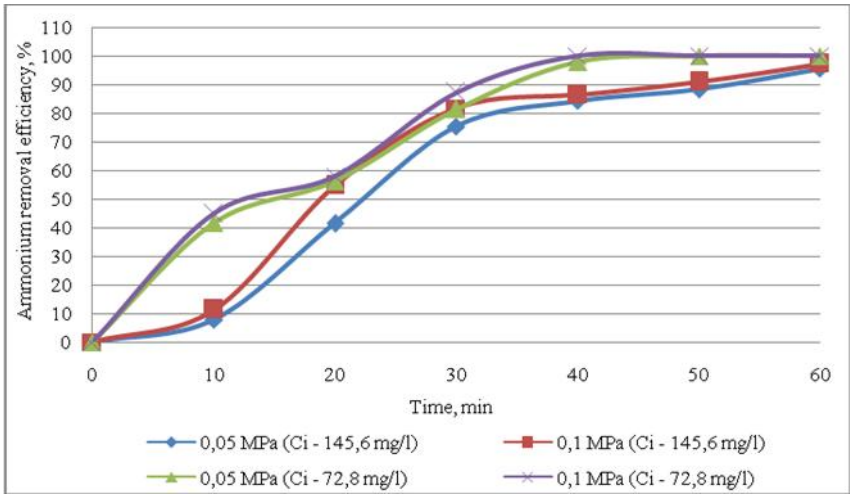

Fig. 8.21. The ammonia removal efficiency, with heating, depending on the air supply pressure and the initial concentration

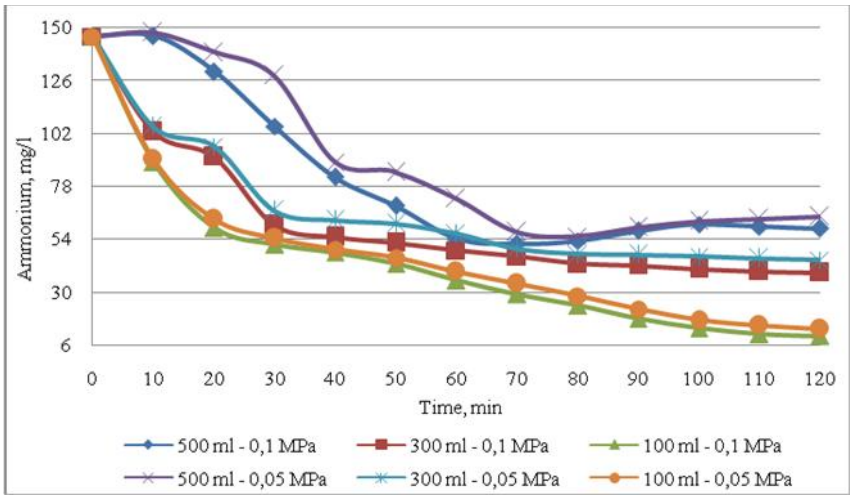

Fig. 8.22. The variation of the ammonia concentration, depending on the air pressure supply and the sample volume, without heating (Ci – 145,6 mg/l)

the reaction yield, are higher when the initial concentration is of 145.6 mg/l. This effect is recorded at the typical temperature of the sonic treatment, 16°C, as well as for the experiments with additional heating.

8.5.2. The effect of the sample volume, depending on sample heating

Without heating, after the 120 minute assigned for the experiment, the final concentration for the pressure with maximum effect, 0.1 MPa, for each sample volume, has the following values: 500 ml - 58.708 mg/l, 300 ml - 38.78 mg/l, 100 ml - 9.92 mg/l (Fig. 8.22).

In the presence of sample heating, the decontamination is complete, but the treatment time varies depending on the sample volume. At a pressure of 0.1 MPa, 80 minutes were required for the 500 ml sample volume, 70 minutes for the treatment of 300 ml of the sample and 40 minutes for the sample volume of 100 ml (Fig. 8.23).

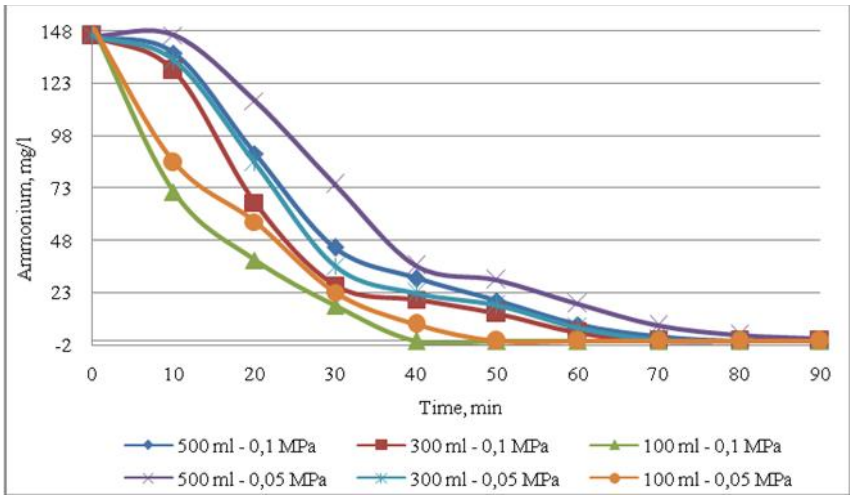

Fig. 8.23. The variation of the ammonia concentration, depending on the air pressure supply and the sample volume, with heating (Ci – 145,6 mg/l)

8.6. Conclusions

In the phase of experimental research realization and interpretation of the results for the sonic technology applied to the ammonia water from industrial processes, the following conclusions resulted:

- The singular sonic treatment performed continuously on the sample volume of 300 ml ammonia water achieved, after 120 minutes, a decontamination efficiency of 59% (29.84 mg/l) for the pressure of 0.05 MPa, and 68% (23.29 mg/l) for the pressure of 0.1 MPa.
- In the presence of heating, for the continuous treatment of a volume of 300 ml ammonia water, for the supply pressure aof the air jet generator, of 0.1 MPa, 40 minutes are sufficient for the complete decontamination of the sample, which corresponds to the temperature of treated solution of 58°C. This type of sonolysis allows the discharge of the treated wastewater directly into natural receivers, after 30 minutes of treatment [3].
- The pressure value of 0.05 MPa, in the presence of heating for the sample of 300 ml, generates the complete removal of ammonia after 50 minutes of sonic treatment, when the sample temperature is of 62°C.
- Regarding the intermittent treatment in the presence of sample heating , the time required for the complete removal of ammonia from the wastewater is extended to 100 minutes regardless of the air supply pressure utilized.
- When the sonic treatment is applied to the ammonia water with the initial concentration of 145.6 mg/l, in the presence of heating, the complete decontamination effectiveness is reached after 70 minutes at the pressure of 0.1 MPa and after 80 minutes at the pressure of 0.05 MPa.

Chapter 9

Exerimental results of sulfide wastewater treatment by ultrasonic technology

9.1. The dynamics of pH values during the sonic treatment of sulfide wastewater

When the sonic treatment was applied to the sulfide wastewater, the pH values were reduced proportionally to the treatment time increase, to the air supply pressure of the sonic air jet generator increase, and to the sample volume decrease. This effect of an acceleratrd reduction in pH during the sonic treatment is beneficial in the process of sulphide wastewater decontamination, as the sulfide oxidation to sulfoxide is favored.

9.2. The effect of the generator air supply pressure on the efficiency of sulfide wastewater decontamination

9.2.1. The effect of treatment time and the optimum time intervals establishment

After several preliminary experiments, the sampling interval for reading the sulfide concentration was established at intervals of 10 minutes. The time needed to perform experiments was determined by the evolution of the decontamination regime, but within 120 minutes.

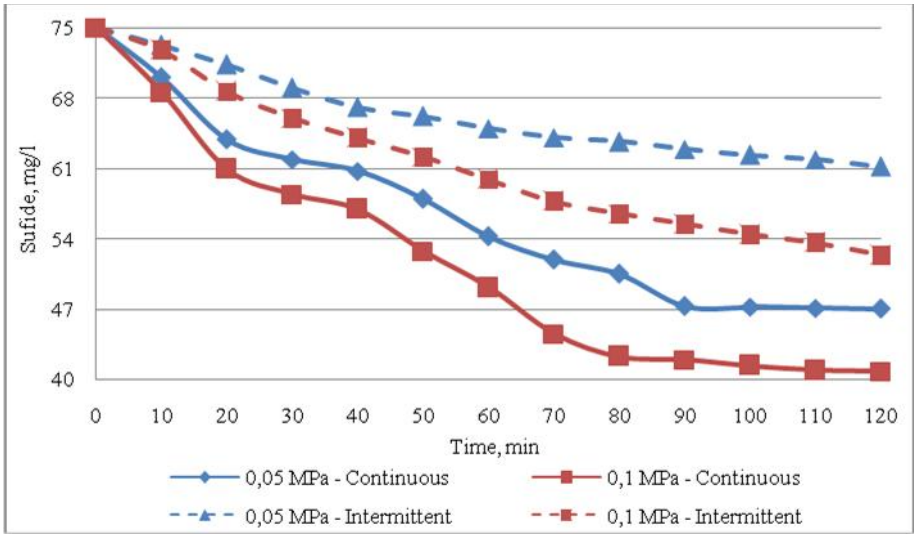

Fig. 9.4. The variation of the sulfide concentration, depending on the air supply pressure and the operating mode

9.2.2. The effect of treatment regime and the optimum regime establishment

As shown in Figure 9.4 (C- 75 mg/l, v- 300 ml, T- 16°C), by applying the sonic treatment continuously, in the first 90 minutes the present sulfides oxidation is constant both due to aeration and OH cavitational radicals, until the concentrations of 47.08 mg/l and 41.97 mg/l for the pressures of 0.05 MPa and 0.1 MPa respectively. The possibility of efficient energy consumption on the sonic treatment application was studied for the sulfide wastewater also. After 120 minutes, the decontamination efficiency is reduced by 20.8% (0.05 MPa), and 15.41% (0.1 MPa), compared to the continuous treatment.

9.3. The effect of the generator air supply pressure on the efficiency of sulfide wastewater decontamination, in the presence of sample heating

9.3.1. The effect of treatment time and the optimum time intervals establishment

Due to the known volatility characteristics of the inorganic sulfides present in water, the treatment in the presence of the sample heating compared to the treatment at the constant temperature of 16°C (specific to the sonic technology), generated the reduction of the necessary treatment time.

9.3.2. The effect of treatment regime and the optimum regime establishment

The evolution of the sulfide concentration by the application of sample heating is shown in Figures 9.6 and 9.7, for sonic treatment under continuous or intermittent operation.

Raising the temperature to 62°C at the supply pressure of 0.05 MPa, and to 60°C at the supply pressure of 0.1 MPa, produces in the case of continuous sonic treatment an increase of the decontamination efficiency, compared to the treatment without heating. During 90 minutes, the reaction yield increases in the presence of heating by 20.33% (0.05 MPa) and 20.02% (0.1 MPa), compared to the results of the sonolysis in the absence of heating.

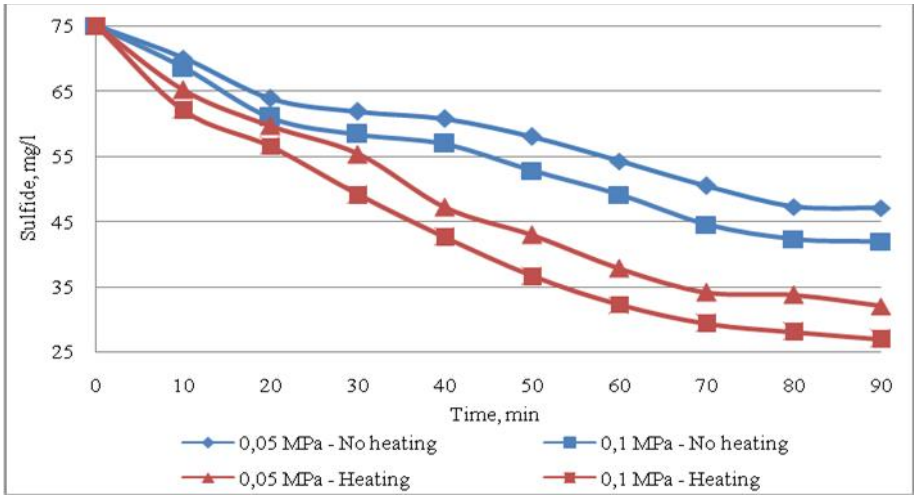

Fig. 9.6. The variation of the sulfide concentration, in continuous mode, depending on the air supply pressure and the sample heating regime

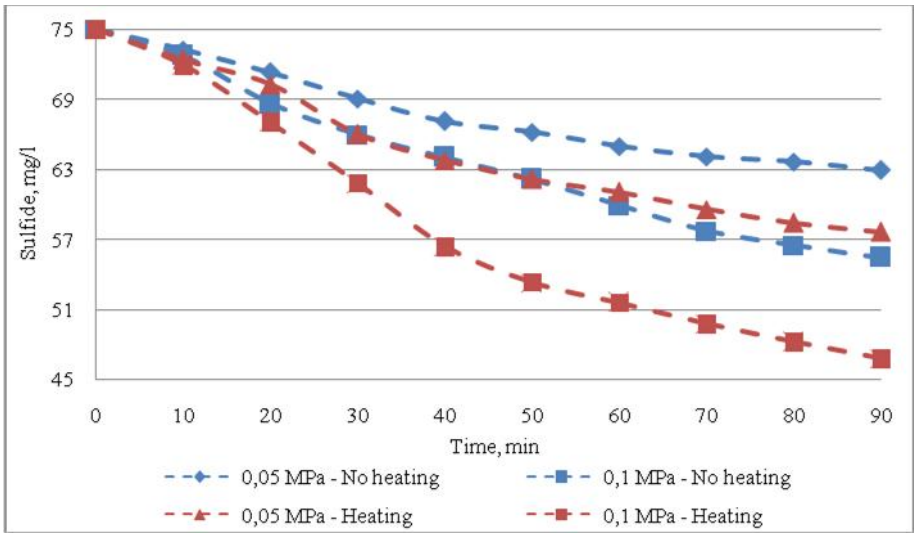

Fig. 9.7. The variation of the sulfide concentration, in intermittent mode, depending on the air supply pressure and the sample heating regime

For the intermittent sonic treatment, the decontamination efficiency is significantly reduced, values of 23.18% and 37.64% to the supply pressures of 0.05 MPa and 0.1 MPa respectively, being recorded after 90 minutes. The break periods during the functioning of the sonic air jet generator, imply the interruption of the acoustic parameters effect, of intensity and frequency, that are responsible for the production of the cavitational events and of the oxidizing free radicals.

9.4. The effect of the sample volume

9.4.1. The sulfide wastewater sample volume of 500 ml

Corresponding to the volume of 500 ml, for both the supply air pressures of the sonic generator, a more rapid decrease of the concentration was observed in the first 40 minutes, up to values of 66.21 mg/l for 0, 05 MPa and 61.37 mg/l for 0.1 MPa.

In the next time interval, the sample degassing process intervenes and thus the reduction of the reaction rate. If the studied wastewater sample is sonicated with heating, an extension of the time interval in which the sulfide removal yield is accelerated, to 60 minutes, is noted.

9.4.2. The sulfide wastewater sample volume of 100 ml

For the volume of 100 ml, a decrease of the concentration until the final values of 25.06 mg/l for 0.05 MPa and 19.86 mg/l for 0.1 MPa is recorded after 120 minutes. The sample heating, which is up to 72°C (0.05 MPa) and 70°C (0.1 MPa) within 30 minutes, make the volume of 100 ml to obtain the highest degree of sulfide removal, to the values of 11.94 mg/l and 8.02 mg/l, after 90 minutes.

In the Figures 9.12 and 9.13 is shown a comparative evolution of the sulfide concentration based on the sample volume, for each of the studied supply air pressures. The results contained in the two graphs were obtained for the continuous operation of the sonic gasodynamic generator while heating the sample. These conditions for carrying out the

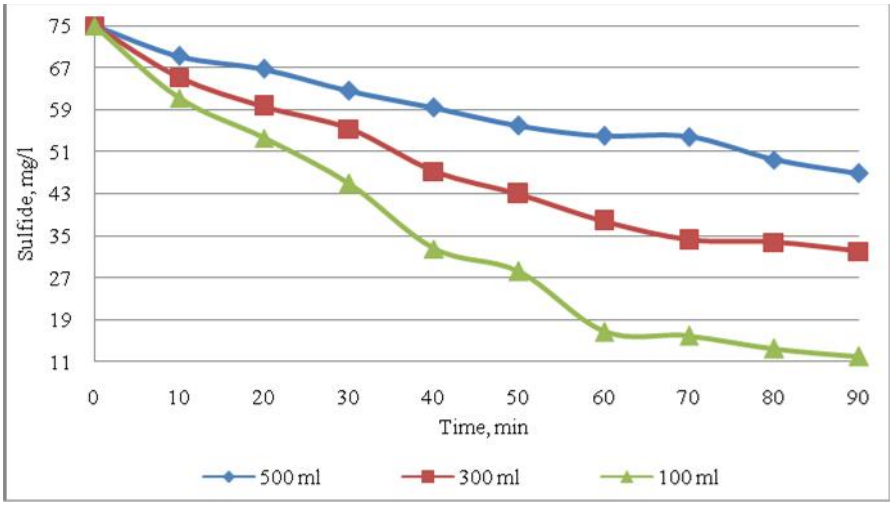

Fig. 9.12. The variation of the sulfide concentration depending on the sample volume, with heating, at the air supply pressure of 0,05 MPa

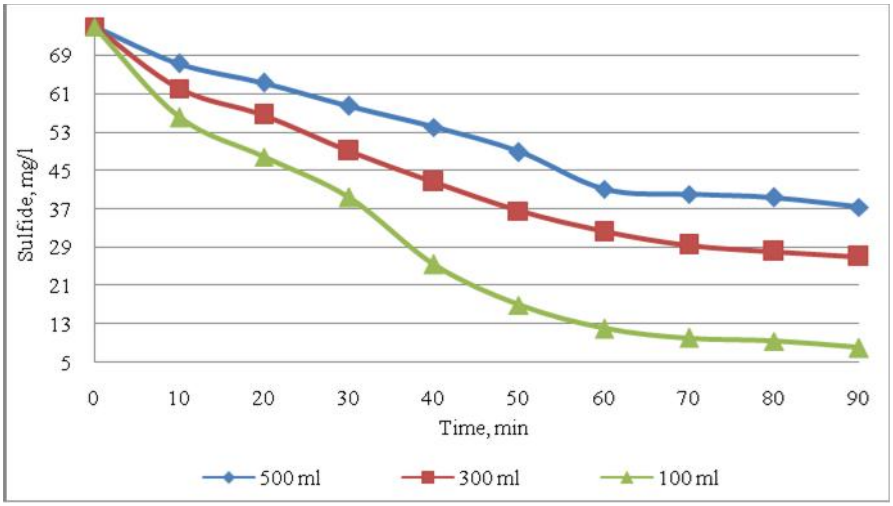

Fig. 9.13. The variation of the sulfide concentration depending on the sample volume, with heating, at the air supply pressure of 0,1 MPa

experiments indicated a higher decontamination efficiency of the sulfide wastewater, by reducing the amount of wastewater.

9.5. The effect of the initial concentration

9.5.1. The effect of the generator air supply pressure, depending on sample heating

Compared to the wastewater with lower initial concentration, of 75 mg/l, the decontamination efficiency varies for the initial concentration of 120 mg/l, as in Figure 9.15, in the case of the sonic treatment without heating, and as in Figure 9.16 in the case of sonic treatment with heating. According to these graphs, the oxidation reaction yield of the present sulfides in the wastewater, decreases with increasing the solution concentration.

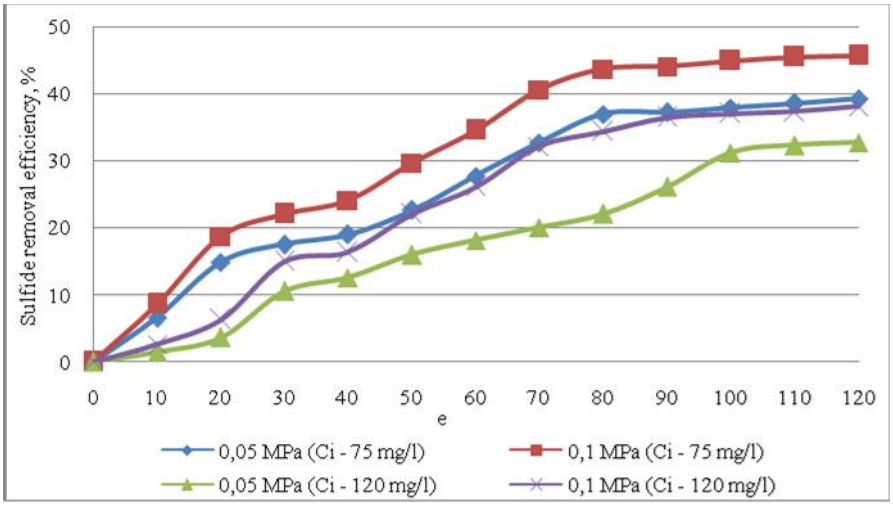

Fig. 9.15. The sulfide removal efficiency, without heating, depending on the air supply pressure and the initial concentration

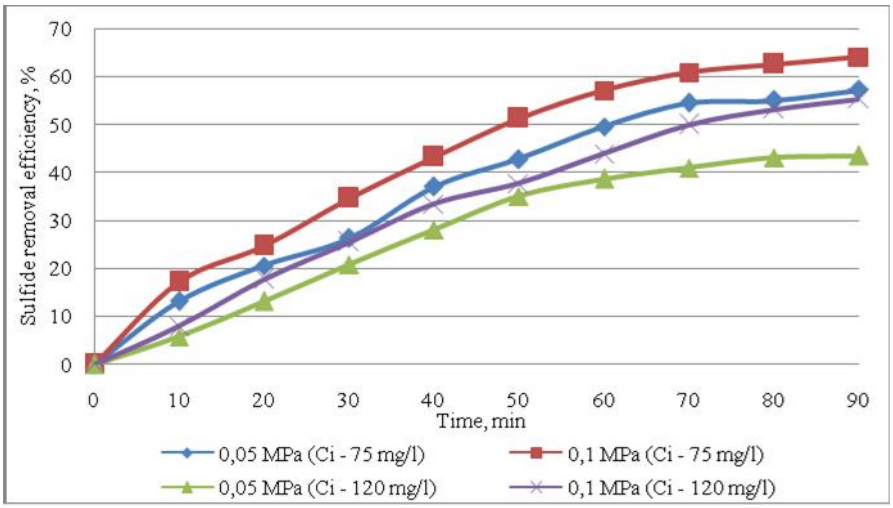

Fig. 9.16. The sulfide removal efficiency, with heating, depending on the air supply pressure and the initial concentration

In the presence of sample heating, after 90 minutes and by maintaining the temperature of 60°C, the sulfide oxidation is carried out by 55.28% efficiency for the initial concentration of 120 mg/l.

9.5.2. The effect of the sample volume, depending on the sample heating

The reaction rate increases proportionally to the sample volume reduction for the both supply air pressures of the sonic generator (0.05 MPa and 0.1 MPa). Therefore, the highest decontamination efficiency is achieved for the sonic treatment of the volume of 100 ml, at a pressure of 0.1 MPa.

However, without heating, after two hours of treatment, the sulphide concentration decreases to the value of 44.38 mg/l, which is not within the permissible values for discharge to natural receptors or public sewerage systems [3]. However, this value represents a

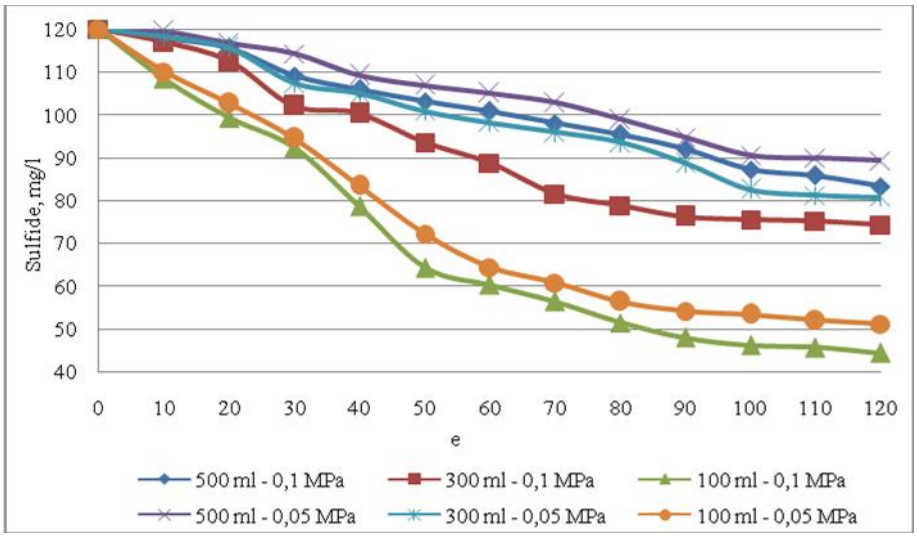

Fig. 9.17. The variation of the sulfide concentration, depending on the air pressure supply and the sample volume, without heating (C_i – 120 mg/l)

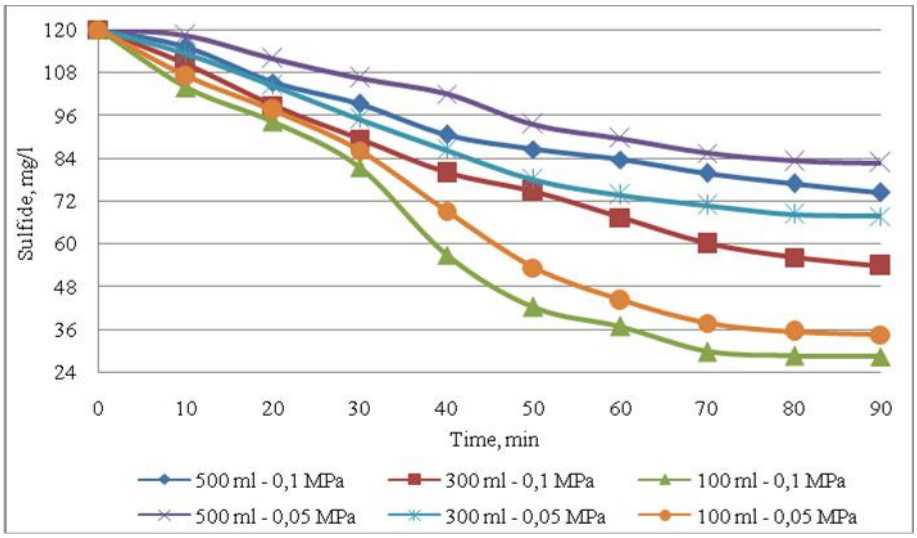

Fig. 9.18. The variation of the sulfide concentration, depending on the air pressure supply and the sample volume, with heating (C_i – 120 mg/l)

considerable reduction of sulfide, which during the experiment of 2 hours showed a reduction of 63.016% from the initial concentration of 120 mg/l (Fig. 9.17).

The reaction rate is higher as the temperature rises, so that after 90 minutes, the decontamination efficiencies for each sample volume for the air pressure of 0.1 MPa are: 38.04% (74.35 mg/l) for the volume of 500 ml, 55.28% (53.66 mg/l) for the volume of 300 ml and 76.47% (28.23 mg l) for the volume of 100 ml, as shown in Figure 9.18.

9.6. Conclusions

In the phase of experimental research realization and results interpretation of the application of the technology sonic to treat sulfide wastewater contaminated similarly to the wastewater

from industrial processes, the following conclusions resulted:

- The sonic treatment performed at the constant temperature, of 16°C, (C - 75 mg /l, V - 300 ml), generates a constant oxidation of the sulfides present in the studied wastewater, during the first 90 minutes, both by aeration and the OH cavitation radicals, up to the concentration of 47.08 mg/l and 41.97 mg/l, for the pressures of 0.05 MPa and 0.1 MPa.
- The reduction of the sulfide content by the intermittent treatment of a 300 ml volume of wastewater of 75 mg/l initial concentration, within 120 minutes, was of 20.8% at a pressure of 0.05 MPa and of 15.41% at pressure of 0.1 MPa.
- Raising the temperature to 62°C at a supply pressure of 0.05 MPa, and to 60°C at a supply pressure of 0.1 MPa, in continuous operation of sonic treatment, over the course of 90 minutes, produces an increase of the reaction yield in the presence of heating of 20.33%, and 20.02% respectively, compared to the results in the absence of heating, obtained by the same treatment time.
- The break periods during the air jet sonic generator functioning, imply the interruption of the acoustic parameters effect, of intensity and frequency, responsible for the production of the cavitation events and of the free radicals with oxidizing character. Also, the periodic stop of the sample aeration and oxygenation through the supplying air of the generator, leads to a decrease of the present sulfides removal degree.
- For the sonic treatment applied to the sulfide wastewater with initial concentration of 120 mg/l, a time interval for the removal of a certain amount of excess sulfide is necessary. The amount of hydroxyl radicals produced by the sonic generator operation is specific to each supply pressure used, and also it is constant for each experimental repetition. So as, in the case of a higher density of sulfide in solution, the oxidation process is carried out in a more extended period of time.

Chapter 10

General conclusions, original contributions and perspectives

10.1. General conclusions

Summing up the aproched issues and the conclusions of the documentation research, the directions of the thesis were oriented to the design and development of two experimental facilities based on sonic or ultrasonic technology, for the decontamination of wastewaters and technological liquids.

The contaminated waters which were the subject of this study are the industrial ammonia water and the sulfide wastewater simulated in the laboratory. The choise to study ammonia and sulfides as water contaminants, is based on their origin in the most modern technological processes. These compounds are responsible for decomposition processes and eutrophication and thus the destruction of aquatic flora and fauna, once in surface waters.

The acoustic irradiation is a process of advanced oxidation which has proven to be effective in removing some drawbacks of the conventional methods for treating the wastewater from industrial processes, such as the strict control of pH and temperature, the addition of chemicals, the regeneration of the materials. the high energy consumption, the long treatment time, etc.

When ultrasound is introduced into a liquid medium, it creates oscillating regions through cycles of attraction and rarefaction between the molecules. The alternation of these cycles generate the appearance of cavities in the liquid in the form of micro bubbles that, by the ultrasonic waves absorbtion, increase their volume and implode. The collapse of the microbubbles in the irradiated liquid is called acoustic cavitation and is one of the main oxidation processes. This phenomenon generates a large amount of energy released in microseconds and is involved in many beneficial effects on many technological processes.

The effects of cavitation are both physical (shock waves, microjets, turbulence, shear forces) and chemical, by the appearance of free hydroxyl radicals, which are highly reactive. At the same time, the acoustic frequency waves generated by the pyrolytic reactions, leads to extremely high pressures and temperatures within the cavitation bubbles formed during the treatment by ultrasound.

The use of ultrasound is an area that has deepened in various fields, including the wastewater cleaning processes. The usual ultrasonic emitters are electromechanical based, particularly those relying on the convertion of the electric energy into mechanical energy by a piezoelectric material. However, the literature is very limited in terms of singular applications of electromechanical generators (in the absence of numerous chemical reagents), regarding the toxic compounds covered by this study, especially on waters with high sulfur content.

Therefore, one of the proposed facilities, designed and built to treat wastewater without further addition of chemical reagents or oxidants, was the experimental facility with

piezoelectric generator that works in ultrasonic field of fixed frequency (30 kHz). This pilot plant operated by the ultrasonic generator, uses the electric energy, converted into electromechanical energy in the form of oscillation of the piezoelectric crystal. The electromechanical energy becomes ultrasonic energy and generates stationary acoustic waves, in nonresonant regime. The experimental tests were conducted for the variations of several parameters, namely acoustic parameters (ultrasonic intensities of 90 W/cm^2 and 460 W/cm^2), geometric parameters (sample volumes of 50 ml, 100 ml, 300 ml and 500 ml; different heights and diameters of the liquid in the treatment vessel) and functional parameters (variations in operating regime (continuous or intermittent), variations of the sample heating regime, variations in the initial concentration of the pollutant, etc.).

The main innovative element of this study is the design and realization of the sonic gasodynamic stem-generator, together with the regretted Prof. Dr. Eng. George Balan. The calibration of the air jet generator can be performed depending on the supply air pressure, by means of a software and a sound analysis system.

It has been found that the maximal values of the acoustic parameters do not exceed the sonic domain (<20 kHz) and they are reached for the distance between nozzle-resonator Δ_R = 1.2 mm, for the both values of the air supply pressure, namely:

- the pressure of of 0.05 MPa, for which the acoustic frequency is of 18.25 kHz and the dound intensity level is of 102.4 dB (acoustic intensity of 0.017 W/m^2);

- the pressure of of 0.1 MPa, for which the acoustic frequency is of 19.16 kHz and the dound intensity level is of 107.1 dB (acoustic intensity of 0.0512 W/m^2);

On the bases of the air-jet generator a sonic treatment plant for water and technological liquids was designed and built practically and the operating conditions for which the effect of applying the sonic technology is maximum were determined. The experimental installation operated by sonic air jet generator uses the mechanical energy to produce acoustic vibrations. The supersonic jet of gas is transmitted by the mechanical generator, loses its stability and emits shock waves of high frequency (unsteady), after the interaction with a resonant cavity.

The mechanism of instability of the detached shock wave is due to the interference of the acoustic waves through the participation in the self-oscillation process of the both jets (the primary jet from the nozzle and the secondary jet from the resonator). Similar to the treatment in the ultrasonic field by the piezoelectric generator, the experimental tests by the sonic technology were also carried out based on the acoustic, geometric and functional parameters.

In the following, a summary of the results for each type of wastewater under study, for both sonic and ultrasonic technology, is exposed.

- Some effluents containing ammonia or sulfide, leave the generating process already having high temperatures between 35-45°C [311], which benefits the sonic/ultrasonic technology application, immediately after the effluent disposal, the decontamination efficiency being improved when wastewater temperature is higher.
- The obtained results show that, regardless the type of radiation (sonic and ultrasonic), it is not required an increase in the acoustic sound level, in all the conditions of wastewater treatment, in order to get a better effect. In the case of the ultrasonic treatment, the effectiveness was higher at lower ultrasonic intensity (90

W/cm^2), due to the higher irradiating surface of the acoustic probe and to the higher thermal energy specific to the MS 10 sonotrode.

- However, in the case of the sonic treatment, which typically involves substantially lower acoustic intensities compared to the ultrasonic irradiation, the efficiency of ammonia and sulfides removal from water was higher at the higher supply air pressure (0.1 MPa), which involves the higher acoustic intensity (0.0512 W/m^2) from the two studied for the sonic treatment. This result was due to more intense bubbling of the samples, as well as to the greater amount of air bubbles introduced into the wastewater having the additional role of cavitation nuclei and of accelerated degassing of the solutions.
- Also, it is noted that the use of very high frequencies is not necessary. Comparing the decontamination efficiencies of the ultrasonic technology towards the sonic technology, it can be concluded that for the low frequency domain specific to the sonic irradiation (<20 kHz), the studied pollutants removal is better for all the sample volumes. The ammonia and sulfide extraction are not due to ultrasound, but is the result of cavitation. Cavitational events cause the degassing of wastewater, process accentuated by bubbling.
- The low frequency waves (the sonic technology) produce cavitation bubbles in a small number but large in size, resulting after the collapse in powerful energy and intensity. On the other hand, high frequency waves (the ultrasonic technology) can generate more cavitation bubbles with smaller size and lower power at the time of implosion.

10.2. Original contributions

The realization of the thesis entitled "Research on the use of sonic generators for the extraction of hazardous substances from wastewaters and technological liquids", was made possible by the personal contributions of the author, of which the most important are:

- The realization of the literature study on the conventional or innovative technologies currently used to decontaminate ammonia wastewaters and sulfide wastewaters, and the analysis of the operating parameters and of the decontamination efficiency of these technologies;
- The realization of the literature study on the action of ultrasound on the liquid media, namely on the effect of the cavitation collapse which materializes by phenomena such as the reactive free radicals generation as well as the pyrolysis generation by hot-spot nuclei, both involved in the degradation of pollutants;
- The realization of the literature study on the research conducted with ultrasonic emitters dedicated to industrial wastewater decontamination and on the influence of the frequency (acoustic or ultrasonic) on the process of pollutants elimination; from this study, the objectives and directions of this thesis research resulted and the facility by sonic gasodynamic generator was proposed;
- The achievements of the tests to determine the sound intensity level and the frequency depending on the supply air pressure of the acoustic generator, using the 01dB SOLO-Metravib sonometer, which performe acoustic measurements in accordance with the noise emission standard EN ISO 3744/2009;

- The practical realization of the experimental system based on the ultrasonic technology, equipped with the electromechanical piezoelectric ultrasonic emitter UP100H (Hielscher Ultrasonics GmbH, Teltow, Germany) to determine the decontamination of the studied wastewater. The test realized with the experimental facility by ultrasonic generator were made inside the Laboratory of Polymer Composites, from "Dunarea de Jos" University of Galati;
- The practical realization of the pilot plant based on the sonic technology, equipped with a mechanical air-jet esmitter, to determine the decontamination of the studied wastewater. The test realized by the experimental sonic generator plant were conducted in the Laboratory of Chemistry of the Faculty of Engineering and Agronomy from Braila and in the Laboratory of chemical analysis from SC Setcar SA company;
- Conducting tests to determine the ultrasonic intensity effect on the decontamination of ammonia or sulfide wastewater;
- Conducting the experiments to determine the effect of the operating mode, continuous or intermittent, of the plant equipped with the electromechanical generator and determining the optimum regime;
- Conducting tests to determine the effect of the aeration to the wastewater samples under study, during the ultrasonic treatment by the installation equipped with the electromechanical generator and establishing the optimum regime;
- Carrying out tests to determine the effect of heating the samples of wastewater during the ultrasonic treatments and determining the optimum regime;
- Conducting the experiments to determine the effect of the sample volume on the yield of the oxidation reaction of the studied contaminant compounds, during the ultrasonic treatments;
- Conducting experiments to determine the effect the diameter and the height occupied by the ammonia or sulfide wastewater sample into the working vessel during the ultrasonic treatment;
- Carrying out tests for determining the influence of the initial concentration of pollutant on the decontamination regime of the sulfide or ammonia wastewater samples, during the ultrasonic treatment;
- Conducting tests to determine the effect of the supply air pressure of the mechanical sonic generator and of the frequency and acoustic intensity on the decontamination of the ammonia or sulfide wastewater;
- Conducting experiments to determine the effect of the operating mode, continuous or intermittent, of the installation equipped with mechanical gasodynamic generator and determining the optimum regime;
- Conducting tests to determine the effect of implicit bubbling that occurs during the treatments performed by the sonic installation equipped with the mechanical gasodynamic generator and determining the optimum regime;
- Carrying out tests to determine the effect of heating the wastewater samples during the sonic treatments and determining the optimum regime;
- Conducting experiments to determine the effect of sample volume on the yield of the oxidation reaction to the studied contaminants, during the sonic treatments;

- Conducting the experiments to determine the effect of the diameter and of the height occupied by the ammonia or sulfide wastewater sample in the working vessel, during the sonic treatments;
- Carrying out tests for determining the influence of the pollutant initial concentration on the decontamination of sulfide or ammonia wastewater samples, during the sonic treatments;
- Interpretation of the obtained results from the performed experimental measurements.

10.3. Perspectives

By the obligation of the contemporary society to maintain adequate quality of the water discharged from industrial processes into the natural watercourses, and after following the elaboration of this research, the PhD student is considering a range of perspectives of the thesis:

- Optimizing the utilized experimental equipment, so it is possible to capture and recover the ammonia and the sulfides removed, which become a new source of pollution once released into the atmosphere;
- The ammonia extraction into an acid in order to obtain specific compounds with further uses, such as ammonium sulfate or ammonium nitrate, fertilizers known for use in the agricultural industry.
- Assessment of the treatment effectiveness for the proposed sonic gasodynamic generator, on different types of residual wastewater, contaminated with other inorganic or organic compounds.

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