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CHEMICAL SONOREACTORS IN ENVIRONMENTAL APPLICATIONS

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Abstract

Ultrasounds has a wide range of active applications spreading in solid, liquid and gaseous mediums, embedded in new methods and technologies for preventing, reducing and removing of existing pollution.
This paper deals with the sonochemistry reactors and their combinations with photocatalysis and electrochemistry. Various parameters such as ultrasound frequency, power, number of ultrasound sources, lab-scale or large-scale equipment used for environmental applications of sonochemical reactors have been analysed using examples available in the literature.

Key words: sonoelectrochemistry, sonochemistry, sonoreactors, ultrasounds

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1. Introduction

Nowadays, physical, chemical and biological methods are used to remove contaminants from water or wastewater. The scientific literature comprises many articles and review papers about sonochemistry. The majority of sonochemical systems use piezoelectric ultrasonic transducers which convert electricity in ultrasounds (Iordache and Iordache, 2009). In general, most studies on environmental sonochemistry adopted the "hot spot" model to explain experimental results, because sonochemical reactions are heterogeneous processes that occur due to heat and reactive species formed. The hot spot represents a "microreactor" which encompasses: ultrasonic cavity, gas-liquid interface and liquid in the vicinity of the interface (Serpone and Colarusso, 1994).

Most sonochemical reactions result in formation of H• and OH• by thermal dissociation of water vapour present in the ultrasonic cavitation, ultrasonic irradiation producing water and hydrogen peroxide through hydroxyl radicals and hydrogen atoms. Based on the study of Gogate and Pandit (2004), the magnitudes of collapse pressure and temperature as well as the number of free radicals generated at the end of cavitation events are strongly dependent by the equipment operating parameters.

The present article does not insist about topics already covered, like methods for activity predictions of ultrasonic steam described or reviewed by others authors (Merouani et al., 2015; Tudela et al., 2014). There are numerous studies which indicate the various ways to manipulate cavitating conditions for maxim effect. A brief summary for sonochemical reactors operating conditions are presented in Table 1.

The primary reaction intermediates characteristics have a key role in efficiency determination of the hybrid process and can provide insight into the synergism observed within the process coupling. The performance predicting requires information and knowledge of the chemical and physical properties of the reactants, major intermediates, and their degradation susceptibility.

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Table 1. Optimum operating conditions for chemical sonoreactors

No.	***Property***	***Effect***	***Favorable conditions***
1	Irradiation intensity ($1\times10^4\div300\times10^4$ W m^{-2})	Number of cavities, single cavity collapse pressure	Use power dissipation until achieve optimum values over a wide area of irradiation
2	Irradiation frequency ($20\times10^3\div200\times10^3$ Hz)	Collapse time of the cavity as well as final pressure/temperature pulse	Regular frequency range to gain an optimum value; the latest researches indicate raised values for specific effects
3	Liquid vapor pressure (40÷100 mm of Hg at 30°C)	Cavitations threshold, intensity of cavitations, rate of chemical reactions	Liquids with low vapor pressures
4	Viscosity ($1\times10^{-3}\div6\times10^{-3}$ Pa s)	Transient threshold	Low viscosity
5	Surface tension (0.03÷0.072 N m^{-1})	Size of nuclei, cavitations threshold	Low surface tension
6	Bulk liquid temperature (30÷70°C)	Intensity of collapse, rate of reaction, nucleation, physical conditions	Optimum value exists, generally lower temperatures
7	Dissolved gas		
	- solubility	Gas content, nucleation, collapse phase	Low solubility
	- polytropic constant and thermal conductivity	Intensity of cavitation events	Gases with higher polytropic constant and lower thermal conductivity, monatomic gases

There are some theoretical and mathematical approaches involving mainly liquid-phase chemistry to explain oxidation chemistry of the coupled sources (Destaillats, 2000; Weavers and Hoffmann, 1998). Many experiments and work are focused on understanding the advantages of these coupled or hybrid systems. These past, present, as well as future investigations need to find the degradation kinetics, from initial attack up to total mineralization. The complex models, which include cavitation dynamics and basic chemical and physical principles with the adequate kinetics forms of each individual processes are need for exploration and prediction of the hybrid processes under various assumed circumstances. The models for the hybrid systems will allow the determination of optimal operating regions in the terms of chemical and physical parameters and efficiency for given effluent characteristics and appropriate practical limits (Adewuyi, 2001).

Any individual AOP is limited by slow rate, oxidative potential, or possibility to generate harmful by products. When degradation rates are enhanced, reaction time is reduced which imply a lot of technical advantages: dimension of reactor or installation, numbers of cycles of productions, decreasing of the contaminant concentrations etc. Consequently, the technology costs and its application from laboratory to industry are significantly reduced. In ultrasound irradiation used for hazardous waste treatment on an industrial scale, the associated reaction can be ecologically acceptable. The mineralization of the organic contaminants should be a goal to minimize the survival time of toxic intermediates (Sharma et al., 2016). Generally speaking, economic and technological limitations of processes should be considered in the design stages for a more effective and economical system. Effective treatment of difficult-to-degrade contaminants from wastewater may require a combination of ultrasound irradiation with other available processes, in such a way as to exploit their individual strengths and reduce substantially the treatment costs over a single step process. The global efficiency of the combined processes is a key performance measure of sonochemical systems. Future work is necessary to understand the global efficiency of the appropriate and complementary hybrid ultrasound processes for a given ultimate treatment goal.

The synergism of different ultrasound irradiation hybrid methods is mainly determined by similar or identical controlling reaction mechanism, e.g. the free radicals attack. The combination of two or more advanced oxidation processes leads to an enhanced generation of the hydroxyl radicals and eventually results in higher oxidation rates. The increase efficacy and the extent of synergism depend also on the alteration of the sonochemical reactor conditions and configuration that lead to a better contact of free radicals and substrates (pollutants). The transmission of ultrasound waves in bulk of liquid, mass enhances the turbulences and decreases the mass transfer resistance, which is a major limiting factor in advanced oxidation processes, e.g. ozone, hydrogen peroxide.

There also exists an optimum concentration of oxidant compounds, e.g. ozone, hydrogen peroxide; beyond the combination of ultrasound with oxidation processes. For an adequate treatment it is necessary to establish the optimum quantity of oxidizing agent through adapted laboratory studies for each particular situation (Gogate, 2002). The presence of radical scavengers severely hampers the rates of combination techniques. Pretreatments in terms of pH control or active carbon adsorption, adjust the concentration of these scavengers below an acceptable value.

The most common problem associated with hybrid photocatalytic method is photo catalysts efficiency decrease due to contaminants adsorption at the surface, thus blocking the UV active sites. Other associated problem with photocatalytic processes is severe mass transfer limitations. When these two modes of irradiation are operated together aforementioned problems are minimized and more free radicals are available for the reaction with pollutants. The expected synergism between these two processes can be attributed to: acoustic micro-streaming catalysts surface clean, increased compounds mass transport at the catalyst surface end in the solution, increased catalyst surface area by fragmentation or pitting, pollutant substrates which react directly with the photo-generated surface holes and electrons under cavitating conditions, and other chemical and physical effects associated with the ultrasound cavitation phenomena.

Few important factors should be considered while designing the optimum sonophotocatalytic reactor (Toma et al., 2001): simultaneous irradiation; stability of photocatalyst in terms of shape, size, structure, etc.; reactors design, direct or indirect UV irradiation does not affect the expected synergism, but the geometry, volume, number of irradiante sources, wave length, flow and circulation of mass and uniform irradiation must be considered; the manner of gas bubbling and their presence; the effect of pH on the rate of degradation depends on the state of pollutant molecule; and presence of other oxidant agents, e.g. Fenton, hydrogen peroxide, etc. The presence of hydrogen peroxide or ozone increases the extent of destruction with the stability of photocatalyst playing a major factor in controlling the overall efficiency of destruction. The development of large scale sono-photo reactors appears to be a daunting task as the literature studies are typically restricted to few millilitres and no more than one litter. The development of these types of reactors should be based on multiple transducers and frequencies as well as excellent distribution of UV light (Gogate and Pandit, 2003).

The wet air oxidation is another method used in treating various wastewaters. Sonication followed by wet air oxidation (SONIWO) has been developed for achieving degradation with increasing efficiency. In this hybrid process, sonication is used to convert bigger complex molecules into smaller ones. The chemical oxygen demand (COD) degreases to the lowest acceptable values. A critical analysis of this technique denotes following important considerations: the SONIWO is more beneficial as compared with individual wet air oxidation, presence of catalysts ($CuSO_4$, $NiSO_4$) improve hybrid process, compounds like phenol in small amounts enhances the rate of generation of free radicals, pH play a critical role and addition of acidic agents increase the efficiency, and use of ultrasound irradiation as a pre-treatment stage appears to be an excellent option for wet air oxidation as reported in lab-scale experiments (Ingale and Mahajani, 1995, 2000).

In order to scale-up a sonochemical reactor, studies and tests done in the past must be considered to determine which measures of reactor efficiency best correlate with pollutant destruction rates. The work must also consider optimal combinative systems and hybrid sonochemical reactors taking into account the parameters which influence the efficiency of coupled technologies.

As an example, the lowering of temperature and pressures imply reduction of investment and operating costs (heat exchangers, materials, pumps, energy, preheating or cooling, etc.). The observed result for ultrasonic irradiation at high pressures (5-25 MPa) is close to oxidation without acoustical treatment, and no cavitation effect was observed. However, medium pressure is closer or higher than amplitude pressure of sound wave. An important tool for success sonochemical reactors and installations is the advanced modelling of combinative or hybrid processes such as the coupling of advanced oxidation reactions and kinetics with bubble dynamics, determination of optimal operation regions in the terms of chemical and physical parameters, and design and development of sonochemical reactors.

In order to introduce ultrasounds in a system is necessary to use instrumentation or installation with specific configurations named sonochemical reactors and usually for waste water treatment can have special and complex designs for ultrasonic bath and horn. A significant amount of work has been published concerning the sonochemical effects on both organic and inorganic chemical reactions. The ultrasound irradiation effects in chemical reactions are: (a) reaction initiate, (b) reaction rate acceleration, (c) reaction pathway changes, and (d) little or no effect. The majority effects are included in (b) category.

The classification of sonoreactors (Table 2) depends on many comparison elements such as functions, design, utilizations, etc. On basis of scale application, they can be the laboratory chemical and electrochemical sonoreactors and industrial ones. The field of utilization includes water treatment, emulsions, washing, atomization, extraction, mixture or bonding processes, etc. Ultrasound bath can have one or multiple ultrasound sources, which can produce the same or different frequencies. The wastewater treatment systems can work in continuous or discontinuous ways, and can be coupled with other processes such as electrochemical, UV irradiation, O_3, and Fenton reactions. The irradiation can be direct or indirect.

The sonoreactors used for bonding or welding composite materials were widely spread in recent years. This process is based on ultrasonic wave propagation effects in the joint area, acoustic cavitation related phenomena, the caloric effect of the movement of the two surfaces relative to the ultrasonic frequency and the effect of chemical polymerization in contact area and can be applied to obtain the bipolar fuel cell plates. Today almost chemical and electrochemical sonoreactors use piezoelectric ultrasonic transducers that can convert electricity in sound with high frequency, but sometimes ultrasound can be emitted by mechanical devices (Galton’s pipe and sirens) or by magnetostrictive transducers, also.

2. Design

2.1. Ultrasonic bath and horn

This section presents the utilization of ultrasound baths and horns in the field of chemistry focusing on wastewater treatment and also are being utilized in any kind of research and are commercial available and adjusted or configured for any type of research experiment.

First applications of ultrasonic bath were more physical rather than chemical specifically for cleaning or washing processes. After this "physical" stage, a new step was developed when many researchers used ultrasonic bath in processes that implied sonochemical reactions. Wastewater treatment is one of the most citied applications.

Main component parts of an ultrasonic bath are: vat, ultrasound sources, electronic part and enclosure. In order to understand what is happening in a sonochemical reactor, it is useful to discuss the ultrasonic fountain. This phenomenon describes the mass flow into the reactor environment during ultrasound irradiation, and the literature describes the manner in which can be observed this flow (Gondrexon et al., 1998). When the ultrasound transducer is activated, the directive acoustic streaming is responsible for the fountain effect observed at the liquid-air interface. That fountain effect is usually observed in high frequency systems where the transducer/emitter is at the bottom of the reactor/vessel. It also creates strong convection currents in the liquid volume which can be visualized by using slowly soluble dyes or small suspended particles. The fluid moving along the transducer axis hits the upper free surface and returns via the side of the bath. In this manner, visual studies for experimental velocity values on the transducer axis ranging from 0.01-0.03 m s-1 and limited input power of the transducer can be realized. This traced method is named in literature as residence time distribution (RTD).

The ultrasound baths and horns are the main components of sonochemical experimental installation. Many experiments for wastewater treatment were and are realized in simple experimental installation with any specialized ultrasonic device. After numerous theoretical and experimental progresses, researchers start to develop special sonochemical reactors for customized applications. It must be taken into account, that despite of the many progresses in the field of sonochemistry, traditionally ultrasound baths and horns will also play a significant role in the field of the experimental wastewater sonochemical treatment and sonochemical reactors scale up (Yasui et al., 2004, 2005).

Table 2. Classification of chemical and electrochemical sonoreactors based on the given criteria

No.	***Criteria***	***Type of sonoreactors***	***Usefully mentions, comments***
1.a.	Dimension	Laboratory	Small capacity
1.b.		Industrial	Big capacity and/or high power
2.a.	Functions of reactor	Continuous	Reaction mass flow (wastewater) is fed in and discharged from reactor into a continuous or discontinuous manner.
2.b.		Discontinuous	
3.a.	Sources of ultrasound	Single source	
3.b.		Multiple source	Ultrasound is emitted at the same frequency.
			Ultrasound emitted by different transducers can have different frequencies.
4.a.	Manner of irradiation	Direct irradiation	Usually ultrasound source is in contact with reactants. In many lab experiments chemical compounds are disposed into a vessel and immersed into ultrasonic bath, filled with water, and subjected to indirect irradiation Distance between ultrasonic source and bottom of vessel is a multiple of 1/λ, where λ is sonic wavelength.
4.b.		Indirect irradiation	
5.a.	Transducer design	Bath	Ultrasonic cleaning mostly adopts upside-down the trumpet ultrasonic transducer. It comprises a radiation head closely attached to the reactor's wall.
5.b.		Horn (sonotrode)	This is a transducer with a special design which concentrates unidirectional ultrasound waves, thus increasing their powers. Sonotrodes are immersed into reaction vessels. The recipients can have a specific shape or name (e.g. Suslink cell, Rosett cell).
6.	Field of utilization	Sonoreactor for wastewater treatment	From utilization perspective, it is quite difficult to present a rigid classification criteria, thus only enumeration is given
		Cleaning bath	
		Emulsion bath	
		Atomization devices	
		Reactors for chemical preparations or synthesis	
7.a.	Complexity	Simple sonochemical reactors	
7.b.		Complex, or in combination with other processes	Many sonochemical experiments especially for wastewater treatment, present a combination of ultrasonic irradiation with electrolysis, UV irradiation, oxidation agents, Fenton process, catalysis, microbiology, etc.

The study of micro-mixing due to acoustic activity is called the method of iodide/iodate. Ultrasound power increases the micro-mixing due to micro-jets and shockwaves. The mixing is evaluated with above mentioned chemical method using two parallel-competitive reactions with two different kinetic speeds. In this manner, the tomography can be undertaken in ultrasound bath or juxtaposed emission module (JEM), where one, two or more transducers are fixed at the bottom of the reactor, and acoustic beams are perpendicular to the air-water interfaces. There were identified three zones: 1) very high velocity zone where also the micro-mixing is high, 2) low velocity zone where the micro-mixing is medium, but turbulence (shearing) is significant and 3) very low velocity zone where also the mixing is very low and turbulence is weak, Fig. 1 (Gonze et al., 2002).

2.2. Sonochemical reactor with gas bubbling

Many authors presented specialized literature in wastewater treatment installations which combine ultrasounds and gas bubbling. The gases usually used are: air and ozone due their oxidizing characteristics, but must consider that in sonochemical processes, other gases also play special roles because of theirs sonochemical properties, e.g. argon, helium, krypton, etc. In the installations used for a hybrid treatment of wastewater with ultrasound and ozone, it was generated electrically from dry pure oxygen. Reactor was cooled with water and wastewater is in direct contact with ultrasound generator (Gültekin and Ince, 2006). Zhang reported a facile oxidative conversion of chemical compounds using molecular oxygen in an airlift sonochemical reactor.

The advantage of this system is that, in comparison with above mentioned examples, this manner of gas bubbling facilitates two types of mass flux in reactor, one ascending in the bubble area and the other descending into the exterior zone of bubbling area (Zhang et al., 2006). The quantification of overall gas-liquid mass-transfer in sonochemical reactors has been done by Kumar et al. (2004) using the dynamic method. They optimized the effect of work parameters such as power density into the system, gas flow rate, position of the sparger relative to the ultrasound source, and the presence of electrolytes (e.g. NaCl) on the mass-transfer coefficient. The information provided in their paper are useful for understanding the role of ultrasound energy in the gas-liquid mass reaction. The sparger position along with the distribution of cavitational activity plays an important role in deciding the rates of mass transfer (Kumar et al., 2004).

The organic compound degradation in presence of TiO_2 with gas supply using an ultrasound horn was investigated by Kubo. The reaction vessel was made of glass; irradiation was carried out using an ultrasonic horn; a part of solution was continuously circulated to a dissolved oxygen (DO) electrode detector; gases were supplied by bubbling through a glass filter. The temperature of reaction solution was regulated using a water bath, and in order to avoid activation of TiO_2 by light, the reaction vessel was blinded by a blackout curtain (Kubo et al., 2005).

2.3. Sonochemical reactor with UV Irradiation

Photolysis or photo-catalysis and sonochemical hybrid wastewater treatment experiments are performed in a vessel that have both UV and ultrasound irradiation sources. The most utilized UV-ultrasound sonochemical reactors is represented by a UV lamp immersed into an ultrasound bath. Usually photo-sono-chemical treatment method is combined not only with photo-catalysts but with oxidant agents (e.g. O_3, H_2O_2) as well in order to improve the efficiency of wastewater treatment. In the case of ultrasound and UV wastewater treatment, it is important to have simultaneous irradiation rather than sequential operation.

The expected synergism between these two manner of irradiation is attributed to: acoustic micro-streaming catalysts surface clean, compounds mass transport increased at the catalyst surface end in solution, increased surface area of catalyst by fragmentation or pitting, pollutant substrates react direct with the photo-generated surfaces holes and electrons under cavitation conditions and other chemical and physical effects associated with the ultrasound cavitation phenomena.

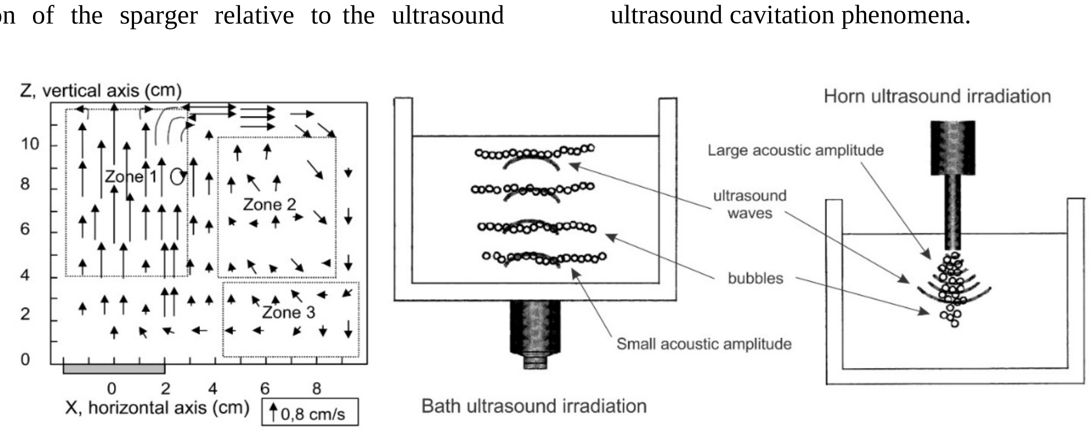

Fig. 1. Example of spatial distribution of the local velocities and comparison of bath and horn ultrasound irradiation

The design of this hybrid reactor can be very diverse. UV irradiation can be done by an immersed lamp or by an external light source. For the latter, the vessel must be made of materials permeable to UV waves. The UV sources can be diverse like in terms of their number or wavelength. Ultrasound sources can also be very diverse such as ultrasound horns or transducers attached on reactor walls or bottom, Fig. 2.

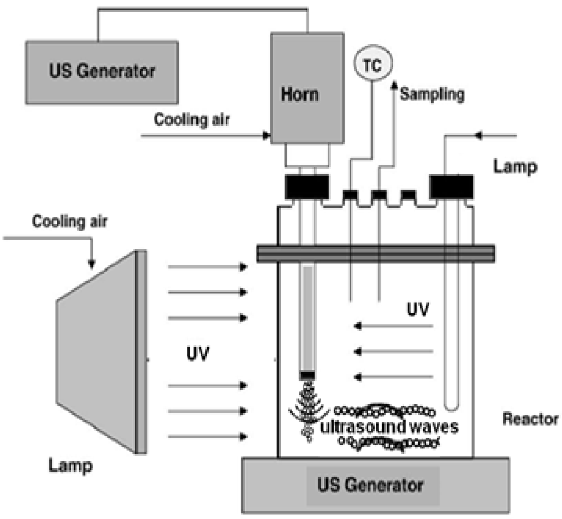

Fig. 2. Schematic illustration multisource UV-ultrasound irradiation system

The diversity of both UV and ultrasound hybrid treatment design is not limited and depends on the imagination and technical knowledge of the researchers. One special design of photo-sono-chemical reactors was realized by Peller for degradation and mineralization of chlorinated aromatic compounds (Peller et al., 2003). Ultrasound assisted destruction of pollutants from wastewater is not limited only to above mentioned example; it includes many categories of organic compounds: aromatics, dyes, herbicides, pesticides, chemical warfare agents, aliphatic carboxylic acids, chlorinated hydrocarbons, alcohols, oxygenates, surfactants, etc. (Adewuyi, 2005). In the hybrid photochemical experiments the shock waves generated by cavitation bubbles, can desorbs the molecules adsorbed on the surface of photocatalyst (Chakma and Moholkar, 2015).

2.4. Sono-electrochemical reactors

Numerous fundamental aspects and applications of ultrasound power in electrochemistry are currently in rapid development due to the most important effects of ultrasounds in an electrochemical system: mass transport enhancement owing to turbulence and micro-streaming; general improvement of hydrodynamics and species movement; continuous activation of the electrode surface, cleaning and abrading effect on electrode surface, product desorption; variation of the concentration gradients and consequently change of the reaction mechanism; sonochemical species formation that react electrochemically in conditions where the silent system is electro-inactive; and formation of ions, radicals and other high energy intermediates (Hardcastle et al., 2000; McMurray et al., 1998; Walton, 2002). The capacity of ultrasound to enhance the electrochemical degradation of pollutants compounds from wastewaters is also mentioned in literature. Like many other electrochemical processes, the efficiency of the process at constant values of ultrasound frequency depends by current density value. Moreover, sono-electro-chemistry has been successfully applied as a technique for the removal of organic pollutants (especially dye residues) from wastewater and effluents (Foord et al., 2001; Lorimer et al., 2001).

One of the simplest sono-electrochemical reactors for wastewater treatment is an ultrasonic bath with two immersed electrodes (Yasman et al., 2004). The electrodes dimensions, geometry or materials could be adapted to any application, considering the work conditions or desired results. In this manner, any type of sonochemical system can be converted to a sono-electro-chemical type. This kind of installation, used by Trabelsi for phenols oxidation in wastewaters (Trabelsi et al., 1996), presented in Fig. 3, consists a cylindrical cathode made by nickel foam and an anode, also a cylinder, realized by a platinised titanium grid of expanded metal. The installation is with gas bubbling system and a dual frequencies generator. Sono-electrooxidation was achieved in the galvanostatic mode at a well definite value of the current density.

Another approach in preparing a sono-electrochemical reactor is the use of one system device as electrode. For example, the bath of the apparatus can be anode or cathode and the second electrode can be immersed in solution in order to close the electrochemical circuit. For a sonochemical system that uses an ultrasonic horn, the horn itself can be used as an electrode. In this manner was used a sono-electro-chemical for destruction of 1,3-dinitrobenzene and 2,4-dinitrotoluene and electro-coagulation of azo-dyes (Abramov et al., 2002). The electrochemical reaction is conducted in a thermostatic glass cell. A titanium ultrasonic radiator was used as a cathode and an anode was introduced through side of wall of the cell, Fig. 4. a).

In electrochemical experiments it is desirable to direct or focus the ultrasound field towards the electrode surface. A thermostatic cell with an immersion horn probe placed from the top in the centre opposite the working electrode was used by Compton (Compton et al., 1995). In this arrangement, tree electrode cell, the electrically conducting horn probe is in direct contact with the cell interior. The sono-electrochemical cell allows values range changing for ultrasound intensity, distance and position between horn and electrode. An important advantage of the immersion horn is the reproducibility which results from the formation of a macroscopic jet of liquid, being the main physical factor in determining the observed current magnitude. Cell designs suffer from an unpredictable pattern of activity due to reflection and superposition of ultrasound waves and from impurities presence (Compton et al., 1997).

In the Marken study is given a classification for different sono-electro-chemical cell types and experimental results for 'face-on', 'side-on', and 'sonotrode' geometries are compared, Fig. 4. b) (Marken et al., 1996). Minimum decrease in the diffusion layer thinning or maximum increase in the transport-limited current was observed as the ultrasound power is increased. The comparative mass transport characteristics and the effect of solvent viscosity were identified as major physical processes which govern the mass transport in undivided sono-electro-chemical cells employing an immersion horn transducer.

The solvent viscosity effects on the limit of diffusion layer thinning were investigated using the electrochemical reduction of tetracyanoquinodimethane dissolved in dichloromethane, dimethylformamide, acetonitrile and dimethyl sulfoxide.

2.5. Sonochemical installations with specific configuration

Degradation of pentachlorophenol aqueous solutions using a continuous flow multi-bath ultrasound installation was reported by Gondrexon (Gondrexon et al., 1999). The chemicals degradation was done in a three-stage sonochemical reactor, operating in a continuous flow mode.

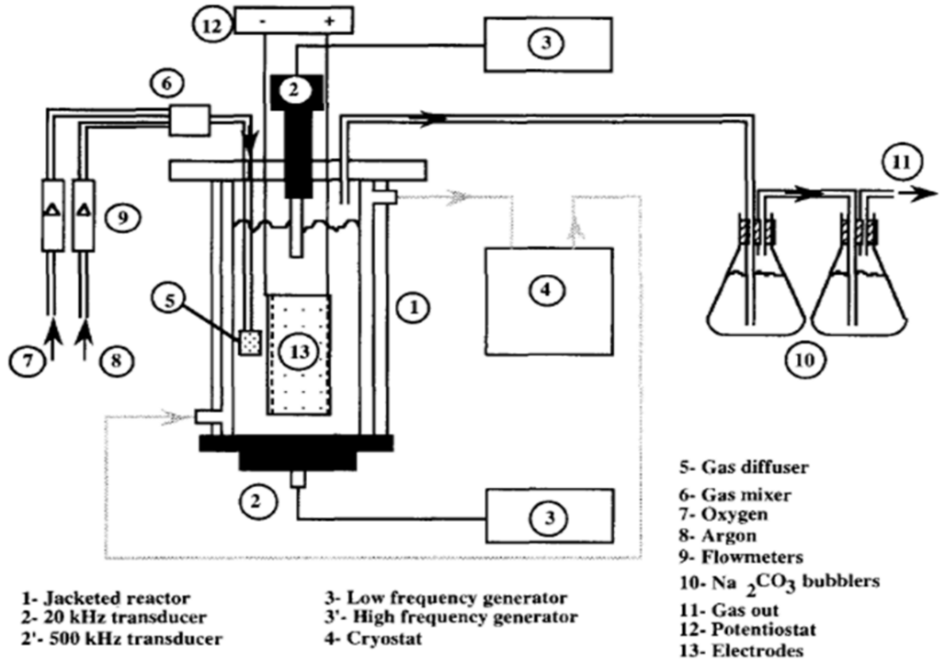

Fig. 3. Schematic diagram of the sono-electro-oxidation apparatus

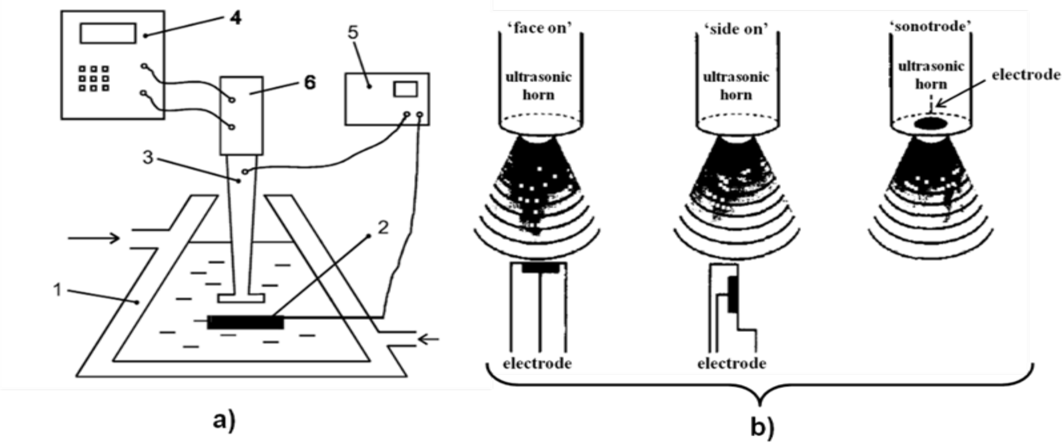

Fig. 4. General view of: a) setup for electrochemical treatment of solutions in ultrasonic field (1 – thermostated vessel, 2 – Al-anode, 3 – waveguide-cathode, 4 – ultrasonic generator, 5 – source of direct current, 6 – piezoceramic transducer; b) electrode geometries types used in sonochemical experiments

The experimental sonochemical reactor may be considered as a series of three high-frequency ultrasonic units. The several parameters influences such as ultrasonic power, volumetric feed flow rate, reactors performances, etc., were reported by the authors. A peristaltic pump is used to feed the sonochemical reactors with wastewater contained in the stirred vessel. Each reactor (unit) was equipped with a 500 kHz piezoelectric source, supplied by its own ultrasound generator. The installation performances were shown to depend on operating parameters such as volumetric feed flow rate and power of ultrasound sources. Taking into account the points outlined in this study, if the ultrasonic power per reactor volume is an important design parameter, a multi-stage installation composed of a series of ultrasonic baths is suggested by above mentioned authors.

Hybrid models of the sono-photo-catalytic installation are used for wastewater treatment (Gogate and Pandit, 2004; Grcic et al., 2017). The idea is to present a universal system for different wastewater effluents treatment. The most important parts of the system considered are: equalization tank, hydrodynamic cavitation set-up, sonochemical reactors and sono-photo-reactors. The proposal is the use of an equalization tank for mixing and homogenization of the wastewater stream coupled with addition of photo-catalyst as well as appropriate amount of pH adjusting chemicals. The wastewater is pumped through hydrodynamic cavitation set-up consisting of orifice plates, which generate cavitations due to sudden change in pressure. One bypass line can be used to adjust the pressure and the flow rate. The sonochemical reactor is a flow cell equipped with transducers that work at multiple frequencies and serve as a multi-purpose unit. The dose of Fe (III) ions, hydrogen peroxide or ozone in proper concentrations should be adjusted depending on pollutants concentration and characteristics in wastewater. The sono-photo-reactor is a tubular device irradiated by sunlight with the help of reflectors. The UV light is placed at the annular location and ultrasonic sources at the bottom of the reactor. The design of both, reactor and reflector, should be done properly, in a manner to achieve incident light uniform distribution.

Depending on the mineralization degree achieved after the oxidation step, wet air oxidation or biological oxidation may be used. The filtration equipment may be used for the separation and reuse of the catalysts. In the above paragraph, the hydrodynamic cavitation set-up process was mentioned, which represents a novel energy efficient hydrodynamic cavitational technique for wastewater treatment. Hydrodynamic cavitation occurs when a wastewater or liquid undergoes a dynamic pressure reduction due to construction devices like orifice plates. The hydrodynamic cavitation phenomenon results in cavities formation, filled with a steam-gas mixture inside of liquid flow. Mixing, homogenization, dispersion etc. caused by substantial plurality of acting forces on the wastewaters causes the cavitational bubbles collapse. The orifices on plate should be distributed in large numbers of smaller diameter holes and the free area should be at a minimum so as to generate intense cavitations. The position and distances between orifice plates and design of hydrodynamic cavitation set-up devices should be adjusted in such way that the cavities generated travel and are available as nuclei in the sonochemical reactor (Sivakumar and Pandit, 2002, Sivakumar et al., 2002).

2.6. Sonochemical reactors with multi-ultrasound sources

To increase the active zones existing in the reactor, it can be easily modified through the transducers number and position. In the case of large scale operation, reactors with multiple transducers are being used due to the fact that it is quite difficult to successfully operate single transducer with very high power and frequency. This is due to the limitations over the transducers material that causes the wave patterns generated by individual transducers to overlap resulting to uniform and increased cavitational activity.

Recent developments employ direct bonding of the transducer to the reactor surface. These improvements and a move to transducers with lower individual outputs have enabled the shift to installations with large numbers of transducers to obtain an acoustic pattern that is uniform above the cavitational threshold throughout the working volume. It is of utmost importance to have uniform distribution of the ultrasonic activity in order to get increased cavitational effects. The low-output transducers use gives the additional advantage of avoiding the cavitational blocking phenomenon (acoustic decoupling), which arises when power densities, close to the delivery point, are very high. In addition, these multi-transducer units, effectively concentrate ultrasonic intensity towards the central axis of the cylinder and away from the vessel walls, thus reducing problems of erosion and particle shedding (Gogate, 2008).

One of the simplest sonochemical reactors with multi-ultrasound sources is a bath with two or more piezoelectric transducers attached on the bottom area or walls. A multi-transducer pilot-station, UES 4000-C, used in sonochemical degradation of chemical contaminants from wastewater was presented by Destaillats et al. (2001). The schematic diagram of their experimental setup consists of a (6 L) stainless steel flow vessel containing four piezoelectric transducers (with frequency 612 kHz) attached to it. Each transducer is excited by a tunable generator. The transducer surfaces were individually cooled by chilled water circulation on their internal surfaces. A thin (0.1 mm) PTFE window, parallel to each transducer separate the solution under irradiation from the chilled water. The four acoustic windows are located between each cooling jacket and the bath allowing the ultrasound waves to reach to wastewater. A pump circulates wastewater from the bath to reservoir tank and heat exchanger. A chiller was used to circulate a refrigerant liquid through the heat exchanger in order to control the operation temperature. Three thermometers were used to monitor the wastewater temperature during the experiments.

In his works, Gonze presents three sonochemical reactors types, composed of glass or stainless steel body and several transducers (Gonze et al., 1999). A piezoelectric ceramic disc made of titanate/lead zirconate (diameter 40 mm) is stuck under a stainless steel plate and is connected to a high frequency (500 kHz) generator whose electrical power can be varied from 0 to 100 W. The transducers were excited with the same frequency: juxtaposed emission module (JEM), combined emission module (CEM), directed beam module (DBM), Fig. 5.

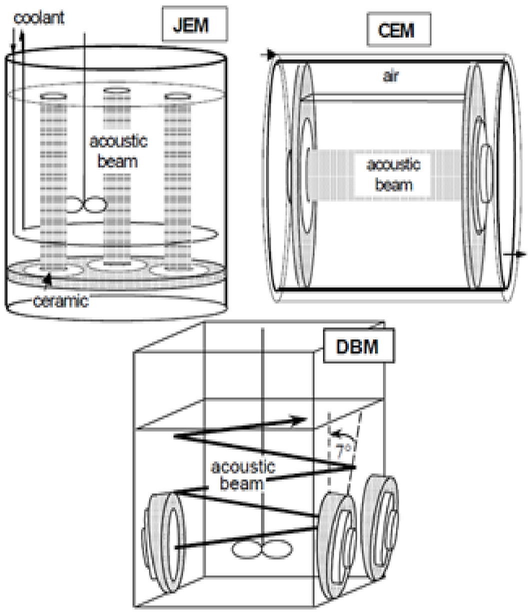

Fig. 5. Schematic description of sonochemical reactors: JEM, CEM and DBM

A juxtaposed emission module (JEM) is a vertically positioned cylindrical glass with two or three transducers fixed side by side to the reactor bottom. The acoustic beams are perpendicular to the air-water interface forming acoustic geysers. These geysers disturb heavily the solution surface and prevent the onset of standing waves. Whatever the liquid height is above the transducer and the wave is always progressive. A combined emission module (CEM) is a horizontally positioned glass cylinder whose extremities are closed with two plates on which transducers can be fixed. The distance between these plates was precisely adjusted. If the liquid length is a half wavelength multiple, a standing wave pattern appears. A directed beam module (DBM) is a rectangular stainless-steel vessel with a cooling coating. Two or three transducers are fixed on its sides and inclined from the vertical by 7°degrees. The acoustic field produces same effects, whatever liquid height is.

A hexagonal sono-photo-chemical reactor is presented in the work of Gogate. These reactor types have ultrasound sources attached on hexagonal walls with UV light sources fitted in the center. The hexagonal shape is used to facilitate the attachment of transducers because it is difficult to mount the transducers on a rounded surface. This sonochemical reactor type can be operated in the batch or continuous mode. The setup has an arrangement for simultaneous irradiation with UV lamp and different ultrasound frequencies (Gogate, 2002).

The principle of the expected synergism in the case of sono-photo-catalytic oxidation, the most common problem observed is the reduced efficiency of photo-catalyst with continuous operation. This is possibly attributed to the pollutants adsorption on catalyst surface, thus active sites covering. Ultrasonic technique can be one method in surface cleaning. The photo-catalytic techniques is severely affected by mass transfer limitations, so ultrasound irradiations and its mechanical effects suggests that simultaneous use of different techniques leads to better results.

2.7. Industrial scale sonochemical reactors

Ultrasound devices are used in sonochemical treatment placed in pipes or itself as component device of a drain-pipe work like sonochemical reactors, but its design is not similar to a classic chemical reactor. The devices can have the shape of tube or pipe and wastewater can cross it or ultrasound elements can be introduced into a pipe and wastewater flow around it. This equipment, together with big sonochemical reactors or baths, has unique techniques for industrial scale ultrasound applications in the wastewater treatment field. The simplest ultrasound device type for wastewater treatment consists in a cylindrical stainless steel tube with an adequate diameter and length. This modular unit reactor type was presented by Vaxelaire and Entezari.

In their works for continuous processing of substances comprises a tubular metallic body with cylindrical inner surfaces and straight circular cross section (open at its feed and discharge ends) and have at least one ultrasonic converter in nodal zone region. For an ultrasonic treatment, one or more devices can be mounted serially along wastewater treatment flow (Entezari et al., 2003; Vaxelaire, 1995).

Tubular sonochemical reactors provide either direct or indirect ultrasound irradiation to wastewater treatment process. Bronson sonochemical reactor has modular units which can be combined in series. Each unit has two ultrasonic horns in contact with wastewater. In fact, this type of ultrasonic treatment uses indirect sonication that prevents process stream contamination with probe fragments which can be incurred during the erosion.

The ultrasounds elements can be introduced into a pipe and wastewater flow around it. This is an effective method for sludge treatment wherein sludge is broken down by the ultrasound irradiation and cavitation effects. This technology was developed by Clark and it is composed by a series of circular ultrasound radial amplifiers introduced into a pipe (Clark, 2007). For sludge treatment, practical results indicated solids reduction and increase gas production in the sludge anaerobic fermentation (Gonze et al., 2003).

Obtaining maximum benefit from water utilized for industrial processes is a top-most priority. The water treatment regimes involve chemical treatments that have negative impact to the environment. One of these specific applications is represented by cooling water systems for many industries that imply a water cyclical circulation in closed regime and some afferent chemical treatments in order to prevent microbiological film formation and corrosion. Using a combination of ultrasonic microbiological control and corrosion inhibitors, not only can environmental performance be enhanced, but also a cost operation decrease can be expected. The new patented technology work was done by passing water through an ultrasonic chamber wherein bacterial cell are exposed to a low-power high-frequency ultrasound combination, UV irradiation and micro-bubble aeration. When exposed to the ultrasound treatment, some bacteria cells die and some become impaired, resulting in the reduction of overall bacteria levels and eliminating bio-film within total cooling water system. An ultrasound device used for treating microorganisms in a liquid medium have an external reservoir which holds the sample and an ultrasound emitter located on the reservoir wall.

The ultrasound emitter producing high-frequency ultrasound with values between 20 kHz and 10 MHz and generates bubbles with an average diameter less than 1 mm. The device is configured to increase the sonoluminescence and inhibit the evolution of the microorganisms. The treatment can be enhanced by using a UV emitter to improve the microbiological treatment (Meulenaer et al., 2007).

The ultrasonic reactor with classical shape, developed by Berger et al. (1996), Fig. 6.a), contains a high transducers number manufactured into the wall and the bottom of a continuously stirred classic chemical reactor. This tank reactor was equipped with a mechanical agitator, an external coating for isothermal control and reaction ports which allow operation in the batch, semi-batch or continuous mode. The ultrasound transducers could be utilized independently from each other and are designed with protecting devices from atmospheric disturbances. The reactor configuration was realized in order to remedy the problems of other reactors types: the efficiency and reproducibility are typical problems associated with ultrasonic bath and small active regions of ultrasound irradiation.

This sonochemical reactor design allows solid-liquid mixtures sonication, which is problematic for vibrating plate systems which only allow liquid-liquid systems (Berger et al., 1996).

Other design for sonochemical reactor was a collaborative effort of many companies. The product name is Harwell sonochemical reactor, Fig. 6. b), a batch reactor with an external flow loop, which sonicates a small fraction of the reaction mixture from the tank vessel volume and returns it in the main vessel reactor tank. The sonochemical module contains an adequate number of transducers which irradiate bulk aqueous solution. Preferably, these transducers are not brought directly in contact with reactive liquid to avoid corrosion and to maintain good equipment condition. The heat exchanger is placed in front of sonochemical active zone in order to reduce reaction mixture ambient temperature, because the high liquid temperatures decrease the sonochemical collapse effects of bubble cavitations (Mason and Berlan, 1992).

2.8. Scale-up considerations

Starting from overall considerations related to performance a few considerations were drawn. Of course, completely new systems can be configured or can start with existing equipment transformed and adapted including piezoelectric ultrasonic devices, but the last is one common method (Gonçalves, 2014). When considering whether to scale-up a reaction and reactor which is developed under ultrasound irradiation, there are several factors to be considered. First, it is important to know ultrasound role in reaction.

The effects are truly chemical (i.e., enhancement due to the formation of free radicals) or they are primarily physical (i.e., enhancement due to the ultrasound astir). If they are physical, it is mandatory to know which effects are most important for wastewater treatment reactions. For example, if particle degradation is the only ultrasound critical role, a sonochemical reactor may not be necessary. The solids can be sonicated before or when they are placed within a conventional reactor. If ultrasound physical effects are important, such as the enhanced rate of mass transfer and/or surface renewal, then sonication will be required over the course of the wastewater treatment.

The fluid and dissolved gases properties are extremely important to ultrasound type and required irradiation amount. The solids presence, their nature, size, and structure will also affect the reactor selection. For example, in liquid-solid reaction system case, a special attention should be given to reactor and its parts, because these could be quickly eroded by the solids presence. The reaction mixture characteristics and the reaction kinetics are necessary to be studied and identified. One must also have acknowledged of the optimum system and ultrasonic conditions, such as the ambient reaction temperature, pressure, frequency, dissipated power, ultrasonic field, and their interactions. Addition of equipment within a reactor (i.e., baffles, stirrers, and cooling coils) affects the distribution of ultrasonic energy because of wave reflection. The many scale-up considerations can be summarized as effect of: dissolved gases (specific heat ratio, conductivity, and solubility), fluid properties (vapour pressure, viscosity, and surface tension), solid particles (materials, size, shape, and density), chemical kinetics, reactor design and operating conditions.

The ultrasound irradiation and its sonochemical effects have been found to enhance the effective diffusivity in a solid-liquid system, increase the intrinsic mass-transfer coefficient, and increase the activation energy and frequency factor of various reaction systems. For scale-up considerations, it is necessary to know the specific system requirements using the aforementioned general guidelines.

2.9. Critical analysis

There is a great and increasing volume of scientific papers related to ultrasound utilization in environment applications, mostly for water and wastewater treatment. The aim of article is to compare the reactors or installations used for water and wastewater sonochemical treatment. In the previous article sections were exemplified these treatment installations, focusing on specific configurations and applications. At the lab scale there is numerous ultrasounds equipment and all of them try to combine ultrasounds with others water treatment methods. The majority of these studied hybrid installations has two water or wastewater treatment systems: first, ultrasound irradiation, and second: Fenton, hydrogen peroxide, UV, gas bubbling, electrolysis; we can conclude ultrasound and another AOP. The most common is ultrasound hybridization with Fenton regent and hydrogen peroxide, a good review about was presented by Bagal and Gogate (2014).

The design and configuration of ultrasound water treatment reactors or installations is not a special one, and generally, this aspect depends by laboratory infrastructure. The installation consists in: ultrasound reactor or bath, electricity, and gas if it is need, supply systems, sampling and analysis (on-line) technique, monitoring and control equipment etc. From elements efficiency perspective, key roles are: the volume of treated water or wastewater, power of ultrasound, ultrasound frequency and the second treatment process.

Closely with those referred above, may be mentioned that sometimes this second water treatment process can be more efficient or even superior to ultrasound irradiation, and in that specific situation the hybridization have no sense. When the researcher discusses about ultrasound scale-up reactors we noticed that it was rather a multiplication. The most common method to increase the water and wastewater workload is to raise the ultrasound devices number, often observed at installations like ultrasound bath.

The main inconvenient for water and wastewater ultrasound treatment is electricity consumptions; therefore it stands to reason that they should be used in the final stage of treatment and where other methods are less effective. Even though the literature abounds with articles about different installation types, it is difficult make a comparison between sonoreactors. One reason is: lack of equipment or experiments standardization and many experimental ultrasound reactors are custom made in laboratory and other: most researchers are focused on experiments that compare different method types for ultrasound hybridization water treatment and not the installations between them. For this kind of experiment the authors use the term of synergy.

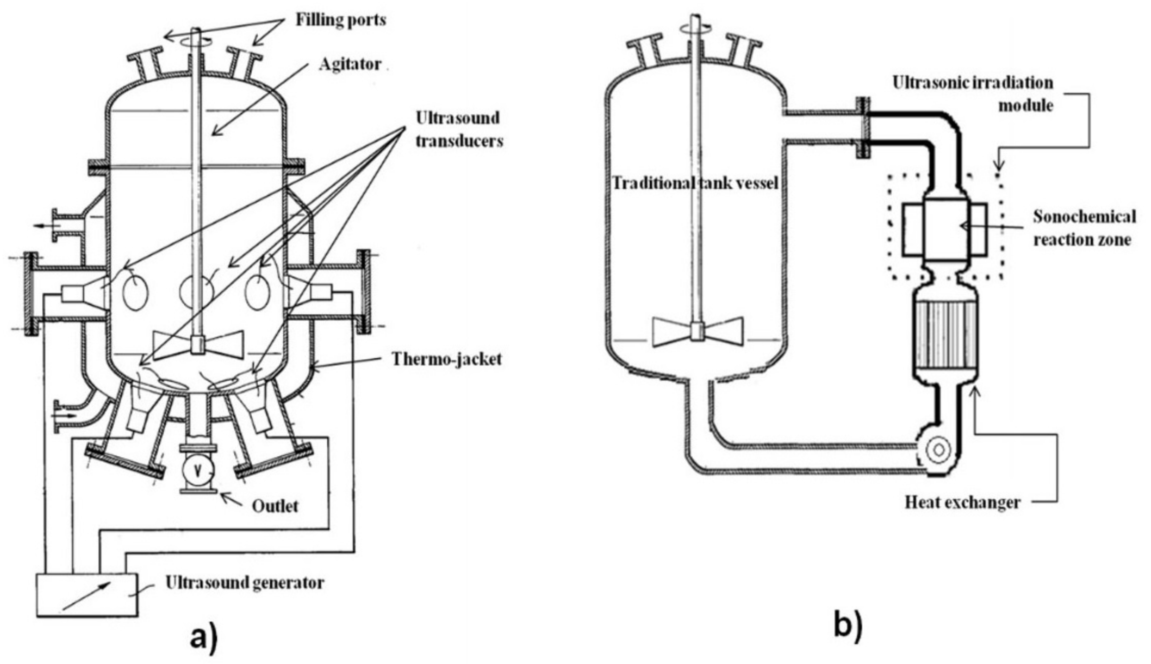

Fig. 6. Comparison of two industrial ultrasonic reactors: a) stirred tank reactor; b) batch reactor with external flow loop sonochemical module

3. Conclusions

The approach of sonochemical installations and reactors can be generally classified as a technological rather than a scientific problem. Science and technology are like two steps closely related, not alternative. After being based on scientific stage, presented into the first paragraphs, technical progress of sonochemical reactors follow them.

Now it is the time to treat these technical parts in the field of sonochemical reactions and installations with scientific tools in order to achieve new elements of progress. This consists of a summary classification and general aspects of the sonochemical reactors. There are presented main type of sonochemical installations and reactors applicable to environment systems in scientific literature: gas bubbling installation, UV hybrid or sono-electro-chemical systems, installation with specific configurations and large-scale sonochemical reactors**.**

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