



Ultrasound Assisted Oxidation Process for the Removal of Aromatic Contamination from Effluents: A Review

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Abstract:

Chemicals are the building blocks for products that meet our most fundamental needs for food, shelter, and health. The chemical industries discharge contaminated waste water that requires appropriate treatment before safe discharge in the environment. Effluent is toxic in nature, due to Presence of aromatic compounds (like benzene, toluene, and xylene). The aim of this study is to check the feasibility of ultrasound technique that has a broad range of industrial applications and its potential for water and waste water treatment. The efficiency of the usual cleaning process to heat carbonaceous compounds (biological or physical / chemical treatment) is limited. In such circumstances, ultrasound seems to be a promising technology for waste water treatment. The heat from the cavity implosion decomposes water in to extremely reactive hydrogen atoms ($H\bullet$) and hydroxyl radicals ($OH\bullet$). Thus in such a molecular environment organic compounds and inorganic compounds are oxidized or reduced depending on their reactivity. This method is highlighted while some of the future challenges like decreasing the cost of operation are considered. Feasibility of ultrasound technique is being evaluated.

Keywords: Aromatic Compounds, Effluent, H_2O_2 , Oxidize, Phase transfer catalyst, Ultrasound

1.0 Introduction:

As a process industries address their growing needs for greater efficiency, new products and reduction in effluents. A wide range of organic compounds is detected in industrial and municipal waste water. These compounds are creating a huge amount of problems to our nature. Indeed up to a few years ago the use of sound in chemistry was something of a curiosity. The basic idea that sounds could influence the rate of chemical reaction. The difference between the sound waves, which are audible, and those which can influence chemical reaction is the frequency and amplitude of sound waves. The sound beyond 18 KHz is called ultrasound. In this range also there are two regions viz. high frequency and power ultrasound. The high frequency or low amplitude propagation finds broad use in medical diagnosis and chemical analysis, the power ultrasound or low frequency used in industry for variety of purposes. It finds large use in emulsification of immiscible liquids, drilling, cleansing of components, deagglomeration powder, machining of hard brittle metals, plastic welding and biological cell wall disruption. The ultrasound technique is mainly concentrated on use of ultrasound for chemical reactions and synthesis.

This sound can also be used to increase rates of heat transfer and mass transfer operations. These reactions are well performed with the combination of ultrasound with oxidizing agent (H_2O_2). (Harman, 1956) proposed the free radical theory and believed that the action of free radicals on large biological molecules, leading to histiocyte injury, is most fundamental reason for aging, tumours, and other diseases in living organisms. The main mechanism of oxidizing function is that generation of highly reactive free radicals, hydroxyl radicals ($OH\bullet$) effecting in destroying organic compounds because they are reactive electrophiles (electron performing) that react rapidly and non-selectively with nearly all electron-rich organic compounds.

1.1 Sound theory

Modern ultrasonic devices rely on transducers which are composed of piezoelectric materials such material respond to the application of an electrical potential across opposite faces with a small change in dimensions. If the potential is alternated at high frequencies, the crystal converts electrical energy to mechanical vibration (sound) energy. At sufficiently high alternating potential, High frequency sound (ultrasound) is generated. When more powerful ultrasound at a lower

frequency is applied to a system, it is possible to produce chemical changes as a result, frequencies above 18 KHz are usually considered to be ultrasound. The frequencies used for ultrasonic cleaning, range 18 KHz to over 100 KHz. The most commonly used frequencies for industrial cleaning are those between 20 KHz and 50 KHz.

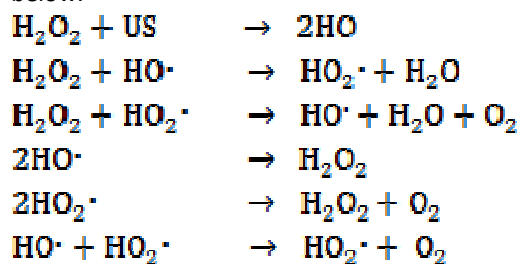
Table 1: Advanced oxidation processes

| | |
|--|--------------------------------|
| Hydrogen peroxide/US | Sonolysis |
| Hydrogen peroxide/UV light | Ozone/Titanium dioxide |
| Hydrogen peroxide/ozone | Fenton reactions |
| Titanium dioxide/UV | Sonolysis |
| Ozone/UV | Ozone sonolysis |
| Ozone/UV/H ₂ O ₂ | Catalytic oxidation |
| Ozone/Titanium dioxide/H ₂ O ₂ | Super critical water oxidation |

Advanced oxidation process are generally used in the treatment of wastewater. The efficiency of this process can be enhanced by the use of ultrasound technique (Stasinakis, 2008). It has been observed that application of ultrasound increases the formation of hydroxyl radicals. Weilin *et al.*, (2010) studied the effect of application of ultrasound on sonochemical degradation of the antibiotics cephalexin in aqueous solution. It was noted that biodegradability of the solution was evaluated by the BOD₅ / COD ratio, which was raised from 0-0.36 after ultrasound treatment, the optimal ultrasound power for cephalexin degradation in the system was 200W and the rate of cephalexin degradation was maximum in the PH range of 6.5- 8.5.

2.0 Hydrogen peroxide / US process

The technique includes H₂O₂ injection with the effluent in reactor. During this process ultrasound is used to cleave the O-O bond in hydrogen peroxide and generate the hydroxyl radicals. The reactions describing US / H₂O₂ process are showing below.



(Maleki *et al.*, 2005) studied the effect of application of ultrasound on ultrasonic degradation of phenol and determination of the

oxidation by-products toxicity. It was noted that phenol was toxic to daphnia magna and resulted in quite low values comparison of treatment of ultrasound of phenol and effluent toxicity showed that treatment of ultrasound value of effluent was 1.65 times less than that obtained for phenol at 48 hours, it was clear that sonication is able to eliminate the toxicity of by-products which were formed during the degradation of phenol. (William, 2007) studied the effect of application of ultrasound on ultrasound biophysics mechanism. It was noted that there are no differences in biological mechanism of injury indicated by ultrasound based on species and age; therefore, structural differences among mammalian species studied were independent of the biological mechanism that causes ultrasound-induced lung damage, and lesions induced by ultrasound were similar in morphology in all species and age group.

3.0 Applications of the ultrasound technique

3.1 Acceleration of rate of reaction:

Ultrasound is also a modest way to increase the energy level of molecules of the chemical or non-chemical components. It provides little energy to the molecules so that it can change its nature. Ultrasound is very cost effective technique, and one time investment. For this process there is no need to add chemicals, and it is environmental friendly process also. (Fogler and Chendke, 1975) studied the current application of sonic and ultrasonic energy in chemical processing and identify the number of application in different sectors such as beverages industry in the area of solid liquid extraction in the process of emulsification in deforming operation, waste water treatment, and chemical reaction etc. It was noted that the sonic and ultrasonic energy has wide potential in different fields of chemical engineering. (Gandhi and Kumar, 1994) studied the effect of ultrasound technique in enhances the yield as well as rate of chemical reactions application results in increases formation of reactive intermediate which causes chemical reaction to occur. (Tuulmets and Salmar, 2001) studied the application of ultrasound on effect of ultrasound on ester hydrolysis in aqueous ethanol. It was noted that kinetics of the acid catalysed hydrolysis of ethyl acetate, ethanol rate increases 1.03 - 2.4 times at 22 kHz ultrasound applied for 18 wt. % minimum and 45 wt. % maximum of ethanol.

3.1.1 Phase transfer catalyst

It has been observed that the reaction rate is dependent on the types of phase. Phase transfer catalyst can play major role in increasing the rate of reactions. The use of these catalyst has certain disadvantages like they are costly and may transfer the toxic chemicals in wastewater. Some application of ultrasound technique has been observed in the alkylation of azo dyes (Li *et al.*, 2002). It enhanced the overall alkylation process.

(Yang and chiu, 2011) studied the effect of application ultrasound technique on ultrasound-assisted phase transfer catalysis: benzoylation of sodium 4-acetylphenoxide by dual site phase-transfer rate catalyst in a tri- liquid system. It was noted that 28 kHz ultrasound irradiation in a batch reactor produced 4- acetylphenyl benzoate, in an organic phase was 98.1% in 2 minute at 30 °C with 250 rpm. (Huo *et al.*, 2011) studied the process of mendelic acid production and utilized ultrasound technique in this process. The parameter for study includes frequency of ultrasound reaction temperature phase transfer catalyst and solvent. It observed that a significant growth in the reaction yield observed during ultrasound treatment.

3.1.2 Change in reaction pathway

Same types of molecules choose different path for their completion of chemical reactions. Since ultrasound plays a roll, like booster, which provides a low energy level to high energy level, that is the cause of reactions diverting from the original path. Jolanda *et al.* (1994) studied the feasibility of ultrasound technique to increase reaction rate and yield of products for both homogeneous and heterogeneous system, the parameter was studied include sound intensity and frequency, solvent and temperature. It was noted that application of ultrasound in this field has promising results. Blake and Panter(2011) studied the effect of application of ultrasound in medical science; It observed that the expose of ultrasound on seeds of phasealus lunatus and lima bean. It was noted that the germination rate increases many time along with enhanced growth. The study may be expanded using diagnostic parameters.

3.1.3 Sono catalyst

The advantages of ultrasound are the use of ambient temperatures to preserve thermally sensitive substrates and to enhance the selectively. Ultrasound also enhances preparation of transition metal carbonyl complexes. These makes a process high like a catalyst and give enormous results. This technique can be used in

different fields like chemical, biological, mechanical processes etc.

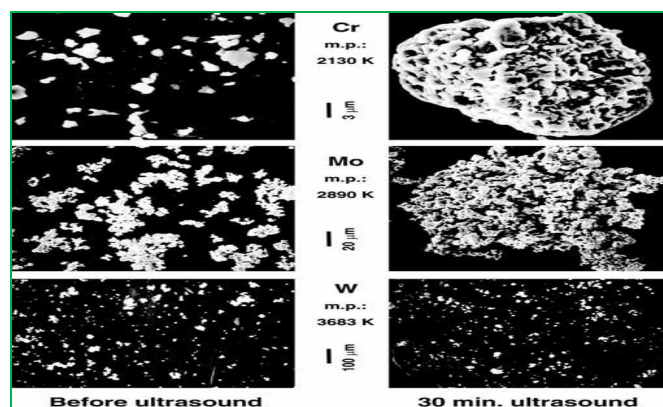


Figure1: Ray diagram

Suslick, (1998) studied the effect of application of ultrasound on Sonochemical reaction and technology. It was noted that sonochemical process affects the reaction rate, activate metal and solid by ultrasound. It was good reactant with liquid phase and it was also capable to remove cavitation from industrial applications. Li *et al.*, (2010) studied the application of ultrasound in the manufacture of Bis (indol-3-yl) methane (BIM), derivative a potential drug in curing cancerous cell and disorder in nerves system. It was noted that lower frequency of ultrasound irradiation increases the yield of product.

Yongli *et al.*, (2012) studied the effect of application of ultrasound on synergistic effects of non-thermal plasma-assisted catalyst and ultrasound on toluene removal. It was noted that ultrasound combined with plasma has been used for toluene removal at atmospheric pressure. A synergistic effects was in the plasma-assisted ultrasound system at the same time, the system increased toluene conversion and reduced ozone emission in the plasma-ultrasound system.

3.2 Water and effluent treatment

Ultrasound is a model process in present era this is increasingly being seen as having potential for use in the treatment of water, waste water and sludge. Ultrasonic sound irradiation effectively destructs the contaminants in water because of the localized high concentrations of oxidizing species. This sound enhances the degradation of various chemical pollutants such as herbicides and pesticides of agrochemical origin or hydrocarbon from industrial effluent. Ultrasound technique is feasible means of disintegrating sewage sludge and degradation or transforming wastewater pollutants. This technique is also used for

anaerobic sludge degradation of aerobic or anaerobic wastewater. Gogate and Pandit,(2004) studied the effect of application of ultrasound techniques on a review of imperative technologies for waste water treatment. It was noted that advanced oxidation processes work on the principle of generation of free radicals and subsequent attack of the same on contaminated molecules. Hydrogen peroxide directly attack to oxidants in the presence of ultrasound. Liu *et al.* (2005) studied the effect of application of ultrasound on enhancement of organic pollutant biodegradation by ultrasound irradiation in biological activated carbon membrane reactor. It was noted that ultrasonic treatment at 10 W for 24 hours could increase organic load of the bioreactor and the removal efficiency of organic substances and enhanced the level of 2,3,5 triphenyl tetrazoliumchloride dehydrogenase activity (TTC-DHA) in the biological activated carbon reactor.

More application of ultrasound technique has been seen in the literature for treatment of wastewater. The effect of application of ultrasound has been studied in breaking of complex organic compounds (Mahvi A.H., 2009). It has been observed that ultrasound technique provides promising results in killing fecal coliform in wastewater. Doosti *et al.*,(2012) studied the effect of application of ultrasound technique on water treatment using ultrasound assistance. It was noted that the main cause of ultrasound efficiency may be the cavitation phenomena that accompanied by generation of high temperature, pressure and reactive radicals species (OH^\bullet , HO_2^\bullet) by thermal dissociation of water and oxygen. (Yaqub *et al.*, 2012) studied the effect of application of ultrasound on electrode material on electrochemical treatment of industrial wastewater. It was noted that concentration of Pb decreased from 11.5 – 0.6 ppm at 80 kHz from battery industries, 95% removed of Cr from tannery industry using lead cathode, and high COD removed using steel anode at 80 kHz. Use of ultrasound is very effective to removal of heavy metals and organic pollutants from industrial wastewater.

3.3 Textile industry

A huge amount of water and electricity is required in the wet processing of textile material which results in germination of large effluent. Application of ultrasound technique enhances induced dispersion and break-up of dye. The acceleration of dye inside the fibers improve dye fixation and

increase the colour yield without affecting properties. Moholkar *et al.*,(2003) studied the effect of application of ultrasound on intensification of mass transfer in wet textile processes by power ultrasound. It was noted that the formation of standing waves assists ultrasonic wet textile processing by raising the power consumption of the system. And also textile fabric in the standing wave field can alter the performance of the ultrasonic system. Karaboga *et al.*, (2007) studied the effect of application of ultrasound on use of ultrasonic technology in enzymatic pretreatment processes of cotton fabrics. It was noted that ultrasound energy during enzymatic treatment of cotton fabric significantly improves enzymes efficiency without affecting the strength of the fabric as well as increased mass transfer towards the textile material. Kamel *et al.*, (2009) studied the effect of application of ultrasound on ultrasonic dyeing of cationized cotton fabric with natural dye, cationization of cotton using solfix E. It was noted that ultrasound technique at 300W extracted cochineal dye and gave maximum extraction values than other conventional methods.

3.4 Medical application

Rapidly growing technologies and sophisticated instruments also create a number of problems. They are also a big problem in itself. Regular and effective sterilization of equipment's and medical implants are extremely important to hospitals. Every year lakhs of rupees invest for this purpose. Most sterilization technology today has disadvantages associated with their use. Ethylene oxide, for instances, which is the current standard for gas sterilization is hazardous to human health and harmful to the environment, parasitic acid, vapor phase hydrogen peroxide and formaldehyde liquids are more costly and difficult to use. Chemicals are not a good substitute of cleaning equipment's since they contribute directly to the evolution of the resistance bacterial strains. Most of the chemicals kill off most of the bacteria but those that survive, because of they are less susceptible to the chemical and sterilization gradually reduces with time. After understanding these problems, there is a possible way to apply ultrasonic technique for the sterilization of medical implants and equipment's.

Number of application of ultrasound technique has been found in literature, for tissue scattering microstructure characterization (Rao and Helguera, 1997). It helps in evaluating the properties more clearly about the microstructure.

Czerwinski *et al.*, (1999) studied the effect of application of ultrasound technique on detection of lines and boundaries in speckle images. It was noted that use of sticks algorithm to enhanced images for boundary detection. The ultrasound could be made more sensitive to thicker lines between speckle suppression and the ability to follow tightly curved boundaries. It provides new information to be incorporated into an image without affecting the gray level value of the original image. Ultrasound technique can be applied in the interventional shoulder (Simmons *et al.*, 2000). Ultrasound guided interventions around the shoulder is relatively easy and growing technique and provide instantaneous relief. Sapna and Vandana, (2010) studied the effect of application of ultrasound on ultrasound in periodontics. It was noted that application of ultrasound in diagnosis and treatment of periodontal diseases shown promising results. It was clear that ultrasonic instruments are here to stay and deserve to play a significant role in periodontal therapy.

3.5 Chemical application

The chemical effects of ultrasound, ultrasound's acting as a catalyst in certain chemical reactions, including oxidation, reduction, hydrolysis, polymerization and depolymerisation, and molecular rearrangement. With ultrasound, some chemical processes can be carried out more rapidly, at lower temperatures, or more efficiently. Ultrasound processes are used as homogenizers, to reduce small particles in a liquid to improve uniformity and stability. These particles (disperse) can be either solids or liquids. Ultrasonic homogenizing is very efficient for the reduction of soft and hard particles. Sonochemical effects can be observed in chemical reactions and processes - increase in reaction speed, increase in reaction output, more efficient energy usage, sonochemical methods for switching of reaction pathway, performance improvement of phase transfer catalysts, avoidance of phase transfer catalyst, use of crude or technical reagents, activation of metals and solids, increase the reactivity of reagents or catalysts, improvement of particle synthesis and coating of nanoparticles. Capelo *et al.*, (2000) studied the effect of ultrasound on degradation of organomercurials, at room temperature, based on oxidation process. It was noted that advanced oxidation process reduce chemicals, high temperature, and pressure. It completes oxidation process within 3 minute using a 40% sonication.

Some application of ultrasound technique has been found on heat transfer rate for thermosymphon heat pipe (wongtom and kiatsiriroat, 2009). It was noted that the heat transfer rate can be increase significantly by applying ultrasound technique. The antioxidant activity of peanut can be improved by the use of ultrasound technique (Yu *et al.*). It has been observed that there is significant increase in antioxidant capacity at a ph of 8.5 and incubation time of 25 minutes. Lin *et al.*, (2012) studied the application of ultrasound extraction in the extraction process of luteolin in taraxacum officinale. It was noted that ultrasound extract 64.84% ethanol at 58.81 minute from leteolin in teraxacum officinale

3.6 Petroleum industry

Petroleum is the largest and most widely used natural resources in the world. Fuels for consumers and industrials use are derived from petroleum, as are the chemicals used as raw materials in a vast array of consumer and industrial products. Today it is very difficult to manage cleaning section and process section of petroleum industry, because of huge amount of chemicals are needed for cleaning purpose. Here ultrasound technology is a promising technology for removal of cavities of instruments and other part of the industry as well as process. David and Isaacs, (1998) studied the effect of ultrasound energy to break-up of oil field emulsion in the petroleum industry. It was noted that ultrasonic treatment not only allowed more water to be separated from the emulsion samples but also separated significantly accelerated the separation process.

Ultrasound can also be used for the treatment of effluent from oil industry. Research literature (Asatekin and Mayes, 2009) indicates the feasibility and potential of ultrasound using different types of membrane. This membrane requires less frequent back washed, easy chemical cleaning. It also reduces energy consumption in to treatment of oil industry wastewater. Some studies (Amani *et al.*, 2011) have been seen in the use of ultrasound technique in changing asphaltic properties in higher boiling fraction of crude oil. It has been observed that ultrasound enhances to formation of asphaltic particles.

4.0 Conclusion:

- Ultrasound technique has to potential to accelerate many reactions.
- It has to ability permits the use of unpurified solvent and reagents.
- The reaction can be conducted at milder conditions
- It helps in improve conversion and yield of reactions and in some cases changes reaction pathway also.
- It can be applied to preparation of emulsions, leaching, grinding etc.
- It is effective in the treatment of effluent containing highly toxic organic pollutant.

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