Chapter 1

INTRODUCTION AND BACKGROUND

1.1 Ultrasound Overview

The industrial sector is progressing at a rapid rate with stiff competition and stringent environmental regulations. With the progress, the needs of the process industries are also increasing at an alarming rate which makes the industries to think about achieving greater efficiency, developing new products and reduction in effluents. The industries are trying to explore innovative ways of making energy work for them in reaction chemistry and the physico-chemical separation of products.

Chemistry is the interaction of energy and matter. The relationship between the rate of a chemical reaction and the electromagnetic radiation is a well established in synthetic chemistry. Traditional sources of radiation include heat, light and electric discharge. The basic idea, that the sound could influence the rate of chemical reaction or form new chemical species has been proved to be correct. The basic difference between the sound waves, which are audible, and those, which can influence chemical reactions, is the frequency and amplitude of sound waves. The sound audible to the human ear falls between 16 Hz to 16 kHz and in this range, it has no effect on chemical reactions [1]. Ultrasound is cyclic sound pressure with a frequency greater than the upper limit of human hearing. This limit varies from person to person, it is approximately 20 KHz in healthy, young adults and thus, 20 KHz is used as a lower limit for describing ultrasound. It has a much shorter wavelength though ultrasound behaves in a similar manner to audible sound. The acoustics spectrum is divided into 3 ranges of frequencies. The high frequency or low amplitude propagation finds extensive use in medical diagnosis and chemical analysis, but have not been found to induce or enhance chemical reactions. The power ultrasound or low frequency normally considered falling in the frequency range of 20 to 100 kHz is used in industry for multiple purposes. The special characteristic of this range of frequencies is that the amplitude can be made reasonably large, resulting in high intensity of sound in the vessel. Ultrasound needs only the presence of a liquid to transmit its power. Ultrasound is propagated by a series of compressions and rarefaction waves generated in the medium through which it passes. Whereas other technologies such as
microwave, electrochemistry and photochemistry require some special attribute for activation for chemical applications which may be dipolar species, some conducting medium or the presence of a chromophore. Rapid movement of fluids caused by variation in sonic pressure subjects the solvent to compression and rarefaction and gives rise to the stirring action of ultrasound called acoustic streaming. Acoustic streaming leads to improved thermal mixing and mass transport within the gases and the liquid and also it reduces the diffusion layers between interfaces. As a result it will be expected to have a marked effect on the process, which is diffusion controlled. The second phenomena and the most important is cavitation which can be in general defined as the phenomena of the formation, growth and subsequent collapse of microbubbles or cavities occurring in extremely small interval of time (milliseconds) releasing large magnitudes of energy. Cavitation as a phenomenon was first identified and reported by Thornycroft and Barnaby in 1895 [2]. Two types of cavitation have been extensively studied i.e. hydrodynamic cavitation and acoustic cavitation [3].

Hydrodynamic cavitation is generated by passing the liquid through a constriction such as orifice plate, venture, throttling valve etc. The kinetic energy/velocity of the liquid increases when the liquid passes through the constriction and simultaneously the pressure decreases. If the pressure around the point of vena contracta decreases below the threshold pressure required for generation of cavities then millions of cavities are formed which collapse after reaching a certain size [4].

Ultrasound waves, like all sound waves, consist of cycles of compression and expansion. Compression cycles exert a positive pressure on the liquid, which pushes the molecules together; and expansion cycles exert a negative pressure, pulling the molecules away from one another. The molecules of liquid are held together by attractive forces, which determine the tensile strength of a liquid. During the expansion cycle of the sound wave a large negative pressure is exerted on the liquid. If this negative pressure overcomes the liquid’s tensile strength then the cavity is formed. This phenomenon is called acoustic cavitation [5-6]. Under the influence of ultrasound, these vapours, gas-filled cavities exhibit variety of behaviour patterns depending on their sizes. Those transient cavitiesenlarge to many times their initial size and collapse violently generating very high temperatures (of the order of 1000–5000 K) and pressures (100–50,000 bar) and heating and cooling rates above 10^{10} K/s. When the compression of bubbles takes place during cavitation, heating is
quicker than thermal transport, which generates a short-lived, local hot spot and in single bubble cavitation, conditions may be even more extreme. These events occur simultaneously at multiple locations in the reactor. Thus, cavitation can create extraordinary physical and chemical conditions in cold liquids and serves as a means of concentrating the diffuse energy of sound into a unique set of conditions to produce unusual materials from dissolved (and generally volatile) solution precursors. With ultrasound the energy dissipated per unit volume for the same energy input is very high as compared to the conventional processes. Thus, energy is concentrated in extremely small zones, but at millions of locations. Since the solvent vapor is trapped in the bubble at each acoustic cycle, the energy concentration can break chemical bonds and yield very reactive free radicals (mainly \( \text{OH}^- \) and \( \text{H}^+ \) for water). These radicals may recombine and/or attack molecules in the liquid or gas phase. This phenomenon is studied in branch of science, which is known as ‘sonochemistry’ [6].

Chemistry is basically the interaction of energy and matter. Chemical reactions require energy to proceed and chemistry stops as the temperature approaches absolute zero. The course of a chemical reaction is decided by the properties of a specific energy source. As compared to conventional energy sources such as heat, light or ionizing radiation, ultrasound differs in energy per molecule, pressure and duration. Exceptional heating and cooling rates associated with bubble collapse provide a distinctive mechanism for generating high energy chemistry [7]. The molecules of the vaporized reaction mixture within the bubbles are fractured, forming highly reactive free radicals [8]. In aqueous liquids, acoustic cavitation leads to the formation of reactive species such as \( \text{OH}^- \), \( \text{H}^+ \) and \( \text{H}_2\text{O}_2 \). These short lived species are capable of effecting secondary oxidation and reduction reactions [9]. As a result ultrasound has been shown to have positive effects on many physical and chemical transformations and it is extensively used in chemical processing, material synthesis, wastewater treatment, polymer chemistry etc. The reactivity of metal powders increase by more than 100,000 times by application of ultrasound. Ultrasound can force metal particles together at such a high speeds that at the point of collision the solids melt and ultrasound can generate microscopic flames in cold liquids.

Positive effects of ultrasound are found for both homogeneous and heterogeneous reactions, such as enhancing the selectivity, increasing the conversion, and improving the yield. During the chemical processing ultrasound results in reduction in reaction
time, use of moderate conditions as compared to the conventional route and decrease in the induction period. Novel findings of the effects of ultrasound on mass transfer parameters are reported [10]. Ultrasound can enhance the rates of mass transfer and reaction through the mechanical effects. Power ultrasound, having frequency between 20 kHz and 1MHz, have proven its significant effects on the rate of various processes in the chemical industry such as cleaning, homogenization and emulsification, sieving, filtration, crystallization, extraction, degassing and stripping. But the most remarkable effect is the increase of rate and selectivity of many different chemical reactions. Enhancements due to ultrasound are attributed to its chemical or mechanical effects or to both simultaneously.

The high intensity sound encountered in the power ultrasound range has been found to show interesting and many times unusual chemical effects. Such chemical effects have been reported not only for homogeneous reactions, but also for heterogeneous systems. The chemical effects of ultrasound are attributed to the implosion of microbubbles formed during the rarefaction, or negative pressure period of sound waves. When solid particles are in the vicinity of the cavitation bubble, the implosion may occur symmetrically or asymmetrically [8]. The chemical effects of ultrasound can be divided into three general types: pure liquids, heterogeneous liquid-liquid and heterogeneous liquid-solid systems. Because cavitation can only occur in liquids, chemical reactions are not generally seen in the ultrasonic irradiation of solids or solid-gas systems.

Mechanical effects are caused by shock waves formed during symmetric cavitation, or by microjets formed during asymmetric cavitation. Symmetric cavitations create shock waves which propagate to the surrounding solids causing turbulence on microscopic level and/or thinning of the solid-liquid film. This phenomenon is called microstreaming and it is responsible for increasing the rate of mass transfer of reactants and/or products through the film. When solid particles are in close vicinity to the bubble, it cannot collapse symmetrically. This is known as asymmetric cavitation and it is responsible for the formation of microjets of solvent which bombard the solid surface, leading to pitting and erosion [11-14]. Microjets and shock waves considerably affect the chemical composition and physical morphology of solids that enhances chemical reactivity. The interparticle collisions inducenoticeable changes in reactivity, composition and surface morphology.
1.2 Role of Cavitation in Physical and Chemical Transformations

Some of the applications of ultrasound in different physical and chemical transformations are discussed here. Role of cavitation for polymer degradation, waste water treatment, sonocrystallization, chemical reactions and synthesis of inorganic materials is elaborated in the following sections.

1.2.1 Polymer degradation

Degradation of polymers can occur due to the application of heat, light, chemical reagents or ultrasonic radiation. During the degradation of polymer the scission of the polymer backbone occurs randomly at any bond, at the end of the chain or at the midpoint of the chain. Thermal degradation occurs principally due to chain-end and/or random-chain scission and in ultrasonic degradation the chain cleavage is preferentially near the middle of the chain. There are several unique features of ultrasound that make it viable option from practical and theoretical viewpoints. Degradation of polymers by ultrasound is unique because only polymers above the limiting molecular weight (MW) break. The rapid growth and violent collapse of bubbles is responsible for degradation. Relative motion of the polymer segments and solvents produces stresses in polymer chains leading to scission of chain [15-17]. Passage of ultrasonic waves through the solution creates the localized shear gradient which tear off the molecules leading to chain scission and decrease in molecular weight [18]. The degradation rates of polymers vary with concentration, initial molecular weight, temperature, frequency and intensity of ultrasound [19]. The nature of the solvent has a major effect on the degradation rates. The degradation of poly(vinyl acetate) was investigated by Madras et al. [17] by using different solvents and the mixtures of these solvents. The rate of degradation was related to the volatility and the kinematic viscosity of the solvent. It has been observed that more volatile the solvent is lesser is the degradation rate of polymers [19]. This is attributed to the cushioning effect on the bubble collapse when more vapour enters the cavitation bubble [20].

The initial molecular weight of the polymer is important for the degradation kinetics because it provides insights into degradation mechanisms for macromolecular reactions. The ultrasonic degradation of poly(ethylene oxide) (PEO) of different initial molecular weights was studied and the results indicated that the degradation
rate coefficient was independent of the initial molecular weight. The effect of different solvents was also studied and it was found that PEO could not be degraded in acetone, acetonitrile and methanol whereas mixture of toluene and water effectively degraded PEO [21]. Similar work based on ultrasonic degradation of poly(vinyl-pyrrolidone) (PVP) of different initial molecular weights was done by Taghizadeh et al.[22]. The results indicated that the rate of ultrasonic degradation increased with increasing molecular weight and the decreased with solution concentration. The ultrasonic degradation of polystyrene (PS) and ethylene-propylene diene monomer (EPDM) melts was conducted by Jiang Li et al. [23]. They concluded that the molecular weight or intrinsic viscosity of polymer melts decreased with ultrasonic irradiation time and approached a limiting value, below which no further degradation took place. The temperature of the operation is another important factor which needs to be optimized. The degradation of polyacrylamide and poly(ethylene oxide) in solution at different temperatures was studied. The degradation rate coefficient decreased with increasing temperature which was attributed to higher vapour pressure and lower viscosity at higher temperatures [19].

The ultrasonic degradation of polystyrene and poly(vinyl acetate) in chlorobenzene was studied by Madras et al.[15] to calculate degradation rate coefficients. The ultrasonic degradation of poly(vinyl acetate) was carried out in the presence of an oxidizing agent, benzoyl peroxide. The degradation rate coefficient of the polymer decreased with increasing benzoyl peroxide concentration [16]. The influence of the alkyl group substituents on the ultrasonic degradation of different polymers was studied by Daraboina et al. [24]. The rate coefficient increased with an increase in the number of carbon atoms in the alkyl group. Additionally the sonochemical degradation of poly (butyl methacrylate) (PBMA) using different various solvents at varying temperatures and ultrasound intensities was also studied. Lorimer et al.[25] have studied the effect of ultrasonic intensity, reaction temperature and solution concentration on the degradation of dextran in aqueous solution. They observed that the ideal conditions for ultrasonic degradation are high ultrasonic power, low reaction temperature and low solution concentration. The effect of ultrasonic intensity on the degradation mechanism, degradation kinetics and the molecular weight distribution of high-density polyethylene (HDPE) melt were studied. With the increase of ultrasonic intensity the average molecular weight of HDPE decreased [26]. The plausible
The mechanism of ultrasonic degradation of polymer was also proposed in this work. Polymerization and degradation of styrene was investigated by Kobayashi et al. [27] to study how the reactors positions affected weight-average molecular weight, number-average molecular weight and polymer yield. They demonstrated that the varying the position of the reactor polymer characteristics could be controlled. Biodegradable polymers are used as biomaterials in tissue engineering and controlled drug delivery systems hence their degradation patterns are important for biomaterial selection and design. Ultrasound has been used for the degradation of biodegradable polymers [28].

1.2.2 Waste water treatment

Similarly ammonia was removed from simulated industrial wastewater by using high frequency ultrasound waves [32]. High frequency ultrasound waves were used for degradation of dissolved diazinon pesticide in water. The degradation process for diazinon followed a pseudo-first-order reaction model [33].

Among the many organic compounds found in wastewaters, the pollution caused by dyestuffs has been a serious environmental problem for years. Inoue et al. [34] used different frequency ultrasound probes for dyestuffs degradation. Methylene blue (MB) which is typically found in textile effluents is difficult to degrade by conventional methods. Byun and Kwak [35] studied the degradation of Methylene blue in aqueous solution under ultrasonic field. They reported that the sonochemical degradation of dye was faster than the the photocatalytic degradation because of the OH’ radicals generated due to cavitation.

Ultrasound is often coupled with other techniques for the waste water treatment. Those combined processes are called hybrid techniques. The hybrid techniques are extensively used for degradation of phenolic compounds [36-39]. Kidak et al. [36] and Gogate [37] reviewed the work done on application of cavitation for treatment of phenolic compounds. They concluded that cavitation when used alone for wastewater treatment cannot be economical. The different ways in which the cavitation phenomena can be intensified by using additives and/or combining cavitation with other oxidation processes was explained in this work. Hybrid methods viz. Ultrasound/H$_2$O$_2$ or ozone, cavitation assisted by use of catalysts/additives,
sonophotocatalytic oxidation and cavitation coupled with biological oxidation are successfully employed for wastewater treatment.

Hoffman et al. [30] have investigated sonochemical degradation of chemical contaminants in water. They found that substrates such as chlorinated hydrocarbons, pesticides, phenols, TNT, and esters are transformed into short-chain organic acids, CO$_2$ and inorganic ions as the final products. Mahamuni et al. [38] used additives such as salt and carbon tetrachloride for the phenol degradation for intensifying the degradation process. Sonochemical and photochemical oxidation of phenol was carried out with improvement in the degradation rate of phenol. Further the same process was successfully tested for the reduction of chemical oxygen demand of a municipal wastewater [39-40]. The degradation of 4-chlorophenol (4-CP) in aqueous media by ultrasonic irradiation was investigated and the results indicated that OH radicals generated during cavitation are the primary reactive species responsible for 4-CP degradation [41].

Perez et al. [42] have carried out a comparison of sonolytic, photocatalytic and sonophotocatalytic processes of malachite green in presence of carbon tetrachloride under ultrasonic environment with titanium dioxide as a photocatalyst. The effect of different parameters such as ultrasonic intensity, TiO$_2$ crystalline structure and the presence of CCl$_4$ were studied with enhanced rates of degradation of malachite green. Sonochemical degradation of azo dyes in aqueous solution was tried by Okitsu et al. [43]. Their results indicated that azo dye molecules were mainly decomposed by OH radicals formed from the water sonolysis. Additionally they studied the effect of radical scavenger and it was found that the sonochemical decolorization was also depressed by the addition of the t-butyl alcohol radical scavenger.

1.2.3 Sonocrystallization

Crystallization has been used in various industrial sectors such as chemical, petrochemical and pharmaceutical industries and it involves the nucleation and crystal growth. Supersaturation or supercooling are important conditions for the initiation of crystallization. Apart from these minute solid bodies, embryos, nuclei or seeds are also required to act as centres of crystallization and nucleation may be spontaneous or it may be induced artificially [44]. Nucleation of solid crystals from a number of liquids ranging from organic fluids to metals is affected by the presence of ultrasonic
waves. Ultrasound can initiate primary nucleation in particle-free solutions at lower supersaturation levels as compared to other crystallization techniques. The early nucleation because of early supersaturation attained in the presence of ultrasound is attributed to rapid local cooling rates, in the range of $10^7$–$10^{10}$ K/s playing an important role in enhancement of supersaturation. The crystallization temperature is reduced due to localized pressure increases and the cavitation events help in surmounting the excitation energy barriers necessary for nucleation [45]. It is even believed that the nucleation caused by scratching the side of containing vessel could be the result of cavitational effects. Another effect of US on nucleation is shortening the induction time between the establishment of supersaturation and the onset of nucleation and crystallization. The metastable zone width (MZW) can also be reduced by application of ultrasound and the size of the crystals can be customized by suitable sonication conditions [44-46]. Because of the large number of nuclei that can rapidly be created, cavitation can also be applied to obtain large numbers of ultrafine particles or to create nuclei of another polymorph [47].

There are many reports on ultrasound being utilized for the crystallization of various compounds. Lyczko et al. [48] have studied the effect of ultrasound on primary nucleation of potassium sulphate by measuring the induction time and metastable zone width of unseeded solutions. They found that in the presence of ultrasound, induction time and metastable zone width were significantly reduced. Reactive crystallization of 7-amino-3-desacetoxy cephalosporanic acid (7-ACDA) was done by using power ultrasound to control supersaturation, nucleation and crystal growth [49]. The results showed the reduction in induction period and metastable zone width as well as the agglomeration was also reduced. Virone et al. [47] made first attempt to correlate the collapse pressure of the cavitating bubbles with the nucleation rate for ammonium sulphate crystallization. Ultrasound resulted in large reduction in induction times and increased the nucleation rate. Influence of power ultrasound on crystallization of potash alum was investigated by Amara et al. [50]. It was found that ultrasonic waves decreased the supersaturation limit and modified the morphology of the crystal. The average crystal size decreased with ultrasonic power, indicating that the nuclei appear during shorter time in presence of ultrasound. Same authors in another work have compared the growth rate of potash alum crystals in presence of ultrasound and silent conditions. They found that growth rate of potash
alum crystals was faster in presence of ultrasound. The shape of the crystals remained unaltered but size was reduced by ultrasound [51]. Power ultrasound was applied during the process of salting-out crystallization (anti-solvent based crystallization process) and the process was completed in seconds. The results indicated that the mean size and size distribution of formed crystals can be controlled by changing mixture volume, ultrasonic energy and duration. Perfectly shaped crystals were formed with negligible agglomeration. Based on the results, the authors have suggested the possible scale up of this process for industrial application [46]. Although ultrasound has been applied in salting-out process, most of the time it has been used for only initial stages of crystallization (nucleation). However, Bund and Pandit [52] in their work carried out the whole process of lactose crystallization with the aid of ultrasound in the presence of ‘ethanol’ as an anti-solvent. The lactose recovery and crystal properties from sonicated samples were compared with non-sonicated samples. For optimization of the sonocrystallization process for rapid lactose recovery the variation of time of sonication, lactose concentration, protein concentration and pH were tried.

Miyasaka et al. [53] investigated the effects of ultrasound on acetylsalicyclic acid crystallization. In this work the number of crystals formed after primary nucleation was counted and an attempt was made to develop a relationship between the final product size and the number of crystals. They concluded that ultrasound energy not only controls the primary nucleation but plays a role in perfection of the crystal shape. Xie et al. [54] used ultrasonic crystallization for preparing ZnAl-Hydrotalcite compounds with small particle size, narrow particle size distribution and high crystallinity. The effect of ultrasound parameters was also studied and the results indicated that both ultrasonic frequency and ultrasonic power affects the particle size. Increasing of the ultrasonic power decreased the median particle size.

1.2.4. Chemical reactions

There are several reports available where the ultrasound has been used to carry out the chemical reactions. In many cases the comparison of either the rate of reaction or the conversion has been done with the conventional processes. The major portion of application of sonochemistry deals with acceleration of reaction rates. Normally, these would involve reactions with two phase’s viz. liquid/liquid or solid/liquid. The
successful application of sonochemical reactors for chemical processing applications has been due to the generation of highly reactive hydroxyl radicals and local hotspots. Intensification of hydroxyl radical production in sonochemical reactors for the oxidation of salicylic acid in the presence of different additives has been studied by Chakinala et al. [55]. It was observed that optimized power dissipation conditions in the presence of iron powder and oxygen resulted in maximum liberation of hydroxyl radicals for production of 2,5- and 2,3-dihydroxybenzoic acid. One of the major advantage of ultrasound is the use of less forcing conditions for carrying out the reactions. Cavitation was effectively used for the synthesis of biodiesel at ambient conditions of temperature and pressures as against the requirement of high pressures and reflux conditions for the conventional route of synthesis [56]. Classical methodology for the production of transition metal carbonyl anions from metal halide, sodium and tetrahydrofuran (THF) requires high pressure (200 atm) and high temperature (2000°C). These forcing conditions can be reduced to just 100°C and 4.4 atm when performed in the presence of power ultrasound [57].

Results are reported for rates and rate enhancements during synthesis of benzyl sulfide from benzyl chloride and sodium sulfide in an organic solvent in the presence of ultrasound and phase transfer catalyst (PTC) by Hagenson et al. [58]. The combination of ultrasound and PTC resulted in acceleration of the reaction rates. Bhatkhande et al. [59] also studied the saponification of vegetable oil using different PTC’s in presence of ultrasound. They concluded that the rate of saponification of vegetable oil was remarkably accelerated in presence CTAB and ultrasound. Wang et al. [60] studied the kinetics of 1, 7-octadiene under the influence of ultrasound in presence of PTC with substantial increment in the reaction rate.

Reductions of aromatic hydrocarbons by calcium in ethylenediamine–n-alkylamine mixture have been investigated under ultrasonic conditions which resulted in faster reaction rate as compared to mechanical stirring [61]. The effect of ultrasound on hydrolysis of methyl acetate was studied in a batch reactor. The reaction rate has been reported to be increased with increasing sonic amplitude, while the frequency had negligible effect on the rate [62]. Sulfoxide was synthesized from sulfide with very high conversion and selectivity using ultrasonic irradiation in the presence of catalyst [63]. Cavitation has been used for the intensification of the sulfone synthesis process and the yield of sulfone was increased by about five to six times against conventional
1.2.5 Synthesis of inorganic materials

One of the most important applications of sonochemistry is in the synthesis of inorganic nanomaterials. Suslick et al. [66] have synthesized nanostructured Fe/SiO\textsubscript{2} supported catalyst under sonication and it showed higher catalytic activity for the Fischer-Tropsch synthesis compared to the conventional Fe/silica catalyst. In the same manner Fe-Co alloys has been synthesized and tested for the dehydrogenation and hydrogenolysis of cyclohexane with higher selectivity for dehydrogenation. Sonochemically synthesized molybdenum carbide has proved to be excellent dehydrogenation catalyst with selectivity and activity comparable to those of Platinum [67]. Yu et al. [68] have synthesized pure TiO\textsubscript{2} particles using ultrasonically induced hydrolysis reaction and they have compared the photocatalytic activity of prepared samples with Degussa P25 and samples prepared by conventional hydrolysis method.

1.3 The Role of Ultrasound in Systems Under Consideration

1.3.1 Hydrogel synthesis

Most of the studies on the effects of ultrasound on polymer systems have concentrated on the depolymerizing effects of ultrasound [69]. However, the polymerization with use of ultrasound has also been studied and reported for many monomers. The conventional emulsion polymerization processes have different disadvantages such as high polydispersity of particles and instability of colloidal particles. Additionally, the separation of the initiator constituents is difficult, which may affect the purity of the final product. This problem can be eliminated by avoiding the use of chemical initiator in the reaction medium. Hence, the use of ultrasound for an initiation of emulsion polymerization has the advantage to synthesize the polymer products with high purity [70 -71]. The first use of ultrasound for polymerization was reported by Lindstrom and Lamm in 1951 [72] where acrylonitrile was polymerized in water without the use of an initiator.

There are many methods available for the synthesis of polymer hydrogels but the ultrasound technique has attracted considerable attention because of the generation of free radicals, activation of free radical initiators and physical mixing of heterogeneous emulsion/suspension in polymerization systems [73]. Ultrasound has been used for synthesis method [64]. The application of ultrasound in the isomerisation of maleic acid to fumaric acid was found to enhance the yield substantially [65].
polymerization of acrylonitrile [72], styrene [74], acrylamide [75] and acrylic acid [76]. During emulsion polymerization, ultrasound is utilized for generation of free radicals and uniform dispersion of monomer droplets. Due to the intense conditions generated by acoustic cavitation, ultrasound acts as an initiator by breaking chemical bonds of molecules and thus enhances the rate of polymerization. In case of hydrogel synthesis using the ultrasonic irradiation, the generation of free radicals due to ultrasound is responsible for initiation of the emulsion polymerization. In such processes the molecular weights of formed hydrogels is controlled by high shear gradients generated due to the acoustic cavitation. Ultrasound was successfully used for polymerization of monomers and for the synthesis of hydrogel in the absence of a chemical initiator [77]. Cass et al. [78] prepared acrylic hydrogels with ultrasonic polymerization of water soluble monomers and macromonomers. In this work ultrasound was used for generating initiating radicals in different monomer solutions using additives. Emulsion copolymerization of styrene and a cationic surfactant was done under ultrasonic environment to prepare copolymer nanolatexes without addition of any chemical initiators. In presence of ultrasonic irradiations cationic surfactant undergoes bond scission between the two alkyl and ionic groups, producing radicals to initiate the emulsion polymerization [79]. Ultrasonically irradiated emulsion copolymerization of styrene and a cationic surfactant was successfully employed to prepare copolymer nanolatexes without addition of any chemical initiators. A radical trapping experiment and gas chromatograph–mass spectrograph analysis proved that under ultrasonic irradiation, cationic surfactant undergoes bond scission between the two alkyl and ionic groups, thereby producing much more original radicals to initiate the emulsion polymerization [79]. Sonawane et al. [80] have prepared polyacrylic acid-nanoclay nanocomposite in an ultrasound environment and its utility for the removal of dye was tested. Shirsath et al. [81] synthesized a poly(acrylic acid) hydrogel composite by incorporation of kaoline clay using ultrasound assisted polymerization process as well as the conventional process. The hydrogels prepared by both the methods were used for removal of Brilliant Green dye from wastewater and it was observed that hydrogel prepared by ultrasound assisted polymerization process showed better dye removal.
1.3.2 TiO$_2$ synthesis

Ultrasound has proven to be highly efficient in the synthesis of different range of nano materials which includes high-surface area transition metals, oxides, carbides and alloys with desired particle size distribution. The extreme conditions created during ultrasonic irradiations can accelerate the hydrolysis or condensation reaction and it can induce many changes in the morphology of TiO$_2$ nano-particles during preparation [82-85]. The sonochemical method has been applied to prepare TiO$_2$ and doped nanomaterials and photocatalytic activity has been evaluated by different researchers [68, 86-89]. Yu et al. [68] synthesized pure TiO$_2$ particles using ultrasonically-induced hydrolysis reaction and compared the photocatalytic activity of prepared samples with Degussa P25 and samples prepared by conventional hydrolysis method. Neppolian et al. [86] also prepared nano TiO$_2$ photocatalysts using sol-gel and ultrasonic-assisted sol-gel methods using two different sources of ultrasonicator, i.e. a bath type and horn type. Further, the effect of ultrasonic irradiation time, power density, the ultrasonic sources (bath-type and horn-type), magnetic stirring, initial temperatures and sizes of the reactors has been investigated. Li et al. [87] used the combination of ultrasonic and hydrothermal method for preparing Fe-doped TiO$_2$ for photo-degradation of methyl orange. Zhou et al. [82] used ultrasonically-induced hydrolysis reaction for the preparation of Fe-doped TiO$_2$. Huang et al. [88-89] synthesized Fe$_x$O$_y$-TiO$_2$ via the sonochemical method. The synthesized samples were characterized by XRD, Mossbauer, Magnetic, DSC, TEM, SEM and BET measurements.

1.3.3 Calcium carbonate synthesis

Inorganic nano-particle synthesis is a growing area of research. The change in the properties of materials with nanometric scale as compared with their bulk counterpart makes them increasingly suitable for variety of applications. Castro et al. [45] have discussed the positive effect of ultrasound on crystallization process in terms of dramatic reduction in induction period, super-saturation and metastable zone. The results obtained showed that crystal size could be tailored by appropriate sonication conditions. The effective utilization of CO$_2$ gas during calcium carbonate synthesis decides the efficiency of the process. Sonawane et al. [90] have suggested an innovative method for effective micro-mixing of CO$_2$ gas and utilization of ultrasonic
power during synthesis of nano-calcite crystals using sonochemical carbonization. Ultrasonic probe was used as gas injector replacing sparger to avoid unnecessary power dissipation. Passing the gas through the probe hole significantly reduced the particle size and introducing CO$_2$ gas through the probe resulted in changing the preferred orientation of calcite crystals. In another work Sonawane et al. [91] synthesized nano-calcite with a hydrodynamic cavitation setup. As compared to conventional carbonation process the reaction rate was faster and the reactor geometry considerably influenced the particle size. Nishida [92] had used ultrasonic irradiation for studying the precipitation of calcium carbonate. In this work mainly the factors related to ultrasound such as ultrasonic intensity, horn tip size and depth of horn immersion were studied. Ultrasonic irradiation accelerated the precipitation of calcium carbonate and the precipitation rate was proportional to diameter of horn tip and ultrasonic intensity. However, they reported that the morphology and the size of the calcium carbonate crystals were not affected by the ultrasonic irradiation. He and Forssberg [93] synthesized calcium carbonate nanoparticles in the presence of ultrasound and compared the results with conventional stirring method. In this work it was concluded that the application of ultrasound resulted in supersaturation of Ca$^{2+}$ ions which may have led to a rapid nucleation of CaCO$_3$ and the improvement in the solute transfer. Additionally the different operating parameters such as temperature, Ca(OH)$_2$ slurry concentration and CO$_2$ flow rate were also investigated and it was found that smaller particles were synthesized with ultrasound.

1.3.4 Natural product extraction

Extraction of active chemical constituents from the natural sources is an important research area for chemical and pharmaceutical industries. Conventionally, different methods like solvent extraction, supercritical fluid extraction, steam distillation, hot and cold percolation etc., are used to recover the natural products. For isolating active components with maximum yield and purity from natural sources, the selection of the process is decided by the nature of compounds and raw material to be handled. Traditional techniques used for the solvent extraction of natural products are associated with high temperature operations, longer extraction times and poor extraction efficiency. These traditional techniques require large amount of organic solvents and result in lower yields as well. Many natural products are thermally unstable and may be degraded during thermal extraction. High energy consumption is
also one of the major disadvantages of conventional extraction processes [94]. Ultrasound can increase the extraction rate by improving the mass transfer rates and rupture the cell wall due to formation of microcavities which results in higher yields with lesser processing time and requires less quantity of solvent as well [95]. Different substances such as aromatic compounds, citrus compounds, proteins, sugars, natural dyes, pigments, essential oils, acids etc. are extracted using ultrasound. Apart from the improvement in yield and kinetics of extraction, the main advantage is that it requires much lower temperature and pressure conditions. This ultimately results in the decrease in the cost of the process. Vinatoru [96] has given an overview of the ultrasonically assisted extraction of bioactive principles from herbs. The article reports the important aspects of classical and non conventional extraction procedures including the use of ultrasound. Vilkhu et al. [97] also has reviewed the applications and opportunities for ultrasound assisted extraction in the food industry. Ultrasound was applied in the extraction of tannins from myrobalan nuts in order to improve the extraction efficiency, to perform the extraction under milder process conditions and to reduce the process time. The results showed a three to five fold improvement with ultrasonic output [98]. Extraction of isoflavone derivatives from freeze-dried ground soybeans was improved by ultrasound [99]. Further the use of ultrasound for the extraction of essential oil has shown to diminish the danger of thermal degradation as demonstrated during the extraction of essential oils from fresh garlic (Allium sativum) cloves [100].

1.4 Motivation and Objectives

Process intensification is becoming an immensely important area in scientific investigations in recent days and is essential for effective sustaining of the chemical process industry. Process intensification can be achieved using multifunctional equipments, increasing the rates of reactions by sophisticated equipments/operating reactor configurations or using completely newer energy sources. Among the available newer energy sources, use of sound energy or energy associated with the liquid flow, can be used to generate cavitation phenomena which can result in significant degree of process intensification [14,101]. As discussed earlier cavitation has got many advantages such as reduction in steps of reaction- one pot synthesis, reduction in time for completion of reaction, less forcing conditions, free radical generation due to dissociation of vapours, generation of local turbulence and liquid
micro circulation, increase in reaction yield, possible switching of the reaction pathways resulting in increased selectivity and increasing the effectiveness of the catalyst [29].

The basic aim of this work is to study the effect of cavitation over the following physical/chemical processes viz. hydrogel synthesis and its use for waste water remediation, synthesis of photocatalyst, ultrasonic crystallization and ultrasound assisted extraction.

Thus, the objectives of this research were:

1. To study the effect of cavitation onto the different chemical and physical processes.

2. Synthesis and characterization of polymer nanocomposite hydrogel using ultrasound assisted emulsion polymerization method and to test the feasibility of this hydrogel for the removal of dye/pollutant from the waste water. To study the combined effect of hydrogel and ultrasound for the removal of pollutant from waste water.

3. Synthesis and characterization of pure and doped TiO$_2$ catalyst by ultrasound and conventional method and to test this catalyst for the degradation of effluent. To study the effect of doping and doping content on photocatalytic degradation of a pollutant.

4. To synthesize calcium carbonate in the presence of ultrasound and to compare the particle size and morphology of the calcium carbonate particles by ultrasound and conventional process. To study the effect of different operating parameters on particle size and morphology of calcium carbonate particles for both the methods.

5. To study the ultrasound assisted extraction of the curcumin from *Curcuma amada* and its comparison with conventional extraction process. To study the effect of various operating parameters such as solvent, temperature, particle size and solid to solvent ratio on the extraction yield.

1.5 Scope of Thesis

The first chapter provides an overview of ultrasound and its applications. Basics of ultrasound, cavitation (acoustic and hydrodynamic), use of cavitation for physical and chemical transformation and its applications in various fields of chemical engineering.
are discussed in detail. Many operations such as homogeneous and heterogeneous reactions, material synthesis, nanomaterial synthesis, waste water treatment, automization, microbial cell disruption, particle breakage can be benefited by using ultrasound. The effects of ultrasound on some of the physical and chemical transformations are discussed. The brief discussion on motivation and objectives of the research work and scope of the thesis is also included in Chapter one.

The comprehensive literature review on applications of ultrasound in four systems viz. hydrogel synthesis, TiO$_2$ synthesis and its doping, calcium carbonate synthesis and ultrasound assisted extraction is reported in second chapter. In this chapter, conventional methods of hydrogel synthesis are discussed in detail and the swelling behaviour and applications of hydrogels for different applications are reported. Titanium dioxide (TiO$_2$) due to its photocatalytic activity has been extensively used for waste water treatment. Dopants, such as transitional metals are added to TiO$_2$ to improve its catalytic response and also reduce the recombination of photo generated electrons and holes. Different synthesis methods and ultrasound assisted synthesis of TiO$_2$ has been reviewed along with its applications for photocatalytic degradation. This chapter also includes the literature review on synthesis of calcium carbonate and the effect of various parameters on the particle size and morphology of calcium carbonate. Finally literature on ultrasound assisted extraction of natural products is reviewed at the end of second chapter.

Synthesis of poly(acrylic acid)-bentonite-FeCo (PAA-B-FeCo) hydrogel nanocomposite via ultrasound assisted in situ emulsion polymerization is presented in third chapter. Use of cavitations generated due to the ultrasonic irradiations during in situ emulsion polymerization improves the dispersion of bentonite-FeCo into PAA matrix. The utility of synthesized nanocomposite hydrogel was evaluated using a cationic dye, crystal violet (CV) under different operating conditions such as temperature, pH, dye initial concentration and cavitation environment. The optimum temperature was found to be 35°C and basic pH (optimum at 11) was responsible for the higher adsorption of dye due to dissociation of COO$^-$ ions at higher pH. Thermodynamic parameters for adsorption indicated that the dye adsorption onto PAA-B-FeCo hydrogel was spontaneous and endothermic in nature. The addition of exfoliated bentonite clay platelets and Fe–Co served the dual purpose of providing the mechanical strength to the hydrogel as well as increasing the adsorption capacity due
to improvement in the electrostatic interaction. Combined effect of ultrasound and hydrogel adsorption was also evaluated. It was found that the combination of hydrogel and ultrasound gives higher dye removal as compared to hydrogel adsorption alone. With hydrogel alone, 87% removal was achieved in 15 h and with combination of ultrasound 97% removal was achieved in only 5 h.

**Chapter four** presents the comparative study of synthesis of titanium dioxide nanoparticles doped with Fe and Ce using sonochemical approach and conventional doping method. The prepared samples were characterized using X-ray diffraction (XRD), FTIR, transmission electron microscopy (TEM), and particle size analysis. Spherical TiO$_2$ particles were formed by the sonochemical method and the particle size was found to be around 100–200 nm. Dopants Fe and Ce were added to TiO$_2$ to improve its catalytic activity and to reduce the recombination of electrons and holes. The effectiveness of the synthesized catalysts for the photocatalytic degradation of crystal violet dye has been reported. It has been observed that the catalysts prepared by sonochemical method exhibited higher photocatalytic activity as compared to the catalysts prepared by the conventional methods. Also the Ce-doped TiO$_2$ exhibited maximum photocatalytic activity followed by Fe-doped TiO$_2$ and the least activity was observed for undoped TiO$_2$. It was found that an optimal dosage of 0.2 g/L of 0.8 mol % Ce and 1.2 mol % Fe in TiO$_2$ resulted in higher degradation for 30 mg/L initial dye concentration. Kinetic studies established that the photo degradation followed the pseudo first-order reaction kinetics.

The continuous production of calcium carbonate (CaCO$_3$) by the precipitation method was carried out in stirred reactor under ultrasonic environment and its comparison with the conventional stirring method is reported in **Chapter five**. The effect of various operating parameters such as Ca(OH)$_2$ slurry concentration, CO$_2$ flow rate and Ca(OH)$_2$ slurry flow rate on the particle size and morphology of CaCO$_3$ was investigated. The calcite particles were characterized by Fourier transform infrared (FTIR), X-ray diffraction (XRD) and particle size analysis. The morphology was studied by using scanning electron microscopic (SEM) images. Only calcite phase of CaCO$_3$ was formed as confirmed by the characterization techniques for both the preparation methods. In most of the cases rhombohedral calcite nanoparticles were observed. The particle size obtained in the presence of ultrasonic environment was found to be smaller as compared to conventional stirring method. The particle size
decreased with an increase in the concentrations of Ca(OH)$_2$ and increased with CO$_2$ flow rate for both the methods. The particle size decreased with increased slurry flow rate.

Curcumin, 1,7-bis(4-hydroxy 3-methoxyphenyl)-1,6-heptadione-3,5-dione, is a dietary phytochemical found in the dried rhizomes of curcuma species. Curcumin is known for its antioxidant, anti-inflammatory, anti-parasitic, antiallergic, antimicrobial, anti-mutagenic and anticancer properties. Extraction of Curcumin from dried rhizomes of *Curcuma amada* is reported in **Sixth chapter**. Ultrasound-assisted extraction (UAE) was evaluated as an effective alternative to conventional extraction methods for the isolation of curcumin. The Ultrasound-assisted extraction of *Curcuma amada* powder was compared with the conventional methods of Soxhlet extraction and batch extraction. The different process parameters affecting the extraction process such as type of solvent, extraction time, extraction temperature, solid to solvent ratio, particle size, ultrasound power and ultrasound frequency were optimized with ultrasound assisted extraction. Ethanol was found to be the most suitable solvent for extraction. The yield obtained with Soxhlet extraction was considered to be 100 %. Maximum 72 % curcumin extraction was achieved in 1 h by using UAE at 35 °C temperature as compared to Soxhlet extraction for 8 h at 78 °C. The maximum extraction was obtained at optimized conditions of 35°C temperature, solid to solvent ratio of 1:25, particle size 0.09 mm, ultrasound power 250 W and ultrasound frequency of 22 kHz.

Overall conclusions of the present work and future perspectives of the current study are reported in **seventh** and **eighth chapter** respectively.

**References**


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