CHAPTER 1

INTRODUCTION

1.1 WATER

Water is an essential natural resource needed for mankind and all other living creatures. Water is necessary for living organisms, next to air. It is involved in many biological processes performed for the survival of living organisms. Water is used in domestic purposes, such as, cooking, washing clothes, cleaning the utensils and bathing. Almost, all industries need water either as a raw material or as a process utility. Today, world is facing severe scarcity of water and fortunately there is an increasing awareness among the people to conserve this precious commodity.

Natural water is seldom chemically pure. However, the organic and inorganic suspended particulate matters, gases, vapors, mists, etc present in air get dissolved in the rain water. In addition, the water gets mixed with surface pollutants and contaminants during their flow over the lithosphere. Different salts get dissolved with water when it percolates through the soil, leading to significant increase in total dissolved solids. Hence, natural water acquires many impurities, when it moves on the earth.

The industries pollute the environment in many ways. The negative impact on the environment is largely due to indiscriminate and unregulated exploitation of both renewable and non renewable resources and the use and
abuse of the environment as a sink for dumping the waste products (Bhatia 2005).

The production of chemical compounds across the world has increased tremendously. This is attributed to the growing population as well as the development of new chemical compounds for the progress of modern society. Thousands of chemical compounds are being released into the environment and many of these chemicals resist decay. Massive industrialization increases the generation of wastewaters, which pollute the surface water and ground water as well (Bhatia 2005). The problem is worse in countries like India, where the population is thickly dense.

In view of the limited availability of water for meeting the growing demand and in the interest of protecting the environment, it is essential to reduce the water consumption, reuse and recycle once used water and minimize the pollution effects on water resulted from variety of uses. Water conservation is one of the most important duties of each human to save the planet, and numerous researches are being performed globally to address this issue.

1.2 INDUSTRIAL WASTEWATER

The major source of contamination is the continuous disposal of wastewaters released from manufacturing industries into the environment. The industries use water as a raw material, heating or cooling medium, carrier for raw material and solvent. It should be noted that only a small fraction of supplied water is present in the end product, the rest are let out as wastewater. This contains unutilized raw materials, products and byproducts. The amount of such materials present mainly depends on the nature of the process employed.
These wastewaters can be disposed safely after the attainment of permitted level of contamination. When the permitted level of contamination is exceeded significantly, the characteristics of natural resources will be affected severely. The main problem stems from the waste coming from process industries due to their large volume and degree of variation.

Often industrial wastewaters are either discharged directly into the surface water bodies or else into the municipal sewers. The presence of contaminants in water causes diseases and makes water unfit for human consumption. Industrial wastewaters contain a variety of recalcitrant organic compounds which are toxic, carcinogenic and mutagenic in nature. Most of the recalcitrant compounds contain one or more aromatic rings which are generally resistant to biological treatment. All these compounds are highly persistent in the environment and have the potential to produce negative impacts to flora and fauna.

The effluents released from textile, leather, paper, plastics, etc., contain various kinds of synthetic dyestuffs. On the other hand, effluents released from pharmaceutical industries contain proteins, antibiotics, endocrine disrupting compounds, etc. Over 100 pharmaceuticals are known to be present in water up to the level of microgram per liter (Rodayan et al 2010).

1.3 TEXTILE EFFLUENT

Dyes are used to impart color to the fabrics. The dyes, in general, are resistant to biodegradation except the ones which are used in the manufacture of food stuff. The raw materials used to manufacture dyes are mainly aromatic hydrocarbons, such as, benzene, toluene, naphthalene, anthracine, pyrene, phenol, pyridine and carbazole (Patwardhan 2008). In addition to these organics, a large variety of inorganic chemicals are also used
which include sulfuric acid, oleum, nitric acid, sodium carbonate, bromine, caustic soda, sodium nitrite, hydrochloric acid, sodium carbonate, sodium bicarbonate, sodium hydrosulphite, manganese dioxide, etc.

The raw materials are converted into a large variety of derivatives or intermediate products, which are then turned into dyes. The unit processes involved in the synthesis of dyes include sulphonation, nitration, halogenation, dehydration, Friedel-Craft’s reaction, etc.

Textile and other related products constitute the second largest industry in the world placed next to the food industry. At least 10% of the world’s productive energy devoted to this industry (Moore and Ausley 2004). Synthetic dyes are one of the important classes of recalcitrant organic compounds and are frequently found in the environment due to their wide industrial applications.

Several industries, such as, food, paper, plastics, textile and cosmetics are using different synthetic dyes to color their products. Among these industries, textile industry utilizes the large portion of dyes produced. The textile industry consumes large volumes of clean and pure water in different wet processes which include washing and bleaching of natural fibers, dyeing, and finishing steps. The consumption of large amount of water and dyes leads to the discharge of large volume of effluents that are colored (Harazono and Nakamura 2005). Approximately, 10 to 15% of the overall production of dyes is released into the environment mainly through wastewater (Tan et al 2000).

A wide range of synthetic dyes are used in the industries, which can be classified on the basis of chromophore as azo, anthraquinone, acridine, arylmethane, cyanine, phthalocyanine, nitro, nitroso, quinine-imine, thiazole or xanthene dyes. The textile dyes can be classified on the basis of dyeing
process as disperse dyes, basic dyes, acid dyes, reactive dyes, direct dyes and vat dyes. Azo, anthraquinone and indigo are the major chromospheres found in commercial dyes (Ghodbane et al 2009b).

The characteristics of textile effluents mainly depend on type of dye employed, type of cloth, such as, cotton, wool, regenerated fiber and synthetic fiber and specifications of the finished cloth (Patwardhan 2008). Apart from color, dye effluents possess a high pH, alkalinity, COD, temperature and toxicity. This nature comes not only from the dye used, but also from the chemicals used in the manufacturing processes. The COD to BOD ratio was found to be very high for these effluents, which make the biodegradation difficult.

Presence of dyes in the effluent streams even in minute concentrations is highly visible and aesthetically displeasing. It affects the reoxygenation capacity of water, which causes severe damage to the living organisms (Song and Li 2009). In addition, it also reduces the sun light penetration, which affects the photosynthesis. Due to high water solubility and low degradability, dyes are identified as most problematic chemical compound present in the industrial effluent.

1.4 PHARMACEUTICAL EFFLUENT

Pharmaceutical industry plays a predominant role in the society as it produces a large group of human and veterinary medicines. This industry produces more than 10,000 speciality chemicals, which constitute the drugs required for humans and animals. The prescription and non-prescription drugs produced across the globe exceed thousands of metric tons annually (Ternes et al 2004).
Products of this industry may be classified as:

- Chemicals – antihistamines or hypnotics
- Antibiotics – narrow spectrum or broad spectrum
- Biologicals – vaccines or sera
- Animal – hormones or extracts
- Vegetable – fluid extracts

The above products are marketed in the form of tablets, pills, capsules, elixirs, extracts, tinctures, emulsions, suspensions, solutions, lotions, syrups, mixtures, sprays, ointments, etc. Some pharmaceutical units produce bulk drugs whereas others make the formulations.

Pharmaceutical industry produces medicines such as vitamins (especially B₂, B₁₂ and C), various antibiotics, organic acids, enzymes by fermentation and organic synthesis. On the other hand, some antibiotics and vitamins are produced by fungi or bacteria in large stirred tanks which contain fairly complex nutrient solution of organic constituents and minerals.

The manufacturing operations include seed production, fermentation to increase the biomass, production of the desired metabolite, filtration of the biomass, pH adjustment, removal of color from the fermented broth, extraction of the end products with solvents or on suitable resin columns, evaporation, filtration and drying. In addition to the solid wastes generated from these methods, mycelium, filter aids, liver pulp and dust from the tabletting section are produced during manufacture. Liquid wastes generated in these industries can be classified as: a) process wastes consisting mainly of used chemicals, spent formulation broth, washings and contaminated batches, b) the sanitary wastes, and c) cooling water.
The drugs manufacturing plants generate different effluents, which can be classified as (Patwardhan 2008):

a) Highly acidic, with pH less than or equal to 1.0

b) Combined wastewaters from all the manufacturing blocks, except those from intermediates

c) The floor washings from all the blocks

d) Sewage from the toilet blocks.

In addition, pharmaceutical industry wastewaters contain varying concentrations of heavy metals, such as, copper, cadmium, zinc, nickel and mercury. Treatment of real pharmaceutical effluent is troublesome due to its complex nature. This is caused due to the fact that, the wide variety of chemical compounds have been produced in the manufacturing facility. The intensity of the problem is further aggravated due to the variations in composition and concentration of the pollutants in the wastewaters (Tekin et al 2006).

The presence of pharmaceuticals in the aquatic environment is recognized as an emerging environmental concern across the world. Certain classes of pharmaceuticals like endocrine disrupting compounds (EDCs) pose a potential threat to reproductive system in humans (Bredhult et al 2007). On the other hand, pharmaceuticals like antibiotics may cause long term changes which are sometimes even irreversible to the microorganism genome.

For many other compounds, their effect on humans and other living organism has not been understood completely. The situation becomes worse when these pharmaceutical compounds are present in mixtures with other chemicals, termed as ‘cocktails’ (Halling-sorensen et al 1998). Sometimes,
the pharmaceutical compounds are metabolized into more hydrophilic molecules which find way to the surface water (Klavarioti et al 2009).

1.5 TREATMENT METHODS

The industries manufacture products which are essential for modern living. They also generate substantial quantities of wastes. Managing these wastes costs billions of dollars each year globally and these costs will continue to escalate due to the population explosion and other reasons.

However, the treatment of wastewater is essential in order to prevent the pollution of surface and ground water. In addition to this, it is highly required to satisfy the stringent act and regulations implemented by the government agencies across the world. These factors enhanced the demand for efficient and environmental friendly green technologies to treat industrial and domestic effluents. The treatment of wastewater can be carried out by physicochemical and biological processes.

The treatment of pharmaceutical and textile wastewater has always been troublesome due to its complex nature. In addition, fluctuations in wastewater composition and pollutant concentrations made the treatment process more difficult. Furthermore, these effluents create serious environmental problems as they are extremely resistant to biological degradation.

The conventional methods used for the treatment of these effluents include biological oxidation, physical and/or chemical treatment. Physicochemical methods, such as, solvent extraction, filtration, chemical oxidation, sorption, coagulation, floatation, etc., have been extensively studied by various researchers. But the decolorization of dyes by these chemical and physical methods is financially and methodologically
demanding, mostly not very effective and time consuming too (Ghodbane and Hamdaoui 2009b). The traditional methods of treating dyes through flocculation, air sparging, adsorption on activated carbon, ultra-filtration and reverse osmosis are quite ineffective because of their low molecular weight and high water solubility, and in most of these methods, the pollutant is merely transferred from water to another phase, resulting in secondary pollution (Tang et al 1997, Lachheb et al 2002, Slokar et al 1998).

On the other hand, the active ingredients present in pharmaceutical effluents are resistant to organisms, such as, bacteria, fungi (Peters 1996). This makes the pharmaceutical effluent extremely resistant to biological degradation and usually difficult to treat using conventional methods.

Several different alternatives including steam stripping, adsorption onto activated carbon, advanced oxidation processes (AOPs), etc were tested to treat these effluents. Among these, AOPs appeared to be the most promising treatment method, in terms of economic and operation aspects (Tekin et al 2006).

1.5.1 Advanced Oxidation Processes

AOPs, considered as non-waste generating technologies, are found to be more efficient on destruction and mineralization of recalcitrant organic chemical compounds present in the wastewaters. These are aqueous oxidation methods, in which highly reactive species, hydroxyl radicals, destruct the target pollutant (Klavarioti et al 2009). These radicals can be generated \textit{in situ} through one or more oxidation processes. These hydroxyl radicals are capable of oxidizing the organic pollutants non-selectively resulting in the production of carbon dioxide, water and inorganic mineral salts (Pera-Titus et al 2004).
The various AOPs were analyzed and reported in the literature for the treatment of various recalcitrant organic pollutants present in the wastewaters. The AOP was found to be more attractive due to two reasons namely diversity of technologies involved and the wide area of potential application. Key AOPs include wet oxidation, sonolysis, ozonation, Fenton’s oxidation, ultraviolet irradiation, solar visible radiation, electrolysis, etc. These oxidation technologies have the capacity to degrade bio-refractory chemical compounds, pesticides, etc, either completely or partially, most importantly at ambient conditions.

The less conventional and evolving processes include persulfate oxidation, ionizing radiation, microwaves, pulsed plasma and the ferrate agent which are employed to treat industrial wastewaters. In addition to wastewater treatment, AOPs can be employed immensely on soil remediation, municipal wastewater sludge conditioning, production of ultrapure water and volatile organic pollutant treatment and odor control.

Among these conventional AOPs, ultrasound is a relatively new process for wastewater treatment; thus it received much attention than other treatment processes. Similarly Fenton’s process is capable of producing hydroxyl radicals and is a more efficient, fast, low-cost and easy to operate technology for destructing the organic pollutants. On the other hand, the persulphate was found to be an alternative oxidant to degrade organic contaminants (Oh et al. 2009).

1.5.1.1 Sonolysis

The sonolysis can be performed through cavitation. Generally, cavitation is defined as generation of cavities, subsequent growth and collapse of these bubbles produce large magnitudes of energy over a very small area resulting in very high energy densities. In the reactor, the cavitation occurs
simultaneously at millions of locations, which generate extreme condition of very high temperature of few thousand Kelvin and pressure of few thousand atmospheres locally. In addition, free radicals are generated during cavitation, due to the dissociation of vapors entrapped within the cavities resulting in process intensification.

There are four types of cavitation, in principle, namely,

1) When the cavitation was affected by the pressure variations in the liquid caused by sound waves, usually ultrasound, the chemical changes occur. This type of cavitation is usually called acoustic cavitation.

2) Hydrodynamic cavitation is a type of cavitation produced by pressure variations caused due to the geometry of the system creating velocity variation.

3) Optic cavitation has been produced by photons of high intensity light (LASER), which ruptures the liquid continuum.

4) Particle cavitation has been produced by the beam of the elementary particles, such as, neutron beam, rupturing the liquid, as in the case of a bubble chamber.

The acoustic and hydrodynamic cavitations generate desired intensity required for chemical and/or physical processing. On the other hand, optic and particle cavitation are typically used for single bubble cavitation, which fails to induce the chemical change in the bulk liquid (Gogate and Pandit 2004). The sonolysis utilizes the benefits of acoustic cavitation.

As early as 1927, Richards and Loomis reported the chemical and biological effects caused by ultrasound irradiation (Suslick 1989). The
frequency of ultrasound ranges roughly from 18 kHz to 10 MHz, which are beyond human hearing. The three ranges of frequencies were frequently reported such as: low frequency ultrasound (20-100 kHz), medium frequency ultrasound (300-1000 kHz) and high frequency ultrasound (2-10 MHz). The low frequency ultrasound is a conventional one whereas high frequency ultrasound has been much used for diagnostic purposes (Peters 1996; Ince et al 2001).

Ultrasound waves can be focused, reflected and refracted similar to electromagnetic waves, but these ultrasound waves require a medium possessing elastic properties for propagation. In addition, ultrasound waves cannot be absorbed by molecules unlike electromagnetic waves (Vajnhandl and Marechal 2005). The acoustic energy can travel through the liquid in propagational direction which is basically a mechanical energy (Peters 1996).

Ultrasonic waves in principle consist rarefaction and compression cycles, which lead to the production of cavitation bubbles in aqueous solution. These bubbles will grow over a few cycles by entrapping the vapor present in the liquid medium to reach a critical size, leading to implosion of bubbles. There are two aspects of cavity dynamics which are of prime importance in the sonochemical reactor. These include the maximum size of the cavity achieved before violent explosion and life span of the cavity.

The life of the cavity determines the distance travelled by the cavity from its generation spot before its collapse and thus the active volume of the reactor can be estimated. The size of the bubble just before the explosion was reported to be several hundreds of micrometers and the time span for the explosion was reported to be less than 100 nanoseconds under 20 kHz irradiation (Kotronarou et al 1992). Suslick (1990) reported that the effective time span is less than 2 microseconds and after which the bubbles start to collapse.
The extreme condition produced by ultrasonic waves results in pyrolytic fragmentation of water molecules and produces hydrogen and hydroxyl radicals (Suslick 1990). In addition, various other radicals may also form (Equations 1.1 – 1.5). Further, the organic compounds present at the bubble-water interface undergo thermolytic decomposition.

\[
\begin{align*}
H_2O &\rightarrow H^+ + \cdot OH \quad (1.1) \\
O_2 &\rightarrow 2 \cdot O \quad (1.2) \\
H^+ + O_2 &\rightarrow \cdot OOH \quad (1.3) \\
O + H_2O &\rightarrow 2 \cdot OH \quad (1.4) \\
H^+ + O_2 &\rightarrow \cdot OH + O \quad (1.5)
\end{align*}
\]

Simultaneously, the dissolved solutes undergo thermal and oxidative degradation through free radical oxidation, or by a combination of thermal and oxidative degradation. In principle, sonolysis can convert the organic pollutants into carbon dioxide and water, or convert them into lower molecular compounds which are less harmful as compared to original pollutants (Gonze et al 1999).

Even though sonolysis has several advantages such as safety, cleanness, high penetrating capacity in the liquid medium, high degradation efficiency without producing secondary pollutants; it is not an attractive avenue for large scale application. This is because it requires highly expensive equipment and consumes large amount of energy. In addition, all the absorbed energy will not be transformed into physical and chemical effects.

These demerits restrict the use of sonolysis in real effluent treatment. Hence, there is a need to couple sonolysis with other AOPs to
increase the degradation efficiency and reduce the operational cost and time required. For example, sonolysis can be coupled with Fenton’s process, persulfate oxidation, sorption, etc.

1.5.1.2 Fenton’s Process

Fenton’s reaction, a homogenous catalytic oxidation process, was discovered by Fenton in 1894 (Fenton 1894). He found that alcohols can be oxidized in the presence of hydrogen peroxide and Fe(H₂O)₆²⁺. In classical Fenton’s process, aqueous ferrous ions react with hydrogen peroxide to generate hydroxyl radicals (Equations 1.6 – 1.7), which are highly reactive and non-selective in nature; oxidize the organic pollutants present in the solution.

\[
\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \cdot\text{OH} + \cdot\text{OH} \quad (1.6)
\]

\[
\cdot\text{OH} + \text{organic pollutant} \rightarrow \text{Oxidized product} + \text{H}_2\text{O} \quad (1.7)
\]

Fenton system is easy to handle and operate, and convenient to employ in the treatment of micro-pollutants, such as, pharmaceutical effluents as well as industrial effluents like textile wastewaters with high organic loading. Despite these advantages, this process has certain limitations, such as, requirement of extreme acidic conditions, high amount of sludge formation, high loss of iron and difficulty in recovering iron.
According to European Union limits, the wastewater cannot be disposed into the environment with high load of iron (>2 ppm). This problem can be minimized and the oxidizing process can be made efficient when this Fenton’s process has been carried out either in heterogeneous way or in combination with other oxidative degradation.

Further Fenton’s reaction is not a universal solution for treating the pollutants as several chemicals are recalcitrant towards Fenton’s reaction, which include acetic acid, acetone, carbon tetrachloride, methylene chloride, n-paraffins, maleic acid, malonic acid, oxalic acid, trichloroethane etc (Gogate and Pandit 2004). In addition to these chemicals, certain compounds present in the waste stream, when oxidized, may produce some of the above-mentioned compounds, which acts as a pollutant (e.g. iso-propanol may be oxidized to acetone) (Bigda 1995).

The degree of oxidation produced by Fenton’s reaction is limited as the dosage of oxidants cannot be increased beyond certain limit. This resists the applicability of Fenton’s reaction as a sole process on treating complex mixture of contaminants like industrial effluents. At the same time, Fenton’s reaction should not be underestimated as it is more capable to produce synergistic effect when it is coupled with other treatment techniques, through which the degree of oxidation can be immensely enhanced.

1.5.1.3 Persulfate Oxidation

The persulfate (S\textsubscript{2}O\textsubscript{8}\textsuperscript{2-}) is one of the strongest oxidants used in aqueous systems and has the higher oxidation-reduction potential (E\textsuperscript{0} = 2.01
V/SHE) than \( \text{H}_2\text{O}_2 \) \((E^0 = 1.76 \text{ V/SHE})\). In addition, persulfate radical has several advantages, such as, ease of storage and transport at ambient conditions, high stability, high water solubility and relatively cost effective. These advantages made persulfate as a promising alternative to conventional oxidants. However, persulfate has a disadvantage that it has limited ability to oxidize the organic pollutants independently. Reactions of persulfate with organic pollutant in water are generally slow at ambient conditions, thus activation is required to accelerate the oxidative degradation process.

The persulfate can be activated using heat, UV light or transition metal ions to produce highly reactive sulfate ions \((\text{SO}_4^{\bullet -})\). These radicals are kinetically fast and have high redox potential \((2.6 \text{ V/SHE})\). They are highly stable in water at ambient conditions than hydroxyl radicals and are harmless (Vicente et al 2011). The higher stability in water made the radical to disperse a greater distance in the bulk medium. These sulfate radicals are capable to oxidize most of the organics (Buxton et al 1988).

Even though sulfate radicals have redox potential slightly lesser than hydroxyl radicals \((2.7 \text{ V/SHE})\), sulfate radicals are more effective than hydroxyl radicals in the following terms: sulfate radicals are kinetically fast; better stability and higher transportation ability compared to hydroxyl radicals (Devi et al 2009, Baciocchi 2008).

1.5.2 Sorption

Majority of the oxidation processes fail to degrade the recalcitrant chemical compounds present in industrial effluents completely. In addition to
this drawback, it is highly difficult to implement these oxidation processes for treating large volumes of wastewater. Thus, these processes could be used to reduce the pollutant level to a certain level beyond which conventional treatment can be employed.

In the past, several conventional physical, chemical and biological methods were reported to treat the industrial effluents. Among these methods, adsorption is widely studied for the removal of color from aqueous effluents and decontamination applications. (Jain et al 2003, Ho and Mckay 2003, Derbyshire et al 2001, Dabrowski 2001; Ahmad et al 2007; Ahmad et al 2009). Adsorption has been reported to be superior to other techniques for water re-use in terms of initial cost, flexibility and simplicity of design and ease of operation (Rafatullah et al 2010).

In adsorption, contaminant is transferred from a water phase where it is dissolved, to the surface of the adsorbate and gets accumulated for its subsequent extraction or destruction. Activated carbon is the widely used adsorbent for the removal of recalcitrant organic compounds as well as residual amounts of inorganic compounds such as nitrogen, sulfides, and heavy metal. Activated carbon is widely employed due to its characteristics, such as high surface area, high adsorption capacity, micro porous structure and special surface reactivity. It is more expensive, which results in high operating cost.

Adsorption was found to be more attractive when low cost adsorbent was employed. This not only reduces the working capital but also reduces the cost incurred for regeneration, which is very much required for conventional sorbents like activated carbon. Many non-conventional low-cost
adsorbents, including natural materials, biosorbents, and waste materials from agriculture and industry, have been proposed. In order to enhance the adsorption ability, these sorbents were activated through physical and/or chemical methods.

1.5.3 Hybrid Methods

Hybridization of advanced oxidation processes was found to give better degradation compared to that of individual processes. This is due to the elimination of demerits associated with individual processes (Gogate and Pandit 2004). Several researchers employed two or three different processes simultaneously and reported remarkable improvement in degradation of pollutants.

The various combinations were tested to accelerate the production of hydroxyl radicals through the synergistic effect. The high operating cost associated with sonolysis can be minimized when it is coupled with other processes. In the case of Fenton’s process, the dosage of chemicals and formation of sludge can be minimized when it is coupled with other processes.

1.5.3.1 Sono-sorption

The inclusion of ultrasound above 20 kHz in sorption process has been found to significantly improve the process (Hamdaoui and Naffrechoux 2009). This has created an unusual condition which favors the degradation of effluent in significant manner (Entezari and Soltani 2009; Entezari et al 2008). In adsorption, diffusion of pollutant has an important role and sometimes it is a rate controlling step. The ultrasonic irradiation is efficient in
providing inter-phase mixing compared to conventional agitation methods (Entezari and Shameli 2000, Entezari and Keshavarzi 2001). In addition, ultrasonication reduces the film thickness attached to the solid phase and thus enhanced the mass transfer rate.

1.5.3.2 Sono-Fenton process

During the Fenton process, Fe$^{3+}$ (Equation 1.6) react to form a complex intermediate (Fe-OOH$^{2+}$) (Equation 1.8). This intermediate is spontaneously decomposed to produce Fe$^{2+}$ and •OOH (Equation 1.9), but this decomposition rate is much slow. This rate can be accelerated under ultrasonic irradiation. Thus regenerated Fe$^{2+}$ also catalyzes the degradation of organic pollutants. The concentration of Fe$^{2+}$ would be held constant as a function of Fe$^{3+}$ concentration. Further, combining ultrasound with Fenton process utilizes the advantages of both the processes in such a way that more hydroxyl radicals were generated and the degradation rate of organic pollutants can be accelerated.

$$\text{Fe}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe-OOH}^{2+} + \text{H}^+ \quad (1.8)$$

$$\text{Fe-OOH}^{2+} \rightarrow \text{Fe}^{2+} + \cdot\text{OOH} \quad (1.9)$$

1.5.3.3 Dual oxidant system

In dual oxidant system (DOX), two effective oxidizing agents, namely hydrogen peroxide and ammonium persulfate, were employed simultaneously to degrade the organic pollutants. In this system, the generation of persulfate radicals was assumed to be initiated by hydroxyl
radicals and similarly sulfate radicals induce the formation of hydroxyl radicals (Baciocchi 2008).

Thus, hydroxyl radicals attack the more reactive organic pollutants whereas the sulfate radicals attack the recalcitrant pollutants. These multi-radical attacks on pollutant enhanced the degradation and the overall reaction mechanism involved is given below.

\[
S_{2}O_{8}^{2-} \rightarrow 2SO_{4}^{\cdot}\quad (1.10)
\]

\[
SO_{4}^{\cdot} + H_{2}O \rightarrow H^{+} + SO_{4}^{2-} + \cdotOH\quad (1.11)
\]

\[
\cdot OH + H_{2}O_{2} \rightarrow HO_{2} + H_{2}O\quad (1.12)
\]

\[
S_{2}O_{8}^{2-} + H_{2}O_{2} \rightarrow O_{2} + HSO_{4}^{\cdot} + SO_{4}^{\cdot}\quad (1.13)
\]

\[
H_{2}O_{2} + HO_{2} \rightarrow O_{2} + H_{2}O + \cdotOH\quad (1.14)
\]

\[
SO_{4}^{\cdot} + H_{2}O_{2} \rightarrow HO_{2} + HSO_{4}^{-}\quad (1.15)
\]

Sulfate radicals can be produced from either sodium persulfate (SPS) or ammonium persulfate (APS). APS is preferred due to its higher solubility (85 g/100 ml of water) compared to SPS (73 g/100 ml of water) at 25°C. In addition to that, excess acidity can be produced even with 1% addition of APS, which is much required for the better use of iron.

1.6 SCOPE AND OBJECTIVES OF THE PRESENT INVESTIGATION

The scope of the present study was to analyze the sonolytic degradation of textile and pharmaceutical industrial effluents. In order to improve the degradation capacity, the sonolysis was coupled with other
treatment methods, such as, Fenton’s oxidation and adsorption. The objectives of the present investigation include:

- To study the treatment of textile and pharmaceutical effluents by sonolysis, Fenton’s process, sorption and persulfate oxidation.

- To study the efficacy of tea waste activated by different methods on sono-sorption of textile and pharmaceutical effluents.

- To study the effect of simultaneous application of ultrasound and Fenton’s process on sorption (sono-Fenton-sorption process) and to optimize the operating parameters.

- To study the effect of activators on persulfate oxidation and compare the performance of different activators.

- To study the effect of coupled persulfate oxidation and hydrogen peroxide oxidation (dual oxidant system) on treating the effluents.

- To study the effect of application of ultrasound irradiation on dual oxidant system (ultrasound/DOX process).