

Chapter 1- Introduction



## **1.1 General introduction**

Water is abundantly available on earth, but ~ 97% of it is trapped in oceans, ~2% trapped in glaciers, and the remaining as fresh water. It is one of the essential elements for all living organisms [1]. Nowadays, in this industrial era, these water resources are severely contaminated due to discharge of unchecked and reckless human activities. A stage will be reached that not a drop of water is drinkable if the water pollution increases at this rate. Water is a basic requirement for all anthropological activities. Wastewater effluent from various industries contains toxic pollutants that are very harmful to all types of animals and plants on the earth [2, 3]. Water pollution has become a worldwide problem and is one of the greatest threats facing humanity today. According to the UN report (2012), two-thirds of the world's population will experience severe water shortages in 2025 [4].

Organic as well as inorganic compounds are found as pollutants in ground and surface water. Major organic pollutants include halo-alkanes, hydrocarbons, alcohols, aromatic compounds, carboxylic acids, detergents, agrochemicals (herbicides and insecticides), etc. Some inorganic hazardous elements like cadmium, mercury, and lead are also found in wastewater, along with pathogens like bacteria, fungi, and viruses [5-7]. Therefore, providing safe water for mankind demands persistent efforts by the government for the conservation of natural water resources. Various stringent environmental regulations, such as developing advanced technologies by the industries for effective removal of pollutants, use of biodegradable products, wastewater cycle volume reduction, and its reuse, have been introduced with this objective by the government. Industry has the authorization to improve or develop new technologies that can effectively remove water pollution for wastewater reuse. It is mainly done by different wastewater treatment methods.

Traditional sewage treatment involves three stages of primary, secondary, and tertiary treatment [8]. The primary treatment involves physical removal of particles, such as sieving larger particles and debris, sedimentation, etc. This greatly reduces the water pollutants as many types of water pollutants are associated with the particles. Effluent from primary treatment undergoes secondary treatment. It is based on biological processes, viz., aerobic and anaerobic treatment processes leading to reduction of organic load (BOD) of wastewater. This treatment mainly treats activated sludge, ponds, and lagoons. Even after the first and second treatments are completed, the wastewater is not sufficient to be used as drinking water, so additional treatment is underway in the third step. Post-treatment processes use different methods depending on the pollutant's nature and the degree of separation needed. Some include coagulation/ agglomeration, chlorination, ion exchange, and membrane processes.

However, traditional treatment methods do not result in complete mineralization of the pollutants, and incomplete breakdown results in forming another type of pollutant [9]. This leads to a secondary burden on the environment, complicating the waste management problem. It is also not appropriate for handling hazardous and non-biodegradable contaminations. As a result, wastewater treatment processes are being modernized with advanced technologies such as Advanced Oxidation Processes (AOPs).

## **1.2 Advanced oxidation processes (AOPs)**

AOPs, proposed by Glaze et al. [10], can be defined as a process for the generation of highly reactive hydroxyl radicals ( $\text{OH}^{\bullet}$ ) near ambient temperature and pressure to affect water purification. AOPs can be helpful in removal of remaining pollutants (trace level) after the treatment with the conventional methods. For example, conventional methods like activated carbon adsorption involve transformation of pollutants into other phases without demineralization leading to other toxic pollutants [11]. Similarly, chemical

oxidation processes can only remove pollutants at high concentrations, and biological treatments take a long degradation time due to prolonged reaction rates. Unlike these conventional methods, AOPs do not create any secondary pollutants and mineralize the water pollutants to carbon dioxide, water and harmless inorganic salts [12]. AOPs can also be used for oxidative destruction of contaminants that are difficult to degrade, such as aromatic compounds, halogenated detergents, pesticides, etc., inorganic contaminants such as cyanide, sulfide, and nitrite can also be oxidized by AOPs [12-14]. According to the literature, AOPs can reduce the concentration of contaminants from hundreds of ppm to less than 5 ppm. It is also called 21st century treatment process due to its high degradation efficiency.

Based on the presence or absence of a light source, AOPs can be classified broadly into two types, namely, photochemical and non-photochemical processes. Photochemical AOPs use a combination of strong oxidizing agents (e.g.,  $\text{H}_2\text{O}_2$ ,  $\text{O}_3$ ) with catalysts (e.g., transition metal ions) and irradiation (e.g., ultraviolet, visible), so it is very promising for removing non-biodegradable wastewater pollutants [15]. They show a high rate of oxidation along with no secondary waste generation. However, the main disadvantages of these processes are high treatment costs, special safety requirements due to use of very reactive chemicals like ozone, hydrogen peroxide, etc., and high-energy sources (eg. UV light) [16]. Therefore, extensive research is underway to develop and improve AOPs.

In the process of AOPs highly reactive free radicals ( $\text{OH}^\bullet$ ) are generated, which are mainly responsible for the breakdown of contaminations due to their electrophilicity and non-selectivity. It is necessary to produce  $\text{OH}^\bullet$  radical continuously through photochemical or chemical reactions because of its high reactivity and exhibits very a high rate constant in the order of  $10^6$ - $10^9 \text{ M}^{-1}\text{s}^{-1}$  [17]. Due to the strong oxidizing nature of hydroxyl radical (second strongest oxidant after fluorine), it reacts with most of the

pollutants, resulting in the formation of peroxy radical, which further initiate a chain reaction, leading to the complete mineralization of the pollutant [3]. Among AOPs, photocatalysis is an attractive technology that can remove water pollutants at normal pressure and temperature by reacting with induced highly reactive free radicals.

Amongst AOPs, a photocatalytic process is an appealing technique that can eliminate pollutants/impurities at normal pressure and temperature employing oxidation triggered by free radicals, and it results in the formation of extremely reactive species, OH<sup>•</sup> radical.

### **1.3 Photocatalysis: Basic principle and its type**

There are two types of photocatalytic processes: homogeneous and heterogeneous photocatalysts. Homogeneous photocatalysts generally include: (i) photochemical irradiation in presence of UV-visible light, strong oxidizing agents (eg., ozone, hydrogen peroxide) with/without catalyst, (ii) electron beam irradiation-based processes (iii) fenton and photo-fenton based processes (iv) ultrasound assisted photocatalyst [18-21].

#### **1.3.1 Homogeneous photocatalysis**

This technique has been used in the water treatment process since 1970s. It has a single-phase system and involves oxidants to generate free radicals resulting in further degradation of organic pollutants via oxidation process. A homogenous aqueous system results in incomplete mineralization by mere primary structural changes. However, a few studies have shown encouraging results by using UV/Ozone and UV/ H<sub>2</sub>O<sub>2</sub> instead of simple light irradiation. Irradiation by UV light can result in either (i) direct photo degradation or (ii) photo-oxidation. In the direct photodegradation process, pollutants are directly excited by UV light; however, in the case of photo-oxidation, degradation is initiated mainly by hydroxyl radicals. Hydrogen peroxide, along with UV light, increases the amount of reactive hydroxyl radicals resulting in a significant improvement in the

rate and strength of the oxidation process. Some of the homogeneous photocatalysis are discussed in the following subsections:

#### **1.3.1.1 UV/hydrogen peroxide (UV/ H<sub>2</sub>O<sub>2</sub>)**

UV/H<sub>2</sub>O<sub>2</sub> process is highly efficient in mineralizing organic pollutants and thus has been widely used for the treatment of industrial wastewater such as textile effluent containing dyes and phenolic compounds [22-25]. The process involves the formation of OH<sup>•</sup> radicals from the photolytic cleavage of H<sub>2</sub>O<sub>2</sub> (Eq. 1.1), which interacts with water pollutants and breaks down.



H<sub>2</sub>O<sub>2</sub> (weak acid) is a powerful oxidant and an oxidizing agent. The rate of aqueous H<sub>2</sub>O<sub>2</sub> photolysis increases at higher pH. H<sub>2</sub>O<sub>2</sub> react with OH<sup>•</sup> (Eq. 1.2) with a maximum rate at a pH equal that is its pK<sub>a</sub> value [18].



By itself, H<sub>2</sub>O<sub>2</sub> is not a very efficient oxidizing agent for mineralization and removal of wastewater [17, 18].

#### **1.3.1.2 UV/ozone (UV /O<sub>3</sub>)**

The UV/ozone process can efficiently work for the degradation of a wide range of water pollutants. This process involves mainly two ways for the oxidation of the compounds. First is the direct reaction between the ozone and the dissolved compounds (Eq. 1.3), and second is the radical route where OH<sup>•</sup> radical reacts with the dissolved compounds. At 254 nm (UV), ozone reacts with water producing H<sub>2</sub>O<sub>2</sub> as an intermediate and further decomposes to give OH<sup>•</sup>. Apart from Eq. 1.3-1.5, OH<sup>•</sup> radicals can also be produced as per Eq. 1.6 [10, 26]:





The free radicals help in the degradation of the pollutants leading to complete mineralization. This process has been used successfully for the removal of different aromatic compounds [26-29].

### 1.3.1.3 UV/ Ozone and Hydrogen peroxide (UV/O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>)

Combination of hydrogen peroxide with UV/O<sub>3</sub> process is considered very powerful and efficient due to the dominant production of OH<sup>•</sup> radical and high rate of TOC removal [18, 30-32]. The mechanism also explains H<sub>2</sub>O<sub>2</sub> is formed due to the decomposition of ozone in the aqueous solution during the process.

### 1.3.1.4 Photo-Fenton system (UV/ Fe<sup>2+</sup>/ H<sub>2</sub>O<sub>2</sub>)

The Photo-Fenton process is often used to degrade wastewater pollutants by adding ultraviolet light to the existing Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub> system (Fenton reagent). According to the literature, Fenton's response rate increases significantly when exposed to visible/light [33]. Fenton's reagent can readily oxidize a wide range of pollutants present in wastewater. Photo-Fenton process on combining with UV radiation show synergistic effect mainly due to photolysis of H<sub>2</sub>O<sub>2</sub> and interaction of iron with UV light, which increase the production of OH<sup>•</sup> radicals leading to increased reaction rate and complete mineralization [34-37].

Ferrous ion reacts with H<sub>2</sub>O<sub>2</sub> readily because the value of the rate constant for this reaction is very high and produces highly active free radical OH<sup>•</sup> and Fe (OH)<sup>2+</sup>, (Eq. 1.7). The complex, Fe (OH)<sup>2+</sup>, further reduced back ferrous ion (Fe<sup>2+</sup>) after interacting with UV light (Eq. 1.8). Further, Fe<sup>2+</sup> react with pollutants and form a complex with the pollutants and photoreduction process takes place (Eq. 1.9).







The light source can be solar radiation, which is a low energy photon, which significantly reduces the operating cost of the treatment [38]. Photo-Fenton system has several advantages for wastewater treatment because of mainly iron is a non-toxic and highly abundant element and environmentally benign hydrogen peroxide oxidant [39]. However, a high Fe concentration is required because it uses a single  $Fe^{2+}$  ion for each  $OH^{\bullet}$  radical production.

### **1.3.2 Heterogeneous photocatalysis**

In heterogeneous photocatalysis, a semiconductor catalyst is excited by a light source in the presence of oxygen, resulting in the formation of bound hydroxyl radicals or free holes. It helps in complete mineralization of organic pollutants[40-43]. The major advantages of this process include inherent destructive nature, involvement of mass transfer, requirement of ambient conditions and can also be carried out in near part of solar spectrum, and complete mineralization.

However, involvement of different phases (solid catalyst in a liquid or gaseous mixtures) for the distribution and utilization of light energy makes this process more complex than a homogeneous process. The heterogeneous photocatalytic reaction requires three components viz., a photon of suitable wavelength, surface of a catalytic which is usually a semiconductor material, and a strong oxidizing agent (usually oxygen). It can be used in different reactions like organic synthesis, metal deposition, splitting of water, water detoxification, transfer of hydrogen, disinfection, anti-cancer therapy, and gaseous pollutant removal. Semiconductors are inexpensive, non-toxic, have a high surface area, exhibit broad absorption spectra with high absorption coefficients, and open for

multielectron transfer reaction processes. Their continued use is possible without substantial loss in photocatalytic activity, and they can regain their native activity after repeated catalytic cycles [44, 45]. They also have tunable properties that can be altered by doping, reduction of size, sensitization, etc. Therefore, semiconductor oxides are widely used in photocatalysis.

#### **1.4 Sonolysis**

Recently, Sonolysis is widely used to treat water pollutants. Ultrasound waves are used in this process, and their frequency refers to more than 16 kHz. The maximum frequency for ultrasound waves is about 5 MHz in gaseous medium and 500MHz in solid /liquid medium. Power ultrasound waves lie between the range of 20 to 100 kHz, and frequencies up to 1 MHz are called high frequency or diagnostic frequencies [46].

Sonolysis of water pollutants is a new field of research, and the effects of ultrasound on the material were first discovered in 1894 by British naval engineers [47]. Ultrasound is a longitudinal wave made up of negative (rarefaction) and positive (compression) pressure regions produced by rotating a propeller. It creates hydrodynamic cavitation by generating alternate cycles of compression and rarefaction. In the cavitation process, there are three steps occur, namely, bubble formation, growth and collapsing in the liquid. The cavitation process begins when a new surface or cavity is created in the fluid. The cavity represents a finite volume that is empty or filled with gas, and at least part of the boundary must be fluid. When the bubbles collapse, it induces a high pressure and temperature (supercritical condition) inside the cavity. The collapsing cavity can generate a temporary condition with a temperature of about ~5000 K in the cavity, and it can also acquire a temperature up to ~2100 K and 500 atmospheres at the bubble liquid interface [47].

On applying ultrasound to the solution, bubbles are produced, as shown in Fig.1.1. During the expansion phase, bubbles oscillate and increase in diameter resulting in the growth of the bubble; however, during the compression phase, bubble diameter decreases, resulting in its shrinkage. Under favorable conditions, bubbles can undergo violent collapse, generating very high pressure and temperature. This implosion results into a rapid compression which allows escape of some heat from the bubble during the process. However, the surrounding liquid can quickly quench the heated cavity [47].

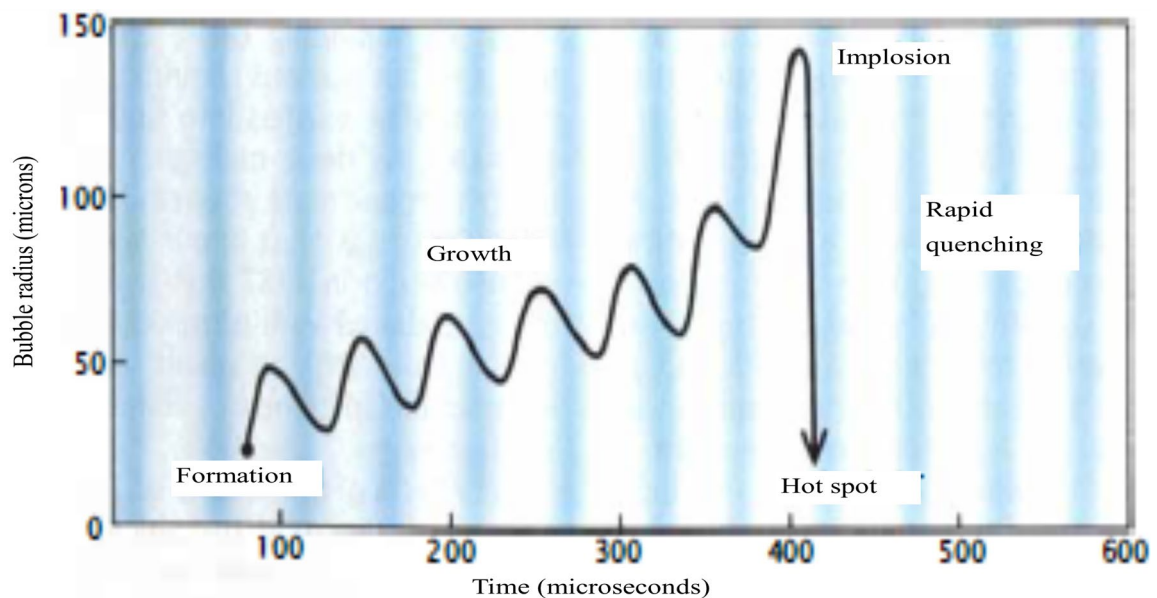


Fig. 1.1 Bubble growth and implosion phenomena [47].

Thus, ultrasound can generate enough mechanical energy leading to permanent physical changes due to cavitation process. Exposure to supersaturated solutions with an ultrasonic field accelerates bubble formation, resulting in smaller bubbles. It has been observed that a lower ultrasonic frequency in 20-30 kHz range is more effective [48]. So, it's a way to produce a variety of microreactors. Despite the local temperature and local pressure conditions created by the cavity explosion, the ultrasonic chemical reaction can

be well controlled. The nature of the reaction depends on factors such as frequency of sound, intensity of sound, temperature of bulk, static pressure, and the selection of liquid. High temperature and pressure induce due to the cavitation process leading to breakage of water molecules resulting in  $\text{H}^\bullet$  and  $\text{OH}^\bullet$  free radicals [49]. Further, these free radicals can react with  $\text{H}_2\text{O}$  and  $\text{O}_2$  during the cooling phase and resulting in production of  $\text{HO}_2^\bullet$  radicals. This cavitation property, which induces active free radicals, has been used in the sonication of water, the water pyrolysis, and responsible for the pollutant degradation [50, 51].

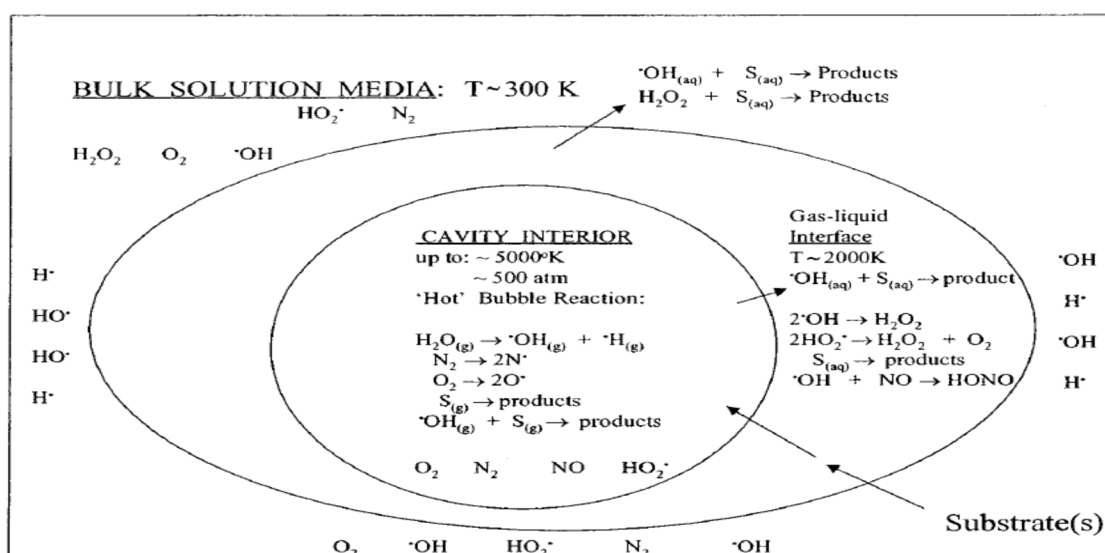
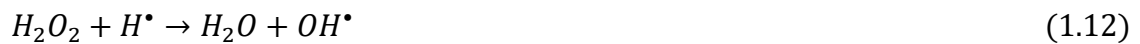


Fig. 1.2 Reaction zones in cavitation process [51].

In sonolytic process, there are three reaction zones created in the aqueous solution, as shown in Fig. 1.2. The first reaction zone is a gaseous region of cavitation bubbles where at high temperature and pressure, gaseous and hydrophobic molecules are readily decomposed by pyrolysis reactions. Here, hydroxyl radicals are formed due to water sonolysis (Eq. 1.10). The second zone is created at bubble/ liquid interface. In this zone, maximum  $\text{OH}^\bullet$  free radical available, leading to free radical reactions predominately. Although, a pyrolytic reaction also occurs due to high temperature (2000 K) and pressure

(500 atmospheres). The third zone of reaction is the bulk liquid where escaped free radicals from bubble/liquid interface take participate in degradation process and also produce hydrogen peroxide on combining hydroxyl free radicals (Eq. 1.11). Hydrogen peroxide may react with hydrogen free radical to reproduce hydroxyl free radical (Eq. 1.12).



The sonolysis of water produce highly reactive free radicals has been examined in various water pollutant degradation, sono-assisted chemical synthesis, sonolytic water splitting, and pyrolytic degradation of hydrophobic molecules [52-56].

In this work, doped-reduced graphene oxide (doped-rGO) and doped-bismuth ferrite (doped-BFO) heterojunctions were synthesized by hydrothermal and solgel method and studied its potential in the photocatalytic degradation of RhB. This work also focuses on understanding the chemical interaction between doped-rGO and doped-BFO, and its effect on photoinduced electron-hole pair recombination. Further, photocatalytic process was coupled with sonolysis process and a comparative assessment of sonocatalytic, photocatalytic and sonophotocatalytic degradation of RhB was studied.

## 1.5 Objectives

Based on the above discussions, in recent years, BFO based materials are extensively studied in the processes, namely photocatalysis, sonolysis, and sonocatalysis, as a practical approach for removing pernicious industrial pollutants from water. Although, a comparative assessment of the processes is required to explore its synergistic effect on BFO based semiconductors for the demineralization of organic pollutants from water.

From this perspective, current study is focused on synergistic effect mediated by BiFeO<sub>3</sub> based semiconductors for the degradation of rhodamine B from water. Specific objectives in accordance with the above general objectives and the corresponding activities performed to achieve them are as follows:

1. Development of nitrogen-doped graphene oxide supported bismuth ferrite (BFO/N-rGO) heterojunction for the degradation of RhB.
2. Development of nitrogen-doped graphene oxide supported Gd-doped bismuth ferrite (BGFO/N-rGO) heterojunction for the degradation of RhB.
3. Carry out a detailed characterization of photocatalysts to understand the microstructure of catalysts.
4. Studied the effect reaction parameters such as concentration of dye, pH, and catalyst loading.
5. Comparative assessment of sonocatalytic, photocatalytic and sonophotocatalytic degradation of RhB.
6. Understanding the kinetics and mechanism of the sonophotocatalytic degradation of RhB.