CHAPTER 1

INTRODUCTION

“Water is the greatest sustainer and hence is like a mother”. To survive, all plants and animals need water. There would be no life on earth if there is no water. Earth's 97% of water is unfit for human consumption and in the remaining 3%, 2% is confined as polar ice caps. The remaining 1% of fresh water present in rivers, lakes, streams and ground water is fit for human consumption. Sadly, even this 1% fresh water is under immense danger due to exploding population growth, urbanization, pollution due to waste chemicals from industries, run-off water from agricultural fields (containing pesticides, fertilizers and soil particles) and sewage from cities and rural areas (Mitch et al. 2003). Water is used in huge quantities in steel, chemicals, fertilizers, textiles, cement, electricity, petrochemicals, paper, mining, thermal power plants and food industries. Hence, the water environment has to be protected by conserving and saving water and adequate supply of water for our future generation has to be ensured. However, recycling of water consumes large amount of power, energy and money. Millions of people around the world are still deprived of clean and safe drinking water. Abundant difficulties were reported due to the scarcity of clean and fresh water (Moosdorf & Oehler 2017).

1.1 SOURCES OF WATER POLLUTION

Water, health and the environment are closely interwoven. Pollution from industrial sources, effluents from textile industries, leather
industries, agricultural sector, sewage and pharmaceutical industries threaten the reliable and safe provision of drinking water (Cramer et al. 2017). Textile mills discharge million gallons of effluents containing toxic, dark coloured organic chemicals and salts. Presence of sulphur, naphthal, vat dyes, nitrates, acetic acid, soaps, chromium compounds and heavy metals like copper, arsenic, lead, cadmium, mercury, nickel, and cobalt and certain auxiliary chemicals all collectively make the effluent highly toxic (Banat et al. 1996). Other harmful chemicals may be formaldehyde based dye fixing agents, hydro carbon based softeners and non-biodegradable dyeing chemicals in the waste water. Depletion of dissolved oxygen which is very essential for marine life in water is the most serious effect of textile waste. In addition, when this effluent is allowed to flow in the fields it clogs the pores of the soil resulting in loss of soil productivity (Verma et al. 2012).

The surface of soil gets hardened and diffusion of roots is prevented. Tannery waste typically contains a complex mixture of both organic and inorganic pollutants. Chlorinated phenols (e.g. 3, 5-dichlorophenol) and chromium are the major pollutants associated with the tanning industry (Brown & Laboureur 1983; Lofrano et al. 2003). Other pollutants of concern within the tanning industry include azo-dyes, cadmium compounds, cobalt, copper, antimony, barium, lead, selenium, mercury, zinc, arsenic, and polychlorinated bi-phenyls (PCB) (Lefebvre et al. 2006). Since tannery wastewater contains a complexity of pollutants including chromium and chlorinated phenols, it is vital to dissect the toxic nature of such wastewater to understand its environmental impacts and identify potential remediation strategies (Suganthi et al. 2013). The agriculture industry covers 76% of the land area in India. Agricultural processes such as uncontrolled spreading of slurries and manure, tillage, ploughing of the land, use of pesticides and fertilizers can cause water pollution.
Accidental spills from milk dairies can also affect the quality of water (De-Bashan et al. 2010; Alexandratos & Bruinsma 2012).

![Figure 1.1 Important sources of water pollution](http://www.waterencyclopedia.com/Po-Re/Pollution-Sources-Point-and-Nonpoint.html)

**Figure 1.1 Important sources of water pollution**

Similarly, pharmaceutical residues, hospital effluents and excretion from humans and livestock are discharged into aquatic environment causing pollution on living environment. Antibiotics have been consumed in high rate by not only humans but also by aquaculture and livestock. The antibiotic residues from various sources account for a large proportion of pharmaceutical contaminations (Archundia et al. 2017). Antibiotic residues discharged into aqueous systems have negative environmental effects even in low concentrations, including antibiotic resistance to bacteria, perturbations in ecosystems and possible risks to human health through drinking water and the food chain. Among them textile dyeing and pharmaceutical industries have created a huge pollution problem because they are the most chemically
intensive industries on earth and the major polluters of clean water (Hashmi et al. 2017).

1.2 DYES /TEXTILE WASTEWATER

Dyes are usually the first contaminant to be recognized in wastewater because they are highly visible and undesirable even in very small amounts (<1ppm for some dyes) (Robinson et al. 2001; Banat et al. 1996). Nevertheless, dyes are still widely used in many modern fields of technology. Over 100,000 commercially available dyes exist and more than $7 \times 10^5$ tons of dyes are produced annually (Pereira et al. 2003; Marco et al. 1997). It has been estimated that 10-20% of the dyes and pigments undesirably end up in wastewater during dying processes.

Figure 1.2 Effluents from dye industry

Dyes make up an abundant class of organic compounds characterized by the presence of unsaturated groups (Chromophores) such as \(-\text{C}=\text{C}^-\), \(-\text{N}=\text{N}^-\) and \(-\text{C}=\text{N}^-\), which are responsible for color of the dyes and the
functional groups which are accountable for their fixation to fibers (-NH₂, -OH, -COOH and -SO₃H) (Molinari 2004; Subramanian et al. 2017).

Textile dyes are classified based on the type of adsorption:

(i) Direct adsorption and attachment of water-soluble dyes.

  e.g. Acid dyes, direct cotton, basic dyes, reactive dyes and disperse dyes

(ii) Adsorption of temporarily solubilized dyes converted to an insoluble form by post-treatment.

  e.g. Vat dyes and Sulphur dyes.

(iii) Adsorption by the fibre which reacts to form an insoluble pigment.

  e.g. azo dyes.

The toxic impacts of textile dyeing industry effluents on plants, soil, aquatic organisms and human health are high. Hence, an immediate solution is essential to treat the textile dyeing wastewater efficiently and economically. It is also crucial to revitalize the textile industry effluent contaminated sites (Shindy 2017).

1.3 ANTIBIOTICS / PHARMACEUTICAL WASTE WATER

In the past years, the use of antibiotics worldwide has afforded substantial development in the treatment of infectious diseases (Graham et al. 2011). The deliberate release of antibiotics in the environment and lack of effective treatments of antibiotic wastewater, antibiotic pollution poses a serious environmental threat to both the aquatic and terrestrial ecosystems.
Antibiotics are a type of antimicrobial used for treating and preventing bacterial infections. Based on the pharmacological properties, the main categories of antibiotics include aminoglycoside, β-lactam, glycopeptide, macrolide, quinolone, sulphonamide, and tetracycline (TC). Untreated effluents from pharmaceutical industries and hospitals leading to water, rivers and streams are an alarming environmental concern and causes water pollution (Bekturganov et al. 2016). The primary route of the introduction of pharmaceuticals into the environment is by the excretion from humans or animals via urine or feces through the sewage system.

1.4 VARIOUS TREATMENT TECHNIQUES FOR THE DEGRADATION OF POLLUTANTS

To alleviate the water pollution by dyeing and pharmaceutical sectors, a tremendous amount of research has to be conducted at lower cost with less energy, while at the same time minimizing the use and impact of
such chemicals on the environment. Many physicochemical and conventional methods have been attempted for the treatment of harmful pollutants. The different conventional treatment techniques are discussed below:

Table 1.1 Various treatment techniques for the degradation of pollutants

<table>
<thead>
<tr>
<th>Methods</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorption</td>
<td>Good removal of a wide range of dyes</td>
<td>Adsorbent requires regeneration or disposal</td>
</tr>
<tr>
<td>Coagulation</td>
<td>Simple, economically feasible</td>
<td>High sludge production, handling and disposal problems</td>
</tr>
<tr>
<td>Flocculation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Membrane separation</td>
<td>Removes all dye types, High efficiency</td>
<td>Membrane fouling, concentrated sludge production, High cost, complex process</td>
</tr>
<tr>
<td>Ion exchange</td>
<td>Regeneration, no adsorbent loss</td>
<td>Not effective for all dyes, chemical reagents cause serious secondary pollution, expensive</td>
</tr>
<tr>
<td>Reverse Osmosis</td>
<td>Removes TDS, heavy metals, fluoride, pesticides, micro organisms</td>
<td>Low recovery, high maintenance cost, pretreatment needed</td>
</tr>
<tr>
<td>Ozonation</td>
<td>Applied in gaseous state, no alteration of volume</td>
<td>Short half-life (20 min), very expensive</td>
</tr>
<tr>
<td>Biodegradation</td>
<td>Economically attractive, publicly acceptable treatment</td>
<td>Slow process, necessary to create an optimal favorable environment, maintenance and nutrition requirements</td>
</tr>
</tbody>
</table>

Although many conventional treatments are available to degrade these hazardous effluents, they have certain limitations. However, advance
oxidation process (AOP) involving photocatalyst is the greener route of detoxifying these carcinogens. When the detoxification is done under sunlight or ambient conditions, it will have an edge over other conventional techniques (Raf Dewil et al. 2017).

1.5 ADVANCED OXIDATION PROCESS (AOP)

Advanced oxidation processes (AOPs) have received increasing attention in the research and development of wastewater treatment technologies over the last two decades. These processes (e.g., Fenton process, low temperature plasma, ozonation and photocatalysis) have been successfully employed for the degradation of organic pollutants. Homogeneous and heterogeneous advanced oxidation processes (AOPs) have been investigated in the area of wastewater treatment. To activate the AOPs, ultraviolet (UV) or visible light, different oxidants (O₂, H₂O₂, O₃), catalysts (TiO₂) are necessary. During the activation process, hydroxyl radicals (·OH) are generated which are very reactive species from adsorbed dissolved oxygen to the degradation of organic compounds (Fujioka et al. 2017). Treatment using Advanced Oxidation Process (AOP) has proven to be a promising technology by various researchers for the degradation of harmful pollutants such as dyes, antibiotics, insecticides, endocrine disruptors, phenols etc (Fenton 1894; Safarzadehet – Amiri et al. 1996; Ollis & Al-Ekabi 1993; Hoigne 1998).

Advanced Oxidation Processes include the following methods:

Among the different AOPs, photo catalysis has been successfully applied to a variety of environmental problems such as water and air purification.
1.6 PHOTOCATALYSIS

Photocatalysis makes use of both light and catalyst. Photocatalysts absorb light quanta when UV or visible light shines on them and increase the reaction rate by forming highly reactive oxidizing radicals. Water treatment using photocatalytic technology has attracted much attention in recent years (Yin et al. 2010). The field of photocatalysis has grown enormously since the demonstration of photocatalytic water splitting on TiO$_2$ by Fujishima and Honda (1972).

Advantages of photocatalysis are: (i) substitute for the energy intensive conventional treatment techniques (ii) results in the formation of harmless products (iii) wide number of pollutants can be detoxified (iv) Pollutants in any physical state (solid, liquid and gas) can be treated by this method (v) Mild reaction conditions and recovery of the catalysts make this technique a greener one and hence does not burden the environment (vi)
converts the pollutants into CO$_2$ and mineral salts, secondary waste generation is minimal.

Source: http://www.airrevolution.co.za/research.html

**Figure 1.5 Mechanism involved in Photocatalysis**

### 1.7 SEMICONDUCTOR PHOTOCATALYSIS

Semiconductor photocatalysis as a “green” technology has been widely used for the treatment of polluted water. But most of the semiconductors suffer from their intrinsic limitations (band gap > 3.1 eV) and hence only ultraviolet radiation can be utilized. In this respect, developing a photocatalyst that efficiently extends photocatalytic activity into visible region for environmental remediation has become a great challenge and one of the most active research topics in photocatalysis. Usually, photo degradation reactions are carried out in heterogeneous systems. The ability to reuse the suspended ultrafine photocatalysts after degradation can result in substantial cost savings (Raf Dewil 2017).

Semiconductor photocatalysts (e.g., TiO$_2$, ZnO, Fe$_2$O$_3$, CdS and ZnS) are often used as photocatalysts due to their favorable electronic structure. They have filled valence band and empty conduction band. When a photon with energy of $hv \geq E_g$ is incident on semiconductor, electrons are promoted from the valence band (VB) to the conduction band (CB) leaving
holes ($h^+$) behind. Excited electrons and holes can recombine to dissipate the input energy as heat, and get trapped in metastable surface states or react with electron acceptors and electron donors adsorbed on the photo catalyst surface. The former process namely recombination is to be prevented and the later process of trapping the electron is to be enhanced for successful degradation. The electron can react with $O_2$ to produce super oxide radical ($O_2^{\cdot -}$) and the hole can react with $OH^-$ ion to produce hydroxyl radical ($OH^\cdot$). Then, these free radicals produced on the photo catalyst surface react with the organic pollutants and oxidize them to $CO_2$, $H_2O$ and mineral salts (Boer 1990; Kudo & Miseki 2009).

1.8 MECHANISM OF PHOTOCATALYSIS

The mechanism of semiconductor photocatalysis involves following steps. When semiconductors are excited by photons with energy equal to or higher than their band gap energy level, electrons receive energy from the photons and are thus promoted from VB to CB if the energy gain is higher than the band gap energy level (Jiuqing wen et al. 2017).

![Figure 1.6 Band gap energy diagram of TiO$_2$ particle](image)
The overall processes in photocatalysis can be described by the following independent steps:

(i) Mass transfer of reactants from the bulk phase to the catalyst surface
(ii) Adsorption of the reactants
(iii) Photon absorption from light source by the catalyst
(iv) Electrons (e⁻) and holes (h⁺) formation
(v) Photo generated charges are transferred to the catalyst surface and induce reaction.
(vi) Product desorption.
(vii) Mass transfer of the products from the interfacial region to the bulk fluid.

1.9 TITANIUM DIOXIDE (TiO₂)

TiO₂ has been the widely studied material among various semiconductors due to its chemical stability, non-toxicity and high photocatalytic activity for the degradation of large number of pollutants such as dyes, phenols and endocrine disruptors (Sayama et al. 2010; Leena et al. 2017). Titanium dioxide is typically an n-type semiconductor which exists in three different polymorphs; namely anatase, rutile and brookite. In all the three forms, titanium (Ti⁴⁺) atoms are co-ordinated to six oxygen (O₂⁻) atoms, forming TiO₆ Octahedra (Michael & Henderson 2011).
Anatase is made up of corner (vertex) sharing octahedra which form (0 0 1) planes resulting in a tetragonal structure. In rutile the octahedra share edges at (0 0 1) planes to give tetragonal structure and in brookite both edges and corners are shared to give an orthorhombic structure (Gong & Selloni 2007). Three polymorphs of titanium dioxide are shown in Figure 1.7.

1.10 BISMUTH VANADATE (BiVO$_4$)

Among various semiconductors, Bismuth Vanadate (BiVO$_4$) has been utilized in the degradation of pollutants due to its excellent physico-chemical and photocatalytic properties. BiVO$_4$ has been used in various fields such as environmental clean-up, hydrogen production, etc. (Huabing et al. 2016). It occurs naturally as the rare minerals pucherite, clinobisvanite and dreyerite. BiVO$_4$ exists in three different polymorphs namely monoclinic scheelite, tetragonal scheelite and tetragonal zircon respectively.
In the monoclinic phase, BiVO$_4$ is an n-type photoactive semiconductor with a band gap of 2.4 eV and acts as a very good water splitting catalysts when doped with W and Mo. BiVO$_4$ photo anodes have been demonstrated to have a record solar-to-hydrogen conversion efficiency of 5.2% (highest for metal-oxide photo-electrode) with the advantage of cheap material (Sleight et al. 1979). BiVO$_4$ has attracted considerable attention due to its photocatalytic activity under visible light irradiation. However, due to reduced photocatalytic activity, poor adsorptive performance and the difficulty of migrating photo generated electron–hole pairs, the wide applications of BiVO$_4$ are restricted in the photocatalytic degradation of organic contaminants.

1.11 NICKEL TUNGSTATE (NiWO$_4$)

NiWO$_4$ have attracted much attention due to its shape and size dependent properties such as magnetic, optical and electronic properties. It also has good catalytic and biological properties (Wang et al. 1992). Ni$^{2+}$ has small ionic radius (0.69 Å) and belongs to the wolframite-type monoclinic
phase. In NiWO$_4$, tungsten atom adopts an overall six-fold coordination (Siti Murni et al. 2013).

![Image of NiWO$_4$ structure]

**Figure 1.9** Structure of NiWO$_4$

NiWO$_4$ is used as gas sensors, optical fibres, humidity sensors and pigments. NiWO$_4$ has many advantages, such as low cost, environmental friendliness, and excellent electrochemical performance and hence it is potential photocatalyst for the detoxification of contaminants. However, its poor adsorption rate, lower surface area and faster recombination rate of charge carriers limit the use of NiWO$_4$ as photocatalyst. To overcome these issues, NiWO$_4$ has been supported with reduced graphene which has the surface area $> 260$ m$^2$ g$^{-1}$ and also has the ability to transport the electron from the conduction band of the photocatalyst to oxygen to generate highly reactive oxidizing species such as superoxide radicals.
1.12 DEVELOPMENT OF PHOTOCATALYST

The development of visible light-driven photocatalysts has attracted great interest. Enormous efforts had been devoted to the studies on the red shift of various photocatalyst such as TiO$_2$, ZnO, BiVO$_4$, NiWO$_4$, etc. Various approaches such as dye sensitizing, anchoring of semiconductors with various supports, such as carbonaceous substances, zeolites, clay and ceramics, polymers and cellulosic materials, semiconductor coupling, Z-Scheme process, doping of metals and non-metals have been applied to improve the visible light activity of photocatalyst (Masakazu & Masato 2003; Pelaez et al. 2012; Akihide et al. 2011). Among these different methods, the most efficient methods were found to be non-metal doping and the usage of graphene as a catalytic support. Hence, these methods were adopted in the present research work.

1.12.1 Doping of Non-Metals

Recent investigations have revealed that the non-metal doping has shown great promise in the field of photocatalysis (Amala Infant Joice et al. 2014; Kanagaraj & Thiripuranthagan 2016; Ramakrishanan et al. 2012; Thamaraiselvi et al. 2017; Joseph et al. 2012).

Higher activity of nitrogen doped TiO$_2$ than bare TiO$_2$ was reported in the degradation of phenol by (Wang et al. 2005). Carbon modified TiO$_2$ was reported as an effective solar photo catalyst towards the degradation of Rh-B (Shao et al. 2010). (Wu et al. 2010) have reported the synergistic effects of nitrogen and fluorine doped TiO$_2$ catalysts towards the degradation of acid orange 7. The enhanced activity of multi element doped TiO$_2$ may be attributed to (i) narrow band gap (Wang et al. 2009) (ii) retardation of phase transition of TiO$_2$ by the doped element (Fagan et al. 2016) and (iii) creation of oxygen vacancies and prevention of recombination of charge carriers (Pan
et al. 2013). (Zaleska et al. 2009) studied the activity of Boron-doped TiO$_2$ and they observed the best photo activity under visible light. (Xie et al. 2007) reported F–N co doped TiO$_2$ in which F–N co-doping extended the absorbance spectra of TiO$_2$ into visible region.

![Diagram](http://pubs.rsc.org/en/Content/ArticleHtml/2016/CS/c5cs00733j)

**Figure 1.10 Electron transfer mechanism in semiconductor oxide**

### 1.12.2 Graphene as Support

Carbon plays a unique role in nature. Graphene was discovered in 2004 by a group of physicists from Manchester University, UK, led by Andre Geim and Kostya Novoselov. Graphene is the mother of all graphitic forms including zero dimensional fullerenes, one-dimensional carbon nanotubes and three-dimensional graphite. Graphene has a single layer of sp$^2$-bonded carbon atoms tightly packed into a two-dimensional honeycomb structure. It has outstanding mechanical, thermal, optical, and electrical properties. Especially, graphene possesses a high thermal conductivity ($\text{B} \ 5000 \ \text{W m}^{-1} \ \text{K}^{-1}$) and therefore offers an excellent mobility of charge carriers at room temperature.
(200000 cm$^2$ V$^{-1}$ s$^{-1}$). It also exhibits an extremely high theoretical specific surface area (B 2600 m$^2$ g$^{-1}$). To date, various methods have been developed for the preparation of graphene, including micromechanical exfoliation, epitaxial growth, chemical and electrochemical reduction of graphite oxide and bottom-up organic synthesis.

Among these methods, the reduction of exfoliated graphene oxide (GO) was proven to be an effective and reliable method to produce graphene nano sheets due to low cost and enormous scalability. Moreover, the surface properties of graphene can be adjusted via chemical modification, which offers tremendous opportunities for the development of functionalized graphene-based materials. Such graphene-based materials show unique electronic, optical properties and good biocompatibility which make these materials attractive for many potential applications including energy storage, catalysis, biosensors, molecular imaging and drug delivery.

Recently, fabrication of ultra-large mesoporous carbon with a controlled pore size and interconnected pore structure has attracted much attention in materials science. Graphitic carbons (GC) loaded on TiO$_2$ can form a TiO$_2$/C core-shell structure, which showed higher photo activity in the photocatalytic degradation of 4-chlorophenol than commercial catalyst Degussa P25 (Shanmugam et al. 2006). Similarly Graphene oxide (GO), an equivalent carbon material, has recently received considerable attention in the environmental clean-up applications as a novel cousin of graphene (Dreyer et al. 2010; Eda & Chhowalla 2010). Graphene oxide (GO), a perfectly functionalized graphene by chemical exfoliation, is a single-atom-thick sheet arranged by localized sp$^3$ defects within the sp$^2$-bonded carbon atoms in a hexagonal lattice with two-dimensional planar sheets. (Kudin et al. 2008) have reported the decolourisation of methylene blue dye using a novel chemically anchored TiO$_2$ nanoparticles on to graphene. Higher photo
catalytic activity of TiO₂/graphene was achieved due to effective charge transfer from semiconductor to graphene as shown in Figure 1.10.

![Figure 1.11 Charge transport process in TiO₂/ rGO photo Catalytic system](source)

Graphene/TiO₂ composites exhibited a better photocatalytic activity under visible light due to the existence of Ti-C and Ti-O-C bonds at the interface.

1.13 PHOTOCATALYTIC DEGRADATION OF TEXTILE DYES

The following azo dyes were chosen for photocatalytic degradation studies.

(i) Congo red (CR)

(ii) Methylene blue (MB)

1.13.1 Congo Red

Congo red (CR, Mol. Wt. 696. 66, λ max - 494 nm) is a water soluble (25 g/ l) diazo dye with the empirical formula C₃₂H₂₂N₆Na₂O₆S₂
(Colour Index No is 22120). The chemical name of congo red is sodium salt of 3, 3’- ([1,1’-biphenyl]-4,4-diyl) bis (4-aminonapthalene-1-sulfonic acid). Benzidine is a toxic metabolite of congo red, which causes cancer in the bladder of humans (Sakkas et al. 2010). Due to its intense and attractive colour, it is used to colour fabrics and it could also be used as a gamma-ray dosimeter since its coloration decays with the intensity of irradiation.

![Figure 1.12 Structure of Congo red](image)

Congo red is used as an indicator, since it turns from red-brown (in basic medium) to blue in acid (Patel & Vashi 2012). Congo red is known to be carcinogenic because of aromatic amine groups. Furthermore, the synthetic origin and complex aromatic structures of azo dyes make them highly intractable to microbial degradation and remain in the environment for a long period of time. Hence, the removal of such a dangerous compound is essential (Harshad Lade et al. 2015).

### 1.13.2 Methylene Blue

Methylene blue, also known as methylthioninium chloride is a formal derivative of phenothiazine. It is a dark green powder that yields a blue solution in water. The hydrated form has three molecules of water per unit of methylene blue. Methylene blue shows pH of 3 in water (10g/l) at 25 °C (77 °F). Methylene blue (MB, Mol. Wt. 319.85 g/mol, λ max – 664 nm) is a
water soluble (25 g/l) diazo dye with the empirical formula \(C_{16}H_{18}ClN_3S\) (Colour Index No is 52015). The chemical name of Methylene blue is [7-(dimethylamino) phenothiazin-3-ylidene]-dimethylanazanium chloride (Bergmann & O’Konski 1963).

![Figure 1.13 Structure of Methylene blue](image)

The major side effects of methylene blue includes mild bladder irritation, dizziness, headache, increased sweating, nausea, vomiting, abdominal pain, diarrhea, upset stomach, frequent urination or stomach cramps. Side effects of large doses of methylene blue include chest pain and confusion (Chan et al. 2017).

### 1.14 PHOTOCATALYTIC DEGRADATION OF ANTIBIOTICS

Among the antibiotics metronidazole and chloramphenicol are widely used compounds. Metronidazole (MTZ) (2-methyl-5-nitroimidazole-1-ethanol) is a well-known antibiotic used to treat several bacterial infections. Continuous usage of metronidazole resulted in the accumulation of this drug in fish and animals. It has also been found to be genotoxic, mutagenic and carcinogenic (Shemer et al. 2006; Fang et al. 2011). Chloramphenicol (CAP) is another kind of antibiotic and owing to its low cost and efficiency, it is used as veterinary drug in animal husbandry (Sarmah et al. 2006; Miao et al., 2016).
The following antibiotics were chosen for the present study

(i) Metronidazole (MTZ) and

(ii) Chloramphenicol (CAP)

Both the antibiotics have high water solubility and hence they have higher potential to leach into soil or runoff in surface water, resulting in soil and water pollution.

1.14.1 Metronidazole (MTZ)

Metronidazole (Mol. Wt. 171.15, λ max – 315 nm) is an antibiotic and antiprotozoal medication. Metronidazole is a nitro-imidazole antibiotic, also known novonidazol. It is a white to slightly yellow crystalline powder. Its chemical Name is 1-(6-chloro-3-pyridylmethyl)-N-nitroimidazolidin-2-ylideneamine and soluble in water (0.9 g/l). It is odorless white to pale yellow crystals or crystalline powder.

![Figure 1.14 Structure of Metronidazole](image)

Metronidazole has common side effects including a metallic taste, loss of appetite, nausea and headaches. It also has high toxicity, potential carcinogenity and mutagenicity effects and hence its removal from wastewater is a vital research issue (Derikvandi et al. 2017).
1.14.2 Chloramphenicol (CAP)

Chloramphenicol (Mol. Wt. 323.1320 g/mol, \( \lambda_{\text{max}} \) – 272 nm) is an antibiotic first isolated from cultures of Streptomyces venezuelae in 1947 but now produced synthetically. It has a relatively simple structure and was the first broad-spectrum antibiotic to be discovered. It acts by interfering with bacterial protein synthesis and is mainly bacteriostatic.

The IUPAC name of chloramphenicol is 2,2-dichloro-N-[(1R,2R)-1,3-dihydroxy-1-(4-nitrophenyl)propan-2-yl] acetamide. The structure of chloramphenicol is shown in Figure 1.14. Due to its effectiveness as well as low-cost, chloramphenicol has been widely used in animal husbandry as veterinary drug.

![Figure 1.15 Structure of Chloramphenicol](image)

The superiority of various catalysts can be understood by comparing the catalysts reported elsewhere, which is clearly shown in Table 1.2.

Table 1.2 Comparison of various catalysts reported in literature

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Quantity &amp; concentration</th>
<th>Parameters</th>
<th>Photocatalytic activity</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-TiO(_2)/NG</td>
<td>80 mg, 10 ppm</td>
<td>Degradation of MB under visible light</td>
<td>87.9% degraded in 180 minutes</td>
<td>Liu et al. 2016</td>
</tr>
<tr>
<td>S-doped TiO(_2) (BM15)</td>
<td>50 mg, 2×10(^{-5})M</td>
<td>Degradation of MB under visible light</td>
<td>4 hours</td>
<td>Ang et al. 2010</td>
</tr>
<tr>
<td>S-doped hollow TiO(_2)</td>
<td>0.5 g, 20 mg</td>
<td>Degradation of MB under solar light</td>
<td>98.6% degraded in 400 minutes</td>
<td>Chaudhuri &amp; Paria 2014</td>
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</table>
### Table 1.2 (Continued)

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Quantity &amp; concentration</th>
<th>Parameters</th>
<th>Photocatalytic activity</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-TiO₂ spheres</td>
<td>0.04 g, 2×10⁻⁵ M</td>
<td>Degradation of MB</td>
<td>60% degraded in 300 minutes</td>
<td>Chi et al. 2007</td>
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<tr>
<td></td>
<td></td>
<td>under visible light</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N- TiO₂</td>
<td>0.150 g, 30 mg</td>
<td>Degradation of MB</td>
<td>95.7% in 540 min and 92.2% in 360 min UV light</td>
<td>Mohamed et al. 2015</td>
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<tr>
<td></td>
<td></td>
<td>under UV and visible light</td>
<td></td>
<td></td>
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<tr>
<td>G- TiO₂-5%</td>
<td>100 mg, 10 mg</td>
<td>Degradation of MB</td>
<td>100% degraded in 90 minutes</td>
<td>Liu et al. 2013</td>
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<tr>
<td></td>
<td></td>
<td>under visible light</td>
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<tr>
<td>Multi element doped TiO₂</td>
<td>0.250 g, 2.5×10⁻⁴ M</td>
<td>Degradation of CR</td>
<td>83% degraded in 2 h</td>
<td>Ramakrishnan et al. 2012</td>
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<tr>
<td></td>
<td></td>
<td>under UV light</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nickel strontium titanate (NiST)</td>
<td>0.25 g, 2.5×10⁻⁴ M for UV &amp; solar, and 2.5×10⁻⁵ M for visible</td>
<td>Degradation of CR under UV, Solar and Visible light</td>
<td>100% degraded in 5.30 h</td>
<td>Joseph et al. 2015</td>
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<tr>
<td>BiVO4/5% rGO</td>
<td>0.1 g, 10 mg/ L</td>
<td>Degradation of MB</td>
<td>30 minutes</td>
<td>Wang et al. 2014</td>
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<tr>
<td></td>
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<td>under visible light</td>
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<tr>
<td>WO₃/ NiWO₄</td>
<td>200 mg, 20 ppm</td>
<td>Degradation of MB</td>
<td>92.5% degraded after 5 hours</td>
<td>Mohammed et al. 2014</td>
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<tr>
<td></td>
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<td>under UV light</td>
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<tr>
<td>ZnSnO₃</td>
<td>0.2 g, 5 mg L⁻¹</td>
<td>Degradation of MTZ under UV and visible light</td>
<td>72.5 % degraded in 180 minutes under visible light</td>
<td>Derikvandi et al. 2017</td>
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<tr>
<td>NiO/ ZnO</td>
<td>0.25 g L⁻¹, 2 mg L⁻¹</td>
<td>Degradation of MTZ under UV light</td>
<td>160 minutes</td>
<td>Dong et al. 2014</td>
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<tr>
<td>V- N doped TiO₂</td>
<td>1 g L⁻¹, 25 ppm</td>
<td>Degradation of CAP under visible light</td>
<td>120 minutes</td>
<td>Eswar et al. 2016</td>
</tr>
</tbody>
</table>

### 1.15 OBJECTIVES OF THE PRESENT WORK

The present work deals with the synthesis of graphene oxide from graphite flakes by modified Hummer’s method. Non-metals doped TiO₂, bismuth vanadate and nickel tungstate photocatalysts supported over graphene were synthesized by single step hydrothermal method. The present work is to investigate the photocatalytic activity of the synthesized catalysts towards the degradation of dyes and antibiotics under visible light irradiation. The textile dyes such as congo red, methylene blue and antibiotics such as metronidazole
and chloramphenicol were chosen for the present study. The combined effect among the components of the catalysts such as non-metals, graphene and semiconductor oxides of the photocatalyst is also discussed. The catalytic activity of the photocatalysts were evaluated and discussed based on reaction kinetics, active free radicals and half-life period of pollutants.

The main objective of the present work is to develop visible light active photocatalysts for the degradation of dyes and antibiotics.

In order to achieve the main objective, the following sub objectives were envisaged.

- To synthesize graphene oxide (GO) from graphite flakes by modified Hummer’s method.
- To synthesize nitrogen doped TiO$_2$ (NT) by hydrothermal method using urea as a nitrogen precursor.
- To synthesize reduced graphene oxide incorporated TiO$_2$ (TiO$_2$/rGO) by hydrothermal method.
- To synthesize nitrogen doped TiO$_2$/reduced graphene oxide (different weight percentages of GO) by one pot hydrothermal method.
- To synthesize nitrogen and sulphur co doped TiO$_2$ (NST) by hydrothermal method using thiourea as a precursor for nitrogen and sulphur.
- To synthesize nitrogen, sulphur co doped TiO$_2$/reduced graphene oxide (different weight percentages of GO) by single step hydrothermal method.
- To synthesize BiVO$_4$/nitrogen doped reduced graphene oxide by simple single step hydrothermal method.
To synthesize NiWO₄/nitrogen doped reduced graphene oxide by one step hydrothermal method.

To characterize the physico-chemical properties of all the synthesized catalysts by X-ray diffraction (XRD), Raman Spectroscopy, N₂ sorption measurements, Fourier transform infrared (FT-IR) spectroscopy, Diffuse reflectance ultraviolet spectroscopy (DRS-UV-vis), Field emission scanning electron microscopy (FE-SEM), High resolution transmission electron microscopy (HR-TEM), X-ray photoelectron spectroscopy (XPS), electrochemical impedance spectroscopy (EIS) and photoluminescence (PL).

To evaluate the photocatalytic activity of all the above synthesized photocatalysts towards the degradation of dyes such as CR and MB and antibiotics such as MTZ and CAP under visible light irradiation.

To propose the degradation mechanism of the dyes and antibiotics.

To determine the active radical species such as OH⁻, holes (h⁺) and O₂⁻ involved in the photocatalytic degradation reactions through trapping experiments.

To study the stability and recyclability of the most active catalyst.

To study the degradation kinetics of dyes and antibiotics.

To analyze the extent of mineralization of dyes and antibiotics using TOC analyzer.

To identify the intermediates using HPLC technique.