CHAPTER-I

Introduction
1.1: History and Principles of Photocatalysis

1.1.1: History of Photocatalysis:

We are surrounded by photochemistry everyday. We see it in the green color of grass and leaves. Photocatalysis in particular has become an increasingly important field and a heavily researched topic by all fields of science, including physicists, chemists, and surface scientists, and is pursued today to solve an ever-widening variety of environmental problems. The term photocatalysis has been used since the year 1920, although the name itself has drawn scrutiny since it incorrectly implies a catalytic reaction driven by light. Photocatalysis, however, broadly defines a photoreaction that is accelerated by the presence of a catalyst. In the mid of year 1920, the semiconductor ZnO began attracting attention for use as a sensitizer for the decomposition of both organic and inorganic photoreactions, and TiO$_2$ was soon after investigated for its photodegradation characteristics [1]. The next major development followed in the 1950 when Markhani and Laidler performed a kinetic study of photo oxidation on the surface of zinc oxide in an aqueous suspension [2]. Most of the primitive work in semiconductor photochemistry took place in the 1960, leading to the first photoelectrochemical cell for splitting water, using TiO$_2$ and Pt coated electrodes [3]. By the 1970's researchers started to perform surface studies on photocatalysts like zinc oxide and titanium dioxide. Titanium dioxide exists in the anatase and the rutile form. Degussa P25 titanium dioxide contains both the anatase and rutile form. Curiously, this mixture long stood as the standard in photocatalysis with high reactivity. In the 1970 solar energy was being studied due to a need for more available renewable resources and environmental concerns; photochemistry was looked upon for the storage and usage of solar energy. In 1972 Fujishima and Honda [3] had a breakthrough for the photolysis of water with a semiconductor electrode, which could also be a solar powered cell. The next big breakthrough in photochemistry occurred in 1976 when Carey and Oliver developed a method for measuring the variation in quantum efficiency with intensity [4]. In the early 1980s, TiO$_2$ was used for the first time to sensitize reactions in the photomineralization of selected organics. Since that time, research in the field of photocatalysis has been
dominated by studies on the photocatalytic oxidation of organic compounds in water, although there is increased interest in oxidizing bacteria and volatile organic chemicals (VOCs) for the purpose of air purification. In the 1980 and 1990 there came an increasing concern for environmental preservation and cleanup. Over the years, many semiconductors with photocatalytic properties have been thoroughly investigated including TiO$_2$ (3.2 eV), SrTiO$_3$ (3.4 eV), CdS (2.5 eV), ZnS (3.6 eV), ZrO$_2$ (5.0 eV), V$_2$O$_5$ (2.8 eV), Nb$_2$O$_5$ (3.4 eV), SnO$_2$ (3.5 eV). However, BiOCl a relatively newer photocatalyst has so far not been investigated. BiOCl an efficient photocatalyst due to its moderate band gap, nontoxicity, high surface area, low cost, recyclability, high photoactivity, wide range of processing procedures, and its excellent chemical and photochemical stability. Thus, BiOCl could be considered an ideal photocatalyst chosen for degradation studies of organic compounds with visible light.

1.1.2: Principles of Photocatalysis:

Photocatalysis, a “green” technique, offers the potential for complete elimination of toxic chemicals in the environment through its efficiency and broad applicability [5]. Photocatalysis can be defined as the acceleration of a chemical reaction by either direct irradiation or by the irradiation of a catalyst that in turn lowers the activation energy for the primary reaction to occur [6]. In order to fully appreciate the characteristics of photocatalysis with semiconductor it is necessary to understand the basic physics of semiconductor materials. “Semiconductors” are characterized by two separate energy bands: a low energy valence band (VB) and high energy conduction band (CB) where each band consists of a spectrum of energy levels in which electrons can reside (see Fig. 1.1). The separation between energy levels within each energy band is small therefore they essentially form a continuous spectrum. The energy separation between the valence band and conduction band is called energy band gap, consist of energy levels in which electrons cannot reside. Light as energy source, can be used to excite an electron from the valence band to conduction band. When an electron in the valence band absorbs a photon, it will increase the energy of the electron and enable the electron to move into the unoccupied energy level in the conduction band. However, since the energy levels of the
valence band are lower than the conduction band, electrons in the conduction band will move back into the valence band and leave the conduction band vacant. When this occurs, energy corresponding to the difference in energy between the bands is released as photon or heat. Semiconductors exhibit photoconductivity because photons can be used to excite electrons and allow conduction process to occur [5].

![Diagram showing the basic principle of photocatalysis.](image)

**Fig. 1.1:** Basic principle of photocatalysis.

The ability of a semiconductor to undergo photoinduced electron transfer to an adsorbed particle is governed by the band energy positions of the semiconductor and the redox potential of the absorbates. From the thermodynamic point of view, adsorbed couples can be reduced photocatalytically by conduction band electrons if the lower redox potential is more negative than the conduction band, and the higher redox potential is more positive than the valence band [7, 8]. The redox potential of the valence band and the conduction band for different semiconductors varies between +4.0 and -1.5 volts versus normal hydrogen electrode (NHE) as shown in Fig. 1.2.
Fig. 1.2: Band gap positions in various semiconductors. The energy scale is indicated in electron volts using either the vacuum level (left) or the normal hydrogen electrode (NHE) (right) as a reference. [9]

The band gap energy and wavelength required to activate the catalyst that produce this gap, the radiation must be of an equal or lower wavelength than that calculated by Planck’s equation (1.1).

\[ \lambda = \frac{hc}{E_{bg}} \]  

(1.1)

where \( E_{bg} \) is the semiconductor band-gap energy, \( h \) is the Planck’s constant and \( c \) is the speed of light.

\[ SC \xrightarrow{hv > Eg} e^- + h^+ \]  

(1.2)

Semiconductor is able to degrade a wide range of organic and inorganic pollutants due to its ability to generate highly oxidizing and reducing species. This is because as a semiconductor (SC), it could be photoexcited by absorbing light of suitable wavelength to generate two types of electronic carriers, the electrons (\( e^- \)) and holes (\( h^+ \)) according to eq. 1.2.
where $h$ is the Planck's constant, $\nu$ is the frequency of light and $h\nu$ is the photon energy.

To achieve photoexcitation, $h\nu$ must be greater than $E_g$, which is known as the optical band-gap of the semiconductor [10]. $E_g$ is defined as the region devoid of energy levels as illustrated in Fig. 1.2. The resulting hole is an oxidizing agent and electron is reducing agent. The pair of photoexcited charges that occurs within a particle is called an electron-hole pair (EHP). The energy required of a photon to generate an EHP in a photocatalyst can be related to its wavelength by:

$$\lambda(\text{nm}) \leq \frac{1240}{E_g}$$  \hspace{1cm} (1.3)

In the general mechanism for the photocatalytic process, the hole can react with water to generate the hydroxyl radical and the electron can reduce molecular oxygen, hydrogen peroxide or some other oxidizing agent in the solution. The positive hole has the strong oxidation power and takes the electron from $\text{OH}^-$ (hydroxide ion) in water. At this time $\text{OH}^-$, that was taken the electron, becomes $'\text{OH}$ of very unstable condition. $'\text{OH}$ takes the electron by the strong oxidation from the nearby organic compound to become stable oneself. In this way the organic compound is decomposed by loss of the electron and finally becomes carbon dioxide and water, and emanated to an atmosphere [10].

1.2: Advanced oxidation processes (AOPs)

Various physical, chemical and biological pre-treatment and post-treatment techniques have been developed over the last two decades to remove color from dye contaminated wastewater. The biological methods based on aerobic and anaerobic digestion are proven to be markedly ineffective for handling wastewater with organics waste. Furthermore physical treatment methods such as reverse osmosis, adsorption on activated carbon and coagulation flocculation are nondestructive and merely transfer pollutants to other phase, thus causing secondary waste [11]. Merely transferring toxic materials from one medium to another is not a long term solution to the problem of hazardous waste loading on the environment. As a result, the use of alternative treatment technologies, aiming to mineralize or transform refractory molecules into others which could be further biodegraded, is a matter of reaction concern. Among them, advanced oxidation processes
(AOPs) have already been used for the treatment of wastewater containing recalcitrant organic compounds. These methods rely on the formation of highly reactive chemical species that degrade more number of organic molecules into innocuous compounds and are called “Advanced oxidation processes” (AOP’s) [12]. They have been successfully used as pretreatment methods in order to reduce the concentrations of toxic organic compounds that inhibit other wastewater treatment processes. The main mechanism of AOPs function is the generation of highly reactive free radicals. Hydroxyl radicals (HO•) are effective in destroying organic chemicals because they are reactive electrophiles (electron preferring) that react rapidly and nonselectively with nearly all electron-rich organic compounds. They have an oxidation potential of 2.80 eV and exhibit faster rates of oxidation reactions [13]. Glaze et al. [14] defined AOPs as “near ambient temperature and pressure water treatment processes which involve the generation of hydroxyl radicals in sufficient quantity to effect water purification”.

The AOPs have proceeded along one of the two routes:

- Oxidation with O2 in temperature ranges intermediate between ambient conditions and those found in incinerators wet air oxidation (WAO) processes in the region of 1–20 MPa and 200–300°C) and
- The use of high energy oxidants such as ozone and H2O2 and/or photons that are able to generate highly reactive intermediates *OH radicals. [15,16]

Promoting the use of the *OH radicals for the detoxification of water pollutants presents two main advantages:

- *OH radicals attack mostly all organic pollutants with rate constants usually in the order of 0.01 to 104 M–1 s–
- The way of production of *OH radicals can be chosen in a better compliance with the specific required treatment process.

However, the term advanced oxidation processes refer to processes in which oxidation of organic contaminants occurs primarily through reactions with hydroxyl radicals.
Hydroxyl radicals are known to be the second strongest oxidants after fluorine. The oxidation potential of the most powerful oxidants is summarized in Table 1.1.

**Table 1.1:** Oxidation potential of oxidants in water.

<table>
<thead>
<tr>
<th>Species</th>
<th>Relative Oxidation Power</th>
<th>Species</th>
<th>Relative Oxidation Power</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorine</td>
<td>3.03</td>
<td>Hypobromous acid</td>
<td>1.59</td>
</tr>
<tr>
<td>Hydroxyl radical</td>
<td>2.80</td>
<td>Chlorine dioxide</td>
<td>1.57</td>
</tr>
<tr>
<td>Atomic oxygen</td>
<td>2.42</td>
<td>Hypochlorous acid</td>
<td>1.49</td>
</tr>
<tr>
<td>Ozone</td>
<td>2.07</td>
<td>Hypoiodous acid</td>
<td>1.45</td>
</tr>
<tr>
<td>Hydrogen peroxide</td>
<td>1.78</td>
<td>Chlorine</td>
<td>1.36</td>
</tr>
<tr>
<td>Perhydroxyl radical</td>
<td>1.70</td>
<td>Bromine</td>
<td>1.09</td>
</tr>
<tr>
<td>Permanganate</td>
<td>1.68</td>
<td>Iodine</td>
<td>0.54</td>
</tr>
</tbody>
</table>

Due to its strong oxidative power, the $^\cdot$OH radical can attack the organic compound by three main mechanisms [16]:

- **Abstraction of hydrogen**
  \[
  ^\cdot\text{OH} + RH \rightarrow R^\cdot + H_2O
  \]

- **Addition reactions**
  \[
  ^\cdot\text{OH} + \text{PhX} \rightarrow \text{HOPhX}.
  \]

- **Electron transfer**
  \[
  ^\cdot\text{OH} + RH \rightarrow [R - H]^+ + \text{HO}^-
  \]

A common reaction is the abstraction of hydrogen atom to initiate a radical chain oxidation

\[
\begin{align*}
\text{RH} + ^\cdot\text{OH} & \rightarrow \text{H}_2\text{O} + R^\cdot \\
2^\cdot\text{OH} & \rightarrow \text{H}_2\text{O}_2
\end{align*}
\]
\[ \text{R}^* + \text{H}_2\text{O}_2 \rightarrow \text{ROH} + \text{HO}^* \]  
(1.6)

\[ \text{R}^* + \text{O}_2 \rightarrow \text{ROO}^* \]  
(1.7)

\[ \text{ROO}^* + \text{RH}^* \rightarrow \text{ROOH} + \text{R}^* \]  
(1.8)

The attack by the \(^{\cdot}\text{OH}\) radical, in the presence of oxygen, initiates a complex cascade of oxidative reactions leading to mineralization of the organic compound. The exact routes of these reactions are quite complex. For example, chlorinated organic compounds are oxidized first to intermediates, such as aldehydes and carboxylic acids, and finally to \(\text{CO}_2\), \(\text{H}_2\text{O}\), and the chloride ion. Nitrogen in organic compounds is usually oxidized to nitrate or to free \(\text{N}_2\), sulphur is oxidized to the sulphate. Cyanide is oxidized to cyanate, which is then further oxidized to \(\text{CO}_2\) and \(\text{NO}_3^-\). As a rule of thumb, the rate of destruction of a contaminant is approximately proportional to the rate constant for the contaminant with \(^{\cdot}\text{OH}\) radical. From Table 1.2 we can see that chlorinated alkenes are treated most efficiently because the double bond is very susceptible to hydroxyl attack. Saturated molecules (i.e., alkanes) react at a much slower rate and, therefore, are more difficult to oxidize.

Table 1.2: Reaction rate constants (\(k, \text{M}^{-1}\text{s}^{-1}\)) of ozone vs. hydroxyl radical [4]

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\text{O}_3)</th>
<th>(^{\cdot}\text{OH})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorinated alkenes</td>
<td>(10^3–10^4)</td>
<td>(10^9–10^{11})</td>
</tr>
<tr>
<td>Phenols</td>
<td>(10^3)</td>
<td>(10^9–10^{10})</td>
</tr>
<tr>
<td>N-containing organics</td>
<td>(10–10^2)</td>
<td>(10^8–10^{10})</td>
</tr>
<tr>
<td>Aromatics</td>
<td>(1–10^2)</td>
<td>(10^8–10^{10})</td>
</tr>
<tr>
<td>Ketones</td>
<td>(1)</td>
<td>(10^9–10^{10})</td>
</tr>
<tr>
<td>Alcohols</td>
<td>(10^{-2}–1)</td>
<td>(10^8–10^9)</td>
</tr>
</tbody>
</table>

AOPs can often achieve oxidative destruction of compounds refractory to conventional ozonation or \(\text{H}_2\text{O}_2\) oxidation. AOPs are suited for destroying dissolved organic contaminants such as halogenated hydrocarbons, aromatic compounds,
pentachlorophenol (PCP), nitrophenols, detergents, pesticides, etc. AOPs can also be used to oxidize inorganic contaminants such as cyanide, sulphide, and nitrite.

1.2.1: **Advanced oxidation methods:**

Several methods are available for generating *OH radicals (see Fig. 1.3).

![Fig. 1.3: The diversity of AOPs.](image)

A common limit to most of the AOP is their high demand of electricity either for ozonation, sonication, electrochemistry, etc. Photochemical oxidation processes, characterized by the generation of *OH radicals initiated by the interaction of the photons of a proper energy level with the molecules of chemical species present in the solution or with a catalyst. AOPs can be classified by the phase where the process takes place. Hence, homogeneous and heterogeneous processes can be differentiated. Non-photochemical and photochemical classifications are based on the methods for generating *OH radicals.

**(A) Non-photochemical methods:**

These AOPs involve the generation of hydroxyl radicals without using light energy. These are three well known methods for generating *OH from this classification. These can be categorized as:
(i) **Ozonation at elevated pH**

As the pH rises, the decomposition rate of ozone in water increases. Oxidation of organic species may occur due to a combination of reactions with molecular ozone and reactions with \(^*\)OH radicals. The reaction between hydroxide ions and ozone leads to the formation of super-oxide anion radical \(O_2^{-}\) and hydroperoxyl radical \(HO_2^*\). By the reaction between ozone and the super-oxide anion radical the ozonide anion radical \(O_3^-\) is formed, which decomposes immediately giving \(^*\)OH radical. Summarizing, three ozone molecules produce two \(^*\)OH radicals [17]:

\[
3O_3 + OH^- + H^+ \rightarrow 2{^*}OH + 4O_2 \quad (1.9)
\]

(ii) **Ozone + hydrogen peroxide (O\(_3\)/H\(_2\)O\(_2\)) – (peroxone)**

Addition of hydrogen peroxide to ozone can initiate the decomposition cycle of ozone, resulting in the formation of \(^*\)OH radicals [17]:

\[
H_2O_2 \rightarrow HO^- + H^+ \quad (1.10)
\]

\[
HO^- + O_3 \rightarrow HO_2^* + O_3^- \quad (1.11)
\]

The reaction continues along the indirect pathway described above and \(^*\)OH radicals are produced [18]

The combination of different reaction steps shows that two ozone molecules produce two \(^*\)OH radicals:

\[
2O_3 + H_2O_2 \rightarrow 2{^*}OH + 3O_2 \quad (1.12)
\]

(iii) **Fenton system (H\(_2\)O\(_2\)/Fe\(^{2+}\))**

The Fenton process was reported by Fenton [19] already over a hundred years ago for maleic acid oxidation:

\[
Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {^*}OH \quad (1.13)
\]

The rate constant for the reaction of ferrous ion with hydrogen peroxide is high and Fe(II) oxidizes to Fe(III) in the presence of excess amounts of hydrogen peroxide. Hydrogen
peroxide decomposes catalytically by Fe(III) and generates again hydroxyl radicals according to the reactions:

\[
\begin{align*}
Fe^{3+} + H_2O_2 & \rightarrow H^+ + Fe-OOH^{2+} \quad (1.14) \\
Fe-OOH^{2+} & \rightarrow HO_2^+ + Fe^{2+} \quad (1.15) \\
Fe^{2+} + H_2O_2 & \rightarrow Fe^{3+} + OH^- + \cdot OH \quad (1.16)
\end{align*}
\]

(B) Photochemical methods:

The oxidizing strength of hydrogen peroxide alone is relatively weak, but the addition of light enhances the rate and strength of oxidation through production of increased amounts of hydroxyl radicals. Photochemical advanced oxidation processes refer both to AOPs that need photons to initiate oxidation process and non photochemical AOPs that increase their efficiency when working with artificial or natural radiations. Conventional ozone or hydrogen peroxide oxidation of organic compounds do not completely oxidize organics to CO\textsubscript{2} and H\textsubscript{2}O in many cases [20]. In some reactions, the intermediate oxidation products remaining in the solution may be more toxic than the initial compound. Efficiency of these processes can be increased by supplementing the reaction with UV radiation. These reactions have been categorized into five main classes shown in Table 1.3:

<table>
<thead>
<tr>
<th>Method</th>
<th>Key reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>UV/H\textsubscript{2}O\textsubscript{2}</td>
<td>H\textsubscript{2}O\textsubscript{2} + hv \rightarrow 2HO\textsuperscript{-}</td>
</tr>
</tbody>
</table>
| UV/O\textsubscript{3}   | O\textsubscript{3} + hv \rightarrow O\textsubscript{2} + O\textsuperscript{(1D)} \  
O\textsuperscript{(1D)} + H\textsubscript{2}O \rightarrow HO\textsuperscript{'} + HO\textsuperscript{'} |
| UV/ H\textsubscript{2}O\textsubscript{2}/ O\textsubscript{3} | O\textsubscript{3} + H\textsubscript{2}O + hv \rightarrow O\textsubscript{2} + H\textsubscript{2}O\textsubscript{2} |
| UV/ H\textsubscript{2}O\textsubscript{2}/Fe (Photo- Fenton) | H\textsubscript{2}O\textsubscript{2} + Fe\textsuperscript{3+} \rightarrow Fe\textsuperscript{2+} + \cdot OH + OH\textsuperscript{-} \  
Fe\textsuperscript{2+} + H\textsubscript{2}O\textsubscript{2} + hv \rightarrow Fe\textsuperscript{3+} + \cdot OH + H\textsuperscript{+} |

Many waste treatment technologies utilize expensive chemicals which are usually toxic in high concentrations. For example, one type of AOPs utilizes ozone and hydrogen
peroxide for oxidizing toxic organic compounds. The use of these chemicals for drinking water treatment could be highly controversial as there are concerns of residues in the treated water. Hence, alternative treatment technologies conforming to the notion of green technology are required in water treatment. Heterogeneous photocatalysis could be a suitable and promising candidate. Photocatalysis could utilize sunlight as the energy source, which is available in abundance to initiate the photodecomposition process of pollutants [21]. The end products of this treatment process are usually harmless compounds such as carbon dioxide, water and inorganic ions. In photocatalysis with the catalyst, electrons in conduction band ($e_{CB}^-$) and holes in the valence band ($h_{VB}^+$) are produced when the catalyst is irradiated with light energy higher than its band gap energy $E_{bg}$ ($h\nu>E_{bg}$). This movement of electrons forms $e^-/h^+$ or negatively charged electron/positively charged hole pairs. The hole can oxidize organic molecules to CO$_2$ and H$_2$O shown in eqs. (1.16) to (1.23) and Fig. 1.4.

\[
\begin{align*}
    SC + h\nu & \rightarrow SC \left( e_{CB}^- + h_{VB}^+ \right) \\
    h_{VB}^+ + H_2O & \rightarrow H^+ + HO^+ \\
    h^+ + HO^- & \rightarrow HO^+ \\
    \text{Organic molecule} + h_{VB}^+ & \rightarrow \text{Oxidation products} \\
    e_{CB}^- + O_2 & \rightarrow O_2^* \\
    O_2^* + H^+ & \rightarrow HO_2^* \\
    \text{Organic molecule} + h_{VB}^+ & \rightarrow \text{Oxidation products} \\
    \text{Radicals (HO } HO_2^* \text{) + organic compounds} & \rightarrow \text{Degradation products}
\end{align*}
\]

Practically all kinds of toxic chemicals are degradable by photocatalytic oxidation. Halogenated hydrocarbons are readily mineralized. Aromatic molecules chlorinated phenols, biphenols, and even dioxins are also completely oxidized yielding CO$_2$ and HCl as final products.
The research activity over the world is mostly devoted to the photocatalytic oxidation of wastewater containing refractory and toxic organics. However, photocatalytic oxidation and other AOPs may play an important role in dealing with today’s challenging demand for new drinking water treatment technologies [14].

1.3: BiOCl, the photocatalyst and selected dyes under investigation

1.3.1: BiOCl, the photocatalyst:
Research over the last three decades has not only confirmed the capability of sunlight for detoxification and disinfection but also accelerated the natural process by the use of catalysts. Semiconductors are usually selected as photocatalysts, because semiconductors have a narrow gap between the valence and conduction bands. In order for photocatalysis to proceed, the semiconductors need to absorb energy equal to or more than its energy gap. This movement of electrons forms e⁻/h⁺ or negatively charged electron/positively charged hole pairs. The hole can oxidize donor molecules. For oxidation reactions to occur the valence band (VB) must have a higher oxidation potential than the material under consideration. Therefore, by careful selection of the semiconductor photocatalyst, a wide range of species can be treated via these AOP processes. There are a number of different semiconducting materials which are readily available, but only few are suitable
for sensitizing the photo-mineralization of wide range of pollutants. The semiconductor to be used as photocatalyst for photo-mineralization of organic pollutants must be (i) photoactive (ii) able to utilize visible and or near UV light (iii) biologically & chemically inert and (iv) photo-stable [22]. Over the years many semiconductor materials have been used for photocatalytic purposes listed in Table 1.4.

Table 1.4: Band positions of some common semiconductor photocatalysts.

<table>
<thead>
<tr>
<th>Semiconductor</th>
<th>Valence band (V vs NHE)</th>
<th>Conductance band (V vs NHE)</th>
<th>Band gap (eV)</th>
<th>Band gap wavelength (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BiOCl</td>
<td>+2.4</td>
<td>-1.1</td>
<td>3.2</td>
<td>378</td>
</tr>
<tr>
<td>TiO₂</td>
<td>+3.1</td>
<td>-0.1</td>
<td>3.2</td>
<td>387</td>
</tr>
<tr>
<td>SnO₂</td>
<td>+4.1</td>
<td>+0.3</td>
<td>3.9</td>
<td>318</td>
</tr>
<tr>
<td>ZnO</td>
<td>+3.0</td>
<td>-0.2</td>
<td>3.2</td>
<td>387</td>
</tr>
<tr>
<td>ZnS</td>
<td>+1.4</td>
<td>-2.3</td>
<td>3.7</td>
<td>335</td>
</tr>
<tr>
<td>WO₃</td>
<td>+3.0</td>
<td>+0.2</td>
<td>2.8</td>
<td>443</td>
</tr>
<tr>
<td>CdS</td>
<td>+2.1</td>
<td>-0.4</td>
<td>2.5</td>
<td>496</td>
</tr>
</tbody>
</table>

Among the possible semiconductors, BiOCl, or Bismuthoxichloride, (Eg = 3.2 eV) is often used because of their unique properties and potential applications. It is inert and resistant to corrosion, and it requires little post-processing, making it inexpensive. Bi(III)-based oxchlorides and oxide compounds have recently attracted particular interest as a photocatalyst [5]. Bismuth oxchloride (BiOCl), with a band gap of 3.2 eV, has industrial applications as a pigment in cosmetic industry, has been used as a catalyst or the oxidative cracking of hydrocarbons and also as photoluminescent and ferromagnetic material [23]. Zhang and Huang [24] reported that BiOCl exhibited better performance than TiO₂ (P25, Degussa) on photocatalytic degradation of methyl orange (MO). Chen et al [25] has also found that BiOCl exhibited high photocatalytic activities for the degradation of rhodamine B, methyl orange and phenol. Recently, Zhang et al [26] reported that BiOCl nanoparticles can be an efficient photocatalyst in decomposing...
methyl orange. This indicates that BiOCl is a potential photocatalyst. The reasons that BiOCl does so well in remediation of wastewater are based on several factors:

- The process occurs under ambient conditions.
- The formation of photocyclized intermediate products, unlike direct photolysis techniques, is avoided.
- Oxidation of the substrates to CO$_2$ is complete.
- The photocatalyst is inexpensive and has a high turnover.

The BiOCl crystal structure is displayed in Fig. 1.5. The crystal structure [24] can derive from the fluorite like (CaF$_2$) structure. Figure shows the Bi atom is coordinated with four O atoms in one base and four Cl atoms in another. The Bi and four O atoms form a tetragonal pyramid; meanwhile the Bi atom and four Cl atoms construct another tetragonal pyramid in the opposite but asymmetric direction and two pyramids are interlaced, clearly shown in Fig. 1.5(b). It can be seen that asymmetric decahedral geometry with a bismuth center is formed. The O atom coordinates with four Bi atoms and the Cl atom is bonded with four Bi atoms. The tetragonal [Bi$_2$O$_2$] slabs “sandwich” by two Cl slabs and a [Bi$_2$O$_2$Cl$_2$] layer forms which are stacked together by the nonbonding (Vander Waals) interaction. From another viewpoint, Fig. 1.5 (a) also shows that the stacking sequence of the crystal is \cdots Cl–Bi–O–Bi–Cl–Bi–O–Bi–Cl \cdots, the five-layered unit (Cl–Bi–O–Bi–Cl)$_n$ ($n$ is an integer) can be considered as a planar macromolecule’. There is a weak nonbonding interlayer (Vander Waals) interaction along the $c$ axis. Therefore, these ‘macromolecules’ tend to form layered structures and also structure is not closely packed in this direction. When one photon excites one electron from Cl 3p states to Bi 6p states in BiOCl, one pair of a hole and an excited electron appear. The BiOCl with layered structure could provide the space large enough to separate and conduct the photogenerated hole-electron pair efficiently, which could enhance their photocatalytic activities. BiOCl has an indirect-transition band-gap so that the excited electron has to travel certain k-space distance to be emitted to valence band. This reduces the recombination probability of the excited electron and the hole. Both the open (loose packed) structure and indirect transitions may benefit the hole–electron
separation and the charge transport. Thus these features are favorable to the photocatalytic reactions. [26, 27].

![Crystal structure of BiOCl](image)

**Fig. 1.5:** Crystal structure of BiOCl.

Heterogeneous photocatalysis can be carried out in various media such as gas phase, pure organic phase or aqueous solutions. The overall process is controlled by several steps like mass transfer of reactants to catalyst surface, adsorption of the reactants, light absorption creating electrons (e\textsuperscript{-}) and holes (h\textsuperscript{+}), transport of photogenerated charges to the adsorption sites, reaction of the adsorbed species, desorption and removal of the products from the catalyst surface [21]. It is of crucial importance for a photoinduced catalytic activity that the photocatalysts absorb photons and adsorb reactants simultaneously.

Upon near UV irradiation, an electron is excited from the valance band to the conduction band, and the subsequent separation of the photogenerated charge carriers occurs. Under influence of electric field, it has been suggested that the majority of the electrons are transferred to the interior of the catalyst particle. It was suggested that prolonged irradiation could result in the accumulation of electrons in the interior. This could cause the flattening of the band near the surface and the narrowing of the space charge layer, easing the transfer of electron from the interior to the surface [28].
When the conduction band $e_{(CB)}$ and valance band $h_{(VB)}^+$ recombination can occur in the bulk (reaction 1a) and/or on the surface (reaction 1b) [29]. When the $h^+$ and $e^-$ are generated following irradiation, they can take part in processes as illuminated in Fig. 1.6.

**Fig. 1.6:** Schematic illustration of the photoexcitation taking place at the catalyst surface.

When a photocatalyst is illuminated with photons with an energy exceeding the bandgap energy $E_{gb} (h\nu - E_{gp})$, an electron ($e^-$) is promoted from the valance band (VB) to the conduction band (CB) with the generation of hole in the valence band as shown in the Fig. 1.4. The resulting hole is an oxidizing agent and the electron is a reducing agent.

$$\text{BiOCl} + h\nu \rightarrow \text{BiOCl} \left( e_{CB}^- + h_{VB}^+ \right) \quad (1.25)$$

Valence band holes ($h_{VB}^+$) react with surface bound $H_2O$ or $OH^-$ to produce hydroxyl radical ($'OH$) as shown in eqs. 1.26 and 1.27.

$$\text{BiOCl} (h_{VB}^+) + H_2O \rightarrow \text{BiOCl} + H^+ + 'OH \quad (1.26)$$

$$\text{BiOCl} (h_{VB}^+) + OH^- \rightarrow \text{BiOCl} + 'OH \quad (1.27)$$
For systems in which oxidation of a compound is desired, the presence of an electron scavenger is important. The most commonly used electron scavenger is oxygen. It has been suggested that conduction band electrons (e$_{\text{CB}}^-$) reduce molecular oxygen to generate superoxide radicals (O$_2^\cdot$). O$_2^\cdot$ is suggested to be further reduced to HO$_2^\cdot$, which could lead to the formation of HO$^\cdot$ which leads to degradation products represented in eqs. 1.28 to 1.34 [30, 31].

$$\text{BiOCl} (e_{\text{CB}}^-) + O_2 \rightarrow \text{BiOCl} + O_2^- \quad (1.28)$$

$$O_2^- + H^+ \rightarrow HO_2^\cdot \quad (1.29)$$

$$\text{HO}_2^- + H^+ + \text{BiOCl} (e_{\text{CB}}^-) \rightarrow \text{H}_2\text{O}_2 + \text{BiOCl} \quad (1.30)$$

$$\text{H}_2\text{O}_2 + \text{BiOCl} (e_{\text{CB}}^-) \rightarrow \cdot\text{OH} + \text{OH}^\cdot + \text{BiOCl} \quad (1.31)$$

$$\text{Dye} + h_{\nu\text{B}}^+ \rightarrow \text{Oxidation products} \quad (1.32)$$

$$\text{Dye} + e_{\text{CB}}^- \rightarrow \text{Reduction products} \quad (1.33)$$

$$\text{Dye} + \cdot\text{OH} \rightarrow \text{Degradation products} \quad (1.34)$$

The mechanism of photosensitized oxidation or photo-assisted degradation suggests that the pathway implicated under visible light irradiation. The mechanism suggest that the adsorbed dye is excited by the visible light radiation to appropriate singlet or triplet states and further followed by electron injection from the excited dye molecule onto the conduction of the BiOCl particles, where the dye is converted to the cationic dye radicals (Dye$^\cdot$) that undergoes degradation to yield products as follows [32,33]

$$\text{Dye} + h\nu(\text{Vis}) \rightarrow _1\text{Dye}^\cdot \text{ or } _3\text{Dye}^\cdot \quad (1.35)$$

$$_1\text{Dye}^\cdot \text{ or } _3\text{Dye}^\cdot + \text{BiOCl} \rightarrow \text{Dye}^\cdot + \text{BiOCl} (e_{\text{CB}}^-) \quad (1.36)$$

$$\text{BiOCl} (e_{\text{CB}}^-) + O_2 \rightarrow O_2^{**} + \text{BiOCl} \quad (1.37)$$

$$\text{Dye}^{**} \rightarrow \text{Degradation products} \quad (1.38)$$

Cationic dye radicals react with hydroxyl ions undergoing oxidation via eqs. 1.38 and 1.39 or interacts with O$_2^{**}$, HO$_2^\cdot$, or HO$^\cdot$ species to generate intermediates that finally lead to CO$_2$ (eqs. 1.40 and 1.43)
A variety of colored compounds have been investigated to act as photosensitizers. In recent studies, it has been suggested that photosensitized degradation on semiconductor surfaces can have important applications for treating a particular class of colored pollutants such as textile dyes. Compared to other AOPs, photochemical oxidation is a very high efficiency treatment also gives no residue, stability to treat a wide range of substances, simplicity of operation and relatively inexpensive [34].

**1.3.2: Selected dyes under investigation:**

In 1856, English chemist William Henry Perkin discovered a way to produce a dye in the laboratory when he tries to synthesize quinine (the only effective antimalaria treatment present) using coal tar. Perkin's discovery showed that dyes and pigments could be produced synthetically [35]. Periodically, a numerous and wide variety of colors have flooded into the world of dye and textile.

---

![Fig. 1.7: Various dye colors.](image-url)
All aromatic compounds absorb electromagnetic energy but only those that absorb light with wavelengths in the visible range (~350-700 nm) are colored. Dyes are classified according to their chemical structure or according to the method of application. Dyes contain two groups which are responsible for their color, called chromophores and the other group is auxochromes. Chromophores, delocalized electron systems with conjugated double bonds, and auxochromes, electron-withdrawing or electron-donating substituents that cause or intensify the color of the chromophore by altering the overall energy of the electron system. Usual chromophores are -C=C-, -C=N-, -C=O, -N=N-, -NO₂ and quinoid rings, while the auxochromes are -NH₃, -COOH, -SO₃H and –OH groups. Based on chemical structure or chromophore, 20-30 different groups of dyes can be discerned. Each different dye is given a Color Index (C.I.) generic name determined by its application characteristics and its color. The Color Index discerns different application classes which are as follows [36]:

**Table 1.5: Classification of dyes based on their application.**

<table>
<thead>
<tr>
<th>Acid dyes</th>
<th>Ingrain dyes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Basic or Cationic dyes</td>
<td>Vat dyes</td>
</tr>
<tr>
<td>Direct dyes</td>
<td>Sulphur dyes</td>
</tr>
<tr>
<td>Mordant or adjective dyes</td>
<td>Disperse dyes</td>
</tr>
<tr>
<td>Azoic dyes</td>
<td>Reactive dyes</td>
</tr>
<tr>
<td>Oxidation dyes</td>
<td>Solvent dyes</td>
</tr>
</tbody>
</table>

**Table 1.6: Classification of dyes based on their Chemical Constitution.**

<table>
<thead>
<tr>
<th>Nitro dyes</th>
<th>Xanthene dyes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitroso dyes</td>
<td>Heterocyclic dyes</td>
</tr>
<tr>
<td>Azo dyes</td>
<td>Indigo dyes</td>
</tr>
<tr>
<td>Diphenylmethane dyes</td>
<td>Anthraquinone dyes</td>
</tr>
<tr>
<td>Triphenylmethane dyes</td>
<td>Sulphur dyes</td>
</tr>
<tr>
<td>Phthalein dyes</td>
<td>Phthalocyanine dyes</td>
</tr>
</tbody>
</table>
The ordinary light consists of electromagnetic radiations of varying wavelengths which can be categorized as Ultraviolet light [100-400 nm], Visible part (white light) [400-750 nm] and Infrared [750-100,000 nm] shown in Fig. 1.8.

**Fig. 1.8:** Electromagnetic radiations of varying wavelengths.

In the case of dye, there is a selective absorption in visible region and reflection in the rest of this region. There is a definite relationship between the color absorbed and color visualized with respect to a given range of wavelength. This is shown in Table 1.7 [37, 38].

**Table 1.7:** Color absorbed and color visualized with respect to wavelength regions.

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Color absorbed</th>
<th>Color visualized</th>
</tr>
</thead>
<tbody>
<tr>
<td>400-435</td>
<td>Violet</td>
<td>Yellow-green</td>
</tr>
<tr>
<td>435-480</td>
<td>Blue</td>
<td>Yellow</td>
</tr>
<tr>
<td>480-490</td>
<td>Green-blue</td>
<td>Orange</td>
</tr>
<tr>
<td>490-500</td>
<td>Blue-green</td>
<td>Red</td>
</tr>
<tr>
<td>500-560</td>
<td>Green</td>
<td>Purple</td>
</tr>
<tr>
<td>560-580</td>
<td>Yellow-green</td>
<td>Violet</td>
</tr>
<tr>
<td>580-595</td>
<td>Yellow</td>
<td>Blue</td>
</tr>
<tr>
<td>595-605</td>
<td>Orange</td>
<td>Green-blue</td>
</tr>
<tr>
<td>605-750</td>
<td>Red</td>
<td>Blue-green</td>
</tr>
</tbody>
</table>
It is interesting to note that a particular dye could be grouped in more than one group. Also, certain groups of dyes may be further classified according to their dyeing properties.

The dyes selected as sample contaminants for the present study belong to the following classes:

**Triphenylmethane Class**
This group of dyes is the oldest known synthetic groups. They are of brilliant color due to resonance of unsymmetrical triphenylcarbonium ions and cover a range of shades from red to blue, including violet and green. Most basic dyes of this series are beautiful, crystalline compounds with a reflex, the color of which is often complementary to the color in solution. However, the color fades rapidly in light and due to this reason they find less uses in textiles but are used for coloring papers, typewriter ribbons and are specially valued for in calico printing and other articles where fastness to light is not of much significance. These dyes have the quinonoid groups as their chromophores. The dye selected from this class is **Malachite green**.

**Phenoxazine Class**
This class of dyes has characteristic oxazine ring system. These dyes include basic, chrome mordant and direct dyes as well as dioxazine pigments. In these dyes the chromophore is the phenoxazonium group while oxochromes are amino or hydroxyl groups para to the ring nitrogen. These dyes range in shade from greenish to reddish blue. The possess brilliant shades, good fasteness to light and moderate fastness to washing. These dyes are chiefly applied to leather and used extensively for dyeing polyacrylonitile. The dye selected from this class is **Nile blue**.

**Phenothiazine Class**
These dyes are analogues of the oxazines, an atom of sulphur replacing oxygen in the heterocyclic ring. These dyes have phenazonium nucleus as chromophore with amino groups para to the ring nitrogen as auxochromes. These dyes have a color range from green to blue and have been used for coloring paper, tannin mordanted cotton and silk.
Fastness to light is usually only fair. Dye selected from this class is **Methylene Green** and **Methylene blue**.

**Phenazinum Class**

These are derivatives of phenazine which act as chromophore. The auxochrome may be –OH or -NH₂ group present in the para position to one of the ring nitrogen; although phenazine dyes without an auxochrome are also known, e.g. flavinduline. The complex phenazine are inexpensive blues, violets, browns and blacks. These are basic blues and may be used for wool, silk and tannin – mordant cotton. Dye selected from this class is **Neutral red**.

The details of the selected dyes and their molecular structure are shown in Table 1.8 and Fig. 1.9:

**Table 1.8:** Details of the dyes under investigation.

<table>
<thead>
<tr>
<th>Dye (C.I. number) Chemical formula</th>
<th>Synonyms</th>
<th>Chromophore</th>
<th>( \lambda_{\text{max}} ) (nm)</th>
<th>MW (g mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Malachite Green</strong> C(<em>{27})H(</em>{27})N(_2)O(_6) (42.000)</td>
<td>Basic Green</td>
<td>Triphenylmethane</td>
<td>618</td>
<td>463.5</td>
</tr>
<tr>
<td><strong>Methylene Green</strong> C(<em>{16})H(</em>{17})ClN(_4)O(_2)S (52020)</td>
<td>Basic Green 5</td>
<td>Phenothiazine</td>
<td>618</td>
<td>364.86</td>
</tr>
<tr>
<td><strong>Methylene Blue</strong> C(<em>{16})H(</em>{18})N(_3)SCl (52015)</td>
<td>Basic Blue 9, Chromosmon</td>
<td>Phenothiazine</td>
<td>663</td>
<td>373.90</td>
</tr>
<tr>
<td><strong>Nile Blue</strong> C(<em>{20})H(</em>{20})ClN(_3)O (51180)</td>
<td>Nile blue A</td>
<td>Phenoxazine</td>
<td>633</td>
<td>353.84</td>
</tr>
<tr>
<td><strong>Neutral red</strong> C(<em>{17})H(</em>{23})ClN(_4) (50040)</td>
<td>Basic Red 5</td>
<td>Phenazinum</td>
<td>540</td>
<td>288.78</td>
</tr>
</tbody>
</table>
Fig. 1.9: Molecular Structure of Selected Dyes.
1.4: Environmental impacts of present research work

The textile dyes and dye intermediates with high aromaticity and low biodegradability have emerged as major environmental pollutants. Nearly 10-15% of the dye is lost in the dyeing process and is released in the wastewater which is an important source of environmental contamination [39, 40]. Decolourization of wastewater has become one of the major issues in wastewater pollution. This is because many industries used dyes to colour their products, such as textiles, rubber, paper, plastics, leather, cosmetics, food and mineral processing industries. Especially, the textile finishing industry has a specific water consumption (approx. 1L/kg of product), part of which is due to dying and rinsing processes. Of current world production of dyestuffs of \( \approx \)10 million kg/ year between 1 and 2 million kg of active dye enter the biosphere, either dissolved or suspended in water, every year [41, 42]. Some dyes are harmful to aquatic life in rivers where they are discharged. Since, dye can reduce light penetration into the water thereby decreasing the efficiency of photosynthesis in aquatic plants and hence having adverse impact on their growth. Dyes also can cause severe damage to human beings, such as dysfunction of kidney, reproductive systems, liver, brain and central nervous system [43-45]. There are various kinds of dyes available in market such as azo, anthraquinone, triarylmethane, diarylmethane, acridine, quinine, xanthenes, and nitro dyes. These dyes are extensively used to impart color to various industrial applications [46, 47]. Synthetic dyestuffs have complex chemical structures which is not easy to degrade biologically. Dyes also usually contain elements such as nitrogen, chlorine, and sulphur. The oxidation products of these elements may be higher in toxicity than the parent molecule. Particularly, synthetic dyes contribute to special environmental concern due to their degradation products such as aromatic amines which are considered as highly carcinogenic substances. As azo dyes represent the largest class of organic colorants listed in the Color Index (60-70% of the total) and their relative share among reactive, acid and direct dyes is even higher, it can be expected that they make up the vast majority of the dyes discharged by textile-processing industries. Anthraquinone dyes are the second largest class (~15%), followed by triarylmethanes (~3%) and phthalocyanines (~2%) of the entries in the Color Index [48]. Azo dyes have found to be carcinogenic and mutagenic in nature. These dyes appear
to cause allergic or intolerance reactions, particularly amongst those with aspirin intolerance and asthma sufferers [49, 50, 48]. Cationic basic triphenylmethane dyes have found to be acutely toxic dyes for algae and fish [51]. Due to the high level risk by untreated dye effluent, many treatment methods and strategies have been used to degrade the dye and minimized the risk. The application of conventional methods; coagulation/flocculation, filtration, activated carbon adsorption, sedimentation, etc. does not totally degrade the dye effluent [52, 53]. Biological and chemical methods produced secondary pollutants that required further treatments. The photocatalytic reaction has advantage over other conventional and classical method for degradation of dyes due to its simplicity and complete degradation based on the generation of highly reactive hydroxyl radicals, appear as emerging alternatives for the mineralization of organic pollutants. Thus, it is very important to initiate the study on five selected dyes since it possessed huge threat to the environment same as the other industrial dyes application. In this study, we have used the BiOCl/Visible system to degrade all selected dyes under ambient condition of temperature and pressure leading to complete mineralization of dyes to inorganic ions.

1.5: Kinetic studies of photocatalytic degradation of dyes

Most of the kinetic studies used in photocatalysis are based on the Langmuir-Hinshelwood mechanism confirming the heterogeneous catalytic character of the system [54-56]. This law successfully explains the kinetics of reactions that occur between two adsorbed species, a free radical and an adsorbed substrate, or a surface-bound radical and a free substrate. The initial rate of substrate removal varies proportionally with the surface coverage, and the adsorption equilibrium of the substrate follows a Langmuir isotherm. Generally, the influence of the initial concentration of the solute to the photocatalytic degradation rate of most organic compounds is described by a pseudo-first kinetic order, which is rationalized in terms of the Langmuir Hinshelwood model, modified to accommodate reactions occurring at a solid-liquid interface [57].
\[
R = \frac{-dc}{dt} = \frac{k_{L-H} K_{ad} C}{(1 + K_{ad} C)}
\]

where \(k_{L-H}\) is the reaction rate constant, \(K_{ad}\) is the adsorption coefficient of dye on the surface of photocatalyst, and \(C\) is the variable concentration at irradiation time \(t\). For pseudo-first order reaction \(K_{ad}C\) is very small as compared to 1 in the denominator of eq. (1.45). So for simplification the denominator becomes 1. Integrating eq. (1.45), we obtain

\[
\ln \left( \frac{C_0}{C} \right) = k_{L-H} K_{ad} t = kt
\]

where \(t\) is the time required for the initial concentration of dye \(C_0\) to become \(C\) and 
\(k = k_{L-H} K_{ad}\) is the pseudo-first-order reaction rate constant.

Half life time \(t_{1/2}\) for the photocatalytic degradation of dye on the BiOCl surface can be calculated by using eq. (1.47)

\[
t_{1/2} = \frac{0.693}{k}
\]

The degradation process is of very complex in nature. As the degradation process proceeds with the illumination of many unstable intermediate species which finally mineralized into inorganic ions and \(CO_2\). Therefore, degradation process is considered under the two parallel branches of photocatalysis \((R_1)\) and photolysis \((R_2)\).

\[
R_1 = k_1[Dye]^{n_1}
\]
\[
R_2 = k_2[Dye]^{n_2}
\]

Several kinetic studies in photocatalyst degradation have been concerned in the power law models in order to find the net rate of degradation of substrate [58-61]. Here an appropriate simple power law model has been examined for photocatalytic degradation of selected dyes as given by eq. 1.48 and eq. 1.49.

\[
R = k_1[Dye]^{n_1} + k_2[Dye]^{n_2}
\]
where $n_1$, $n_2$, $k_1$, $k_2$ are the appropriate orders of the reactions and the rate constants for photocatalysis ($R_1$) and photolysis ($R_2$). To obtain the appropriate parameters the differential method of analysis based on data of dye concentration vs. time has been used. The plot of log (Dye) versus log $R_1$ and log (Dye) versus log $R_2$ have been used to check the goodness of fit of the rate eqs. (1.48) and (1.49) to the obtained data for photocatalysis and photolysis. The values of order of reaction and rate constant have been calculated to find the net degradation rate of selected dyes.

Main objective of the study was to degrade five selected dyes which are persistent non biodegradable priority pollutant and cannot be treated by conventional treatment processes. These dyes are selected as a model compound for the degradation studies to be undertaken with photocatalysis since few scattered reports exist on the treatment of dyes with photocatalytic processes. Another objective is to optimize the photocatalytic process for different parameters and to study their effect on the degradation and decolorization of selected dyes in terms of change in absorbance and COD of the resulting solution.

References: