CHAPTER IV

Results and Discussion
4.1: Analysis and Characterization of BiOCl catalyst

4.1.1: X-ray diffraction analysis:
As is known, XRD technique is a kind of powerful tool to characterize the phase, purity and crystallinity of the sample. The XRD pattern of as-prepared BiOCl is shown in Fig. 4.1.

![XRD Pattern](image)

**Fig. 4.1:** XRD pattern of BiOCl particle (a) before and (b) after the photocatalytic reaction.

The intense and narrow diffraction peaks imply a well-crystallized BiOCl powder material. To test the stability of the sample during the photocatalytic process, we have analyzed it again at the end of the process by XRD. The XRD pattern of BiOCl after the photocatalytic reaction is shown in Fig. 4.1 (b). Figure shows that the XRD pattern of BiOCl did not change even after the reaction was over, confirming that the photocatalyst was stable during the reaction and can be used repeatedly. The XRD pattern shows that all the peaks are well indexed to the tetragonal phase according to the PDF # 850861 data files. The crystal lattice parameters of BiOCl were calculated to be \( a = b = 0.38953 \, \text{Å}, \, c = 0.73734 \, \text{Å} \), which are consistent with the literature [1]. The strong and sharp diffraction
peaks confirmed the highly crystalline nature of BiOCl. The average crystallite size calculated by using the Scherrer formula is 39.6 nm.

**4.1.2: SEM and TEM analysis:**
More information of the structure of the BiOCl crystals was obtained by SEM and TEM observation (Fig. 4.2).

![Fig. 4.2](image)

**Fig. 4.2:** (a) SEM image of BiOCl particles (b) TEM image of an individual plate (c) The selective area electron diffraction of an individual plate (d) TEM image of BiOCl.
The SEM image (Fig. 4.2 (a)) shows the overall morphology of the product. It can be clearly see that the morphology of BiOCl is dominated with plates [1]. The TEM image of the individual plate in Fig. 4.2(b) indicates that plates have a flat surface and tended to form an octahedral shape with about 100 nm in diameter. Fig. 4.2(c) is the selective area electron diffraction (SAED) pattern of one small plate of BiOCl. The (110) and (200) crystal faces can be easily indexed, and the very uniform spot diffraction pattern implies the single-crystal nature of BiOCl. The lattice fringes of BiOCl crystals are found in TEM image (Fig. 4.2(d)) by using Fast Fourier Transform (FFT) and the mask method. It was revealed that the lattice spacing was of 0.27 nm, which is consistent with the (110) plane of BiOCl. This result also confirms the single-crystal structure of BiOCl.

4.1.3 Diffusive reflectance spectra analysis:

Diffuse reflectance spectra (DRS) technique is a useful technique to characterize the optical absorption properties of catalyst. The DRS spectra of as prepared BiOCl is shown in Fig. 4.3.

![Absorbance vs Wavelength](image)

**Fig. 4.3:** (a) UV-Vis absorption spectra for BiOCl particles (b) Plot of $(\alpha \nu)^{1/2}$ versus $\nu$ for BiOCl (Inset).
The result revealed that the sample exhibit significant increase in the photoabsorption at wavelength $\geq 400$ nm. The band gap energy for BiOCl can be estimated from a plot of $(\alpha h\nu)^{1/2}$ versus photon energy ($h\nu$) as shown in Fig. 4.3 (b) (Inset). The intercept of the tangent to the plot can give a good approximation of the band gap energy for BiOCl. The band gap energy estimated from the intercept of the tangent to the plot is 3.2 eV. This observation was also made by Wang et al and Zhang et al [2,3]. Usually, the photoabsorption of the photocatalyst depends on the mobility ability of electron-hole pairs, which determines the probability of electrons and holes to reach reaction sites of the photocatalyst surface [4].

4.2: Effect of metal-ion doping on structural, photophysical and photocatalytic properties of BiOCl

Doping of photocatalyst with various metal ions, particularly transition metal-doped photocatalyst particle has attracted much attention owing to its high photocatalytic activity, because of trapping and subsequent transfer of photoexcited electron onto photocatalyst surface and decreasing the recombination of hole-electron pairs [5]. Mangnese (Mn) was used as a dopant in BiOCl in order to reduce the band gap of the photocatalyst, thus extending the wavelength response a little bit more toward the visible range. The number of photogenerated electrons and holes participating in photocatalytic reactions would be increased, resulting in an enhancement in photocatalytic activity. Consequently, the photodegradation of malachite green (MG) has been employed to evaluate the photocatalytic activity of Mn-doped BiOCl under visible-light illumination.

4.2.1: Preparation of Mn-doped BiOCl:

Mn-doped BiOCl particles were prepared in a manner similar to that used hydrolysis method. The reagent Bi$_2$O$_3$ was dissolved in excessive concentrated hydrochloric acid to obtain a BiCl$_3$-HCl aqueous system. Appropriate amount of MnCl$_2$ was added to BiCl$_3$-HCl solution under vigorous stirring condition. After adjusting the pH value between 2 to 3 with ammonia, the resulting solution was stirred at 323 K for 24 hrs and the centrifugal
machine separated the liquid from the white precipitate, becoming a white powder afterward. The obtained sample was dried at 373 K for 24 hrs and pulverizes [6, 1].

4.2.2: Structural studies:
XRD patterns of the pure and Mn-doped BiOCl particles are shown in Fig. 4.4(a). It was observed that all the peaks are well indexed to the tetragonal phase according to the PDF # 850861 data files. The strong and sharp diffraction peaks indicate a high degree of crystallization. The lattice constants were calculated to be (a = b = 0.38953 Å, c = 0.73734 Å) for undoped BiOCl and (a = b = 0.38892 Å, c = 0.73608 Å) for Mn-doped BiOCl. The crystallite size was obtained 39.6 nm for pure BiOCl while 34.4 nm for Mn-doped BiOCl. This clearly indicates that Mn-doped sample has smaller crystallite size with high surface area.

![Fig. 4.4: (a) XRD scans of pure and Mn-doped BiOCl particles (b) The slow scans of the (001) peaks taken on these two samples (Inset).](image)

As shown in Fig. 4.4(b) (Inset), the (001) peak of the Mn-doped BiOCl shows a clear shift of ~0.12° to the right compared to the pure BiOCl. Also slight shift in the d-spacing observed for the doped BiOCl due to Mn are summarized in Table 4.1. This may be
attributed to the well incorporation of Mn particles in the BiOCl crystal lattice. The shrinkage of lattice constants after doping is due to the substitution of Bi$^{3+}$ (0.096 nm) by smaller Mn$^{2+}$ (0.080 nm) [7–10].

Table 4.1: d values of the Mn doped and undoped BiOCl

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>d$_{(001)}$ (Å)</th>
<th>d$_{(002)}$ (Å)</th>
<th>d$_{(101)}$ (Å)</th>
<th>d$_{(102)}$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure BiOCl</td>
<td>7.416</td>
<td>3.691</td>
<td>3.443</td>
<td>2.676</td>
</tr>
<tr>
<td>Doped BiOCl</td>
<td>7.109</td>
<td>3.672</td>
<td>3.429</td>
<td>2.668</td>
</tr>
</tbody>
</table>

As shown in Fig. 4.5, the SEM images demonstrate that the morphology of BiOCl is dominated with plates, the size of the particles of pure BiOCl (Fig. 4.2(a)) and Mn-doped BiOCl (Fig. 4.5) varies in the range of nearly 1-3 µm and 0.47-5 µm, respectively. It was assumed that Mn doping probably caused aggregation of tiny crystals of BiOCl with small grain size. Also, the aggregation suggests that the size of the particles for Mn-doped BiOCl (Fig. 4.5) could be smaller than calculated particle size (0.47 µm).

Fig. 4.5: Scanning electron micrographs of Mn- doped BiOCl particles.
Usually, smaller the particle size, larger the specific surface area. Increased surface area with decreased particle size is the property of this type of morphology, which provides more exposed area to incident photons/radiations [11].

**4.2.3: Photo physical properties:**

The diffuse reflectance spectra (DRS) spectra of Mn-doped BiOCl is shown in Fig. 4.6 (a). For pure BiOCl (see Fig. 4.3(a)), an absorption edge rising steeply about 378nm, whereas Mn-doped BiOCl exhibit red shifts of absorption edge and significant enhancement of light absorption at 400–600 nm as shown in Fig. 4.6 (a) which clearly indicates the presence of additional energy levels ($\text{Mn}^{2+}/\text{Mn}^{3+}$) of the transition metal ions into the forbidden gap of BiOCl. Therefore, the absorption edge shifting toward higher wavelengths for the Mn-doped BiOCl should come from the electronic transition from the dopant energy level ($\text{Mn}^{2+}/\text{Mn}^{3+}$) to the conduction band of BiOCl. We have calculated the magnitude of these energies with the help of Tauc relation [12, 9].

\[
\alpha h\nu = A(h\nu-E_g)^n
\]  

(4.1)

where, \(A\), \(\alpha\), \(E_g\) and \(\nu\) are proportional constant, absorption coefficient, band gap and light frequency, respectively. Fig. 4.6 (b) (Inset) shows the plot of \((\alpha h\nu)^{1/2}\) versus \(h\nu\) for pure and Mn-doped BiOCl. It could be seen from figure that the band gap for Mn-doped BiOCl was calculated to be 2.7 eV. This indicates that Mn-doped BiOCl possessed narrower band gap compared with that of pure BiOCl. This lower energy value has been attributed to the strong absorption in visible region due to localized levels existing in the forbidden gap because of Mn doping. Upon irradiation with visible light electron-hole pair is generated within the effective band gap, i.e., electron transition takes place from the new additional valence state to conduction state. This transition requires smaller excitation energy as compared to the native band gap (3.2 eV) of BiOCl depending upon the particular dopant level within the band gap [13], therefore it can be used as an efficient photocatalyst under visible light irradiation
4.2.4: Mechanism:

Quite inevitably the degradation rate can be enhanced using more charge carriers. This can be done by doping. Dopant ions make available the charge carriers under visible light exposure conditions by either shifting the absorption edge to higher wavelength side or by increasing the life time of charge carriers [14]. Optical studies (Fig. 4.6) indicate introduction of additional energy level, in Mn-doped sample, at 2.7 eV above the valence band edge in the forbidden gap. The energy level for Mn$^{2+}$/Mn$^{3+}$ is above the valence band edge of BiOCl and the energy level for Mn$^{2+}$/Mn$^{+}$ is below the conduction band edge of BiOCl. Mn$^{2+}$ ions, acting as both electrons and holes traps, can turn into Mn$^{+}$ and Mn$^{3+}$ ions by trapping photogenerated electrons and holes traps, respectively as shown in eqs. (4.2) to (4.4) [14].
Mn-doped BiOCl surface can be represented by the following equations.

\[\text{BiOCl} + h\nu \rightarrow h_{VB}^+ + e_{CB}^- \quad (4.2)\]

\[\text{Mn}^{2+} + h^+ \rightarrow \text{Mn}^{3+} \quad \text{(Holetrape)} \quad (4.3)\]

\[\text{Mn}^{2+} + e^- \rightarrow \text{Mn}^+ \quad \text{(Electrontrape)} \quad (4.4)\]

According to the crystal field theory, Mn\(^{3+}\) and Mn\(^{+}\) ions are relatively unstable as compared to Mn\(^{2+}\) ions, which have half-filled d orbital (d\(^5\)). Therefore, the trapped charges can easily release from Mn\(^{+}\) or Mn\(^{3+}\) ions and then transfer to the surface to initiate the photocatalytic reaction. Mn\(^{+}\) ions can be oxidized to Mn\(^{2+}\) ions by transferring electrons to absorbed O\(_2\) on the surface of BiOCl as given in eq. (4.5). Meanwhile, the adsorbed O\(_2\) is reduced to O\(_2^-\) as given in eq. (4.5), which can further degrade MG shown in Fig. 4.7. Similarly, Mn\(^{3+}\) ions are also reduced to Mn\(^{2+}\) ions by releasing electrons, while surface hydroxyl group translates into hydroxyl radical eq. (4.6) \[14\].

\[\text{Mn}^{+} + \text{O}_2 \rightarrow \text{Mn}^{2+} + \text{O}_2^- \quad \text{(Holetrape)} \quad (4.5)\]

\[\text{Mn}^{3+} + \text{OH}^- \rightarrow \text{Mn}^{2+} + \cdot\text{OH} \quad \text{(Electrontrape)} \quad (4.6)\]

Thus photogenerated superoxide ion (O\(_2^-\)) and hydroxyl radical (\(\cdot\text{OH}\)) are highly reactive and degrade the malachite green.

\[(\text{BiOCl})e_{CB}^- + \text{Dye} \rightarrow (\text{BiOCl})e_{CB}^- + \text{Dye}^{++} \quad (4.7)\]

\[\text{Dye}^{++} + \text{O}_2^- \rightarrow \text{Degradation products} \quad (4.8)\]

\[\text{Dye}^+ + \cdot\text{OH} \rightarrow \text{Degradation products} \quad (4.9)\]

These processes not only accelerate the interfacial charge transfer process, but also enhance the generation of highly reactive oxidative species such as superoxide and hydroxyl radicals. Photodegradation profiles of MG by Mn-doped BiOCl under visible irradiation are shown in Fig. 4.7.
4.2.5: Photocatalytic properties:

The photodegradation experiments that involve visible light irradiation of 25 mgL\(^{-1}\) malachite green (MG) aqueous solution exhibit pseudo-first-order reaction kinetics is represented by the following equation

\[
\ln \left( \frac{C_0}{C} \right) = kt \tag{4.10}
\]

where, \(C\) is the final concentration (mgL\(^{-1}\)) of MG after irradiation, \(C_0\) is the initial concentration (mgL\(^{-1}\)) of MG prior to irradiation, \(t\) is the irradiation time (min) and \(k\) is the apparent reaction rate constant (min\(^{-1}\)). [15, 9].

The plot of the log concentration of malachite green in the presence of 0.7gm of doped and pure BiOCl vs. irradiation time as shown in Fig. 4.8 (a) yielded straight lines indicating pseudo first order reaction. It is observed that the values of rate constants, \(k\), are consistent with the photodegradation of MG. For example, 64% and 98% of 25mgL\(^{-1}\) MG was degraded with pure and Mn-doped BiOCl, respectively, within 120 min (see Fig.
4.8 (b)). The rate constants are 0.0241 and 0.0347 min$^{-1}$, respectively. In general the photocatalytic reaction follows the Langmuir- Hinshelwood mechanism.

**Fig. 4.8:** (a) Pseudo-first-order reaction kinetics curves for photocatalytic degradation of 25 mgL$^{-1}$ MG with (i) Mn-doped BiOCl, and (ii) pure BiOCl, (b) Photocatalytic degradation percentage of 25 mgL$^{-1}$ MG with pure and Mn-doped BiOCl catalyst under visible light irradiation.

**References:**


Malachite green is an organic compound that is used as a dyestuff. It is traditionally used as a dye for materials such as silk, leather, and paper. Malachite green also is used as a direct dye for silk, wool, jute, and leather and to dye cotton that has been mordanted with tannin.
4.3 (A): Effects of various experimental parameters on the degradation rate of Malachite Green (MG)

4.3.1: Photocatalytic degradation of malachite green (MG):

The kinetics of degradation of malachite green (MG) on illuminated BiOCl has been studied extensively and it is already mentioned that Langmuir–Hinshelwood [1] could well describe this phenomenon. In Langmuir–Hinshelwood treatment of heterogeneous surface reactions, the photochemical degradation rate is described by pseudo first order kinetics which has the following mathematical formula [2]:

\[
R = -\frac{dc}{dt} = \frac{k_{L-H} K_{ad} C}{(1 + K_{ad} C)}
\]

(4.11)

where \( k_{L-H} \) is the reaction rate constant, \( K_{ad} \) is the adsorption coefficient of dye on the surface of BiOCl, 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. (4.11). So for simplification the denominator becomes 1. Integrating eq. (4.11), we obtain

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

(4.12)

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 MG on the BiOCl surface can be calculated by using eq. (4.13)

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

(4.13)

The photocatalytic degradation of MG dye follows pseudo first kinetics. The detection was realized at 617 nm. The results for typical run are given in Fig. 4.9(a) and (b). The absorbance of MG dye decreases with an increase in irradiation time. While in dark and during photolysis, no significant changes have been observed (Fig. 4.9(a)).
Fig. 4.9 (a): Decolorization of MG: \([\text{MG}] = 25 \text{mgL}^{-1}, \text{BiOCl} = 0.7 \text{gmL}^{-1},\) Irradiation intensity = \(20 \times 10^3\) lux, pH = 8.0, Temperature = 30 ± 0.3 °C.

The reaction rate constant \((k)\) for the photocatalytic degradation reaction of MG dye by BiOCl catalyst, is obtained from the slope of the linear relationship of the natural logarithm of the ratio between the initial concentration of MG and the concentration after photocatalytic degradation \(\ln(C_0/C)\) versus the corresponding irradiation time as shown in Fig. 4.9(b).

Fig. 4.9 (b): Pseudo first order kinetics: \([\text{MG}] = 25 \text{mgL}^{-1}, \text{BiOCl} = 0.7 \text{gm L}^{-1},\) Irradiation intensity = \(20 \times 10^3\) lux, pH = 8.0, Temperature = 30 ± 0.3 °C.
The value of $k$ gives an indication for the activity of the photocatalyst. The plot of $\ln(C_0/C)$ versus time follows pseudo first order kinetics with regression co-efficient of 0.986, rate constant of 0.0241 min$^{-1}$ and half life time of 28.66 min (Fig. 4.9(b)). Besides the nature of the photocatalyst and the substrate, the rate of photocatalytic reaction is influenced by various parameters, among others but not exclusively, initial pH, catalyst weight, dye concentration, oxidant concentration, salt concentration, FeCl$_3$, Fe$^{3+}$/H$_2$O$_2$, temperature, N$_2$ and O$_2$ purging, light intensity and irradiation time. The effect of varying these parameters will be discussed in the following paragraphs:

### 4.3.2: Influence of initial pH:

The influence of the initial pH of the dye solution was studied as pH is considered to be one of the most important parameters that can affect the photocatalytic degradation process. The initial pH of dye solution was varied from pH 2.3 to 14. The studies were carried out with 25 mgL$^{-1}$ malachite green dye solution and 0.7gm L$^{-1}$ of catalyst dose. The results of pH effect are shown in Table 4.2 and Fig. 4.10. It is quite evident that as the pH of dye solution increase from 2 to 8, the photocatalytic reaction rate increased and the further increase in pH resulted into decrease in rate of degradation. The maximum degradation has been found at pH 8.0. The reaction rate has strong connectivity with the adsorption of MG molecules on BiOCl. The adsorption behavior is influenced extensively by solution pH. The BiOCl surface being positively charged would repel positively charged MG molecules as long as pH was lower than 8.0. In contrast, the two species would attract each other in neutral and alkaline solution. When the solution pH was adjusted to be 2.0, the adsorption was weaker than that of experiments conducted in higher pH values. Based on this principle, the pseudo-first-order reaction rate constants were increased with an increase in pH from 2.3 to 8.0. A possible explanation of this behavior may be the electrostatic interactions between the negatively charged BiOCl particles and positively charged MG led to strong absorption and enhanced the degradation rate in alkaline condition. The phenomenon might be attributed to critically high adsorption on BiOCl surface. The amount of BiOCl particles 0.7 gm L$^{-1}$, which means that the available active site was limited, and catalytic reaction would be a rate-limiting step of overall reaction rate as the quantity of dye adsorption was too high. It
may shelter from the illumination of incident visible light. In other words the increase in rate of photocatalytic degradation might be due to the more availability of OH⁻ ions in basic medium which will generate more •OH radicals by combining with holes which are formed due to the electronic excitation in catalyst. In acidic condition, electrostatic interactions between the positively charged active sites on catalyst surface and cationic dye molecules led to strong repulsion consequently made it difficult for dye molecules to get adsorbed on the catalyst surface [3].

**Table 4.2: Effect of pH**: [MG] = 25 mgL⁻¹, BiOCl = 0.7 gmL⁻¹, Irradiation intensity = 20 × 10³, Temperature = 30 ± 0.3 °C.

<table>
<thead>
<tr>
<th>pH</th>
<th>k(min⁻¹)</th>
<th>t½ (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.3</td>
<td>0.012</td>
<td>53.42</td>
</tr>
<tr>
<td>4.0</td>
<td>0.016</td>
<td>42.30</td>
</tr>
<tr>
<td>6.2</td>
<td>0.021</td>
<td>32.71</td>
</tr>
<tr>
<td>8.0</td>
<td>0.024</td>
<td>28.66</td>
</tr>
<tr>
<td>10.1</td>
<td>0.020</td>
<td>33.87</td>
</tr>
<tr>
<td>12.0</td>
<td>0.018</td>
<td>38.24</td>
</tr>
<tr>
<td>14.0</td>
<td>0.014</td>
<td>47.53</td>
</tr>
</tbody>
</table>

**Fig. 4.10: Influence of initial pH.**
4.3.3: Effect of catalyst weight:

After optimizing pH, the catalyst weight is another important parameter which has strong influence on the degradation rate of the dye molecule. Heterogeneous photocatalytic reactions are known to show proportional increase in photodegradation with catalyst loading [4]. In order to determine the optimal amount of catalyst concentration, a series of experiments were carried out using different concentrations of BiOCl catalyst varying from 0.3 to 1.3 gm, at optimized pH of 8.0 with 25 mgL\(^{-1}\) dye solution and results are presented in Table 4.3 and Fig. 4.11.

**Table 4.3: Effect of catalyst weight:** [MG] = 25mgL\(^{-1}\), Irradiation intensity = 20 ×10\(^3\) lux, pH = 8.0, Temperature = 30 ± 0.3 °C.

<table>
<thead>
<tr>
<th>BiOCl gmL(^{-1})</th>
<th>k (min(^{-1}))</th>
<th>(t_{1/2}) (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3</td>
<td>0.017</td>
<td>38.62</td>
</tr>
<tr>
<td>0.5</td>
<td>0.018</td>
<td>36.78</td>
</tr>
<tr>
<td>0.7</td>
<td>0.024</td>
<td>28.66</td>
</tr>
<tr>
<td>0.9</td>
<td>0.015</td>
<td>45.65</td>
</tr>
<tr>
<td>1.1</td>
<td>0.009</td>
<td>70.85</td>
</tr>
<tr>
<td>1.3</td>
<td>0.007</td>
<td>88.16</td>
</tr>
</tbody>
</table>

**Fig. 4.11:** Effect of catalyst weight.
The graph depicts that as the concentration of catalyst increases from 0.3 to 0.7 gmL$^{-1}$, the degradation rate constant increases from 0.017 to 0.024 min$^{-1}$ but further increase in the catalyst concentration from 0.7 to 1.3 gmL$^{-1}$, the rate constant decreases from 0.024 to 0.007 min$^{-1}$ respectively. So maximum degradation rate was observed with catalyst weight of 0.7 gmL$^{-1}$ and it was considered as the optimum weight for the degradation of malachite green dye solution (25 mgL$^{-1}$) for subsequent analysis. The increased degradation rate that follows the increase in the catalyst weight can be attributed to the fact that the total active surface area increases with increasing catalyst weight, thus accelerating the process. When all the dye molecules are adsorbed on BiOCl no improvement was achieved by adding more catalyst. The decrease in efficiency, which was observed in the Fig. 4.11, may be due to an increasing opacity of the suspension and to an enhancement of the light reflectance, because of the excess of BiOCl particles [5]. Additionally, in the case of high catalyst loads, we observed agglomeration and sedimentation of BiOCl which makes a significant fraction of catalyst to be inaccessible to either absorbing the dye or absorbing the radiation, with consequent decrease in active sites available to the catalytic reaction [4].

4.3.4: Effect of initial dye concentration:

The pollutant concentration is very important parameter in wastewater treatment. The influence of initial concentration of the dye solution has been investigated on the photocatalytic degradation of dye after the optimization of pH and catalyst dose. In order to optimize the initial dye concentrations was varied during the photo catalytic treatment from 10 to 40 mgL$^{-1}$, at constant pH of 8.0 and catalyst dose of 0.7 gmL$^{-1}$. It has been observed from the Table 4.4 and graph (Fig. 4.12) that the rate constant increases from 0.012 min$^{-1}$ to 0.024 min$^{-1}$ with increase in dye concentration from 10 mgL$^{-1}$ to 25 mgL$^{-1}$. Thereafter, rate constant decreases to 0.021 min$^{-1}$ with increased dye concentration up to 40 mgL$^{-1}$. Rate constant was found to be maximal at 25 mgL$^{-1}$ of dye concentration. This may be attributed to the fact that as the concentration of dye was increased, more dye molecules were available for excitation followed by inter system crossing and hence, there was an increase in the rate [5].
Table 4.4: Effect of initial dye concentration: BiOCl = 0.7 gmL^{-1}, Irradiation intensity = 20 \times 10^3 \text{ lux}, \text{pH} = 8.0, \text{Temperature} = 30 \pm 0.3 \text{ C}.

<table>
<thead>
<tr>
<th>MG (mgL^{-1})</th>
<th>k (min^{-1})</th>
<th>t_{\frac{1}{2}} (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.012</td>
<td>56.06</td>
</tr>
<tr>
<td>15</td>
<td>0.019</td>
<td>34.68</td>
</tr>
<tr>
<td>20</td>
<td>0.022</td>
<td>30.23</td>
</tr>
<tr>
<td>25</td>
<td>0.024</td>
<td>28.66</td>
</tr>
<tr>
<td>30</td>
<td>0.023</td>
<td>30.13</td>
</tr>
<tr>
<td>35</td>
<td>0.022</td>
<td>31.50</td>
</tr>
<tr>
<td>40</td>
<td>0.021</td>
<td>33.00</td>
</tr>
</tbody>
</table>

Fig. 4.12: Effect of initial dye concentration.

Further increase in dye concentration, the equilibrium adsorption of dye on catalyst surface active sites increases, which hinders the competitive adsorption of OH^{-} on the same sites, which means a lower formation rate of \cdot OH radical. The increase in dye concentration also decreases the path length of photon entering the dye solution. At high dye concentration a significant amount of visible light may be absorbed by the dye.
molecules rather than the catalyst and this may also reduce the catalytic efficiency. Consequently, the degradation rate decreased as the dye concentration increases [3].

4.3.5: Effect of varying oxidant concentration:

The addition of the other oxidizing species such as H$_2$O$_2$ and K$_2$S$_2$O$_8$ to catalyst suspensions is a well known procedure and leads to an increase in the rate of photo degradation. The effect of the concentration of H$_2$O$_2$ on the initial reaction rate of malachite green degradation shown in Table 4.5 and Fig. 4.13(a). The photocatalytic efficiency found to be increased as the concentration of H$_2$O$_2$ increased from 20 to 60 mgL$^{-1}$ and it reached the optimum at 60 mgL$^{-1}$. Consequently the rate decreased as the concentration of the H$_2$O$_2$ increased beyond the optimum. H$_2$O$_2$ is considered to have two functions in the process of photocatalytic degradation. It accepts a photogenerated electron from the conduction band and thus promotes the charge separation and it also forms *OH radicals according to eqs. (4.14) and (4.15) [6-9].

\[
\begin{align*}
H_2O_2 + e^- &\rightarrow OH^- + \cdot OH \quad (4.14) \\
H_2O_2 + O_2^- &\rightarrow \cdot OH + OH^- + O_2 \quad (4.15)
\end{align*}
\]

Excess H$_2$O$_2$ may act as a hole or an *OH scavenger or react with BiOCl and form peroxocompounds, which are detrimental to the photocatalytic action. This explains the need for an optimal concentration of H$_2$O$_2$ for the maximum effect.

K$_2$S$_2$O$_8$ can also trap the photogenerated conduction band electron results in the formation of sulphate ion (SO$_4^{2-}$), a strong oxidizing agent (standard oxidation potential = 2.6 eV), which can participate in degradation process.

\[
\begin{align*}
S_2O_8^{2-} + e^- &\rightarrow SO_4^{2-} + SO_4^{2-} \quad (4.16)
\end{align*}
\]

From Fig. 4.13(b), with increase in K$_2$S$_2$O$_8$ concentration from 20 to 60 mg L$^{-1}$, rate constant increased from 0.026 min$^{-1}$ to 0.033 min$^{-1}$. At optimal concentration of K$_2$S$_2$O$_8$, rate constant has been found to be 0.033 min$^{-1}$. Consequently degradation rate decreases as the concentration of the K$_2$S$_2$O$_8$ increases beyond the optimum [8].
Table 4.5: Effect of oxidant: \([\text{MG}] = 25 \text{ mgL}^{-1}, \text{BiOCl} = 0.7 \text{ gmL}^{-1}, \text{Irradiation intensity} = 20 \times 10^3 \text{ lux}, \text{pH} = 8.0, \text{Temperature} = 30 \pm 0.3 ^\circ \text{C}.\)

<table>
<thead>
<tr>
<th>Oxidant (mgL(^{-1}))</th>
<th>(\text{H}_2\text{O}_2)</th>
<th>(\text{K}_2\text{S}_2\text{O}_8)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(k) (min(^{-1}))</td>
<td>(t_{1/2}) (min)</td>
</tr>
<tr>
<td>0</td>
<td>0.024</td>
<td>28.66</td>
</tr>
<tr>
<td>20</td>
<td>0.025</td>
<td>27.30</td>
</tr>
<tr>
<td>40</td>
<td>0.028</td>
<td>24.16</td>
</tr>
<tr>
<td>60</td>
<td>0.031</td>
<td>22.04</td>
</tr>
<tr>
<td>80</td>
<td>0.025</td>
<td>26.67</td>
</tr>
<tr>
<td>100</td>
<td>0.024</td>
<td>28.73</td>
</tr>
<tr>
<td>120</td>
<td>0.022</td>
<td>31.47</td>
</tr>
</tbody>
</table>

Fig. 4.13: Effect of oxidant: (a) \(\text{H}_2\text{O}_2\) and (b) \(\text{K}_2\text{S}_2\text{O}_8\).

A possible explanation of this behavior may be the light absorption from dye molecule leads to the photo-sensitization of the molecule, which is accompanied by the excitation of an electron from the lower to the upper energy level. Following this, the excited dye molecule injects electrons to the \(\text{S}_2\text{O}_8^{2-}\) according to eq. (4.16). The resulting \(\text{SO}_4^{2-}\) radicals, strong oxidizing agents, attack the chromophore group in dye leading to the decolorization of the solution. The decrease in rate constant above optimum concentration is due to the adsorption of sulphate ions formed during the reaction on surface of catalyst deactivating a section of photocatalyst \([10,11][8-9]\).
4.3.6: Effect of varying Salt concentration:

Direct or substantive dyeing is normally carried out in a neutral or slightly alkaline dye bath, at or near boiling point, with the addition of either sodium chloride (NaCl) or sodium carbonate (Na$_2$CO$_3$). The effect of presence of NaCl and Na$_2$CO$_3$ is shown in Table 4.6 and Fig. 4.14.

**Table 4.6: Effect of Salt:** [MG] = 25 mgL$^{-1}$, BiOCl = 0.7 gmL$^{-1}$, Irradiation intensity = $20 \times 10^3$ lux, pH = 8.0, Temperature = $30 \pm 0.3^\circ$C

<table>
<thead>
<tr>
<th>Salt (mgL$^{-1}$)</th>
<th>Na$_2$CO$_3$</th>
<th>NaCl</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>k (min$^{-1}$)</td>
<td>t$_{1/2}$ (min)</td>
</tr>
<tr>
<td>0</td>
<td>0.024</td>
<td>28.66</td>
</tr>
<tr>
<td>20</td>
<td>0.022</td>
<td>30.15</td>
</tr>
<tr>
<td>40</td>
<td>0.020</td>
<td>33.18</td>
</tr>
<tr>
<td>60</td>
<td>0.017</td>
<td>40.24</td>
</tr>
<tr>
<td>80</td>
<td>0.015</td>
<td>45.29</td>
</tr>
</tbody>
</table>

As can be seen from Fig. 4.14, an increment in concentration of CO$_3^{2-}$ from 20 mgL$^{-1}$ to 80 mgL$^{-1}$, results in reduction of rate constant 0.022 min$^{-1}$ to 0.015 min$^{-1}$, while with same Cl$^-$ ion concentration variation, the rate constant decreases from 0.024 to 0.012 min$^{-1}$. Half life time increases form 30.15 min$^{-1}$ to 45.2 min$^{-1}$ and 29.24 to 55 min with an increment in concentration from 20 mgL$^{-1}$ to 80 mgL$^{-1}$ for CO$_3^{2-}$ and Cl$^-$ ions respectively.

The inhibition is undoubtedly due to their ability to act as hydroxyl radical (OH$^-$) scavengers. The observed mechanism of hydroxyl radical scavenging is given by eq. (4.17) to eq. (4.20) [12,13].

$$\text{Cl}^- + \cdot\text{OH} \rightarrow \text{Cl} + \text{OH}^- \quad (4.17)$$

$$\text{Cl}^- + h^+_{vb} \rightarrow \cdot\text{Cl} \quad (4.18)$$

$$\text{Cl}^- + \cdot\text{Cl} \rightarrow \text{Cl}_2\cdot \quad (4.19)$$

$$\text{CO}_3^{2-} + \cdot\text{OH} \rightarrow \text{CO}_3^- + \text{H}_2\text{O} \quad (4.20)$$

These ions may also block the active sites on the photocatalyst surface thus deactivating...
the catalysts towards the dye and intermediate molecules. Although, the generated radical anions have been shown to be an oxidant itself, but its oxidation potential is less than that of the hydroxyl radicals [14].

![Fig. 4.14: Effect of Salt: (a) Na$_2$CO$_3$ and (b) NaCl](image)

From this study, it evident that hydroxyl radicals play a very vital role in photocatalytic degradation process.

### 4.3.7: Effect of FeCl$_3$:

In present case, effect of FeCl$_3$ on the photodegradation of MG has been studied by varying the concentration from 20 mgL$^{-1}$ to 120 mgL$^{-1}$ (Table 4.7 and Fig. 4.15). FeCl$_3$ behaves as an electron scavenger ($\text{Fe}^{3+} + e^\rightarrow \text{Fe}^{3+}$) thus preventing the recombination of electron hole pairs. Under the experimental conditions the following reactions become significant.

$$\text{Fe}^{2+} + \text{H}_2\text{O}_2 + \text{H}^+ \rightarrow \text{Fe}^{3+} + \cdot\text{OH} + \text{H}_2\text{O} \quad (4.21)$$

$$\text{Fe}^{2+} + \text{HO}_2^\cdot + \text{H}^+ \rightarrow \text{Fe}^{3+} + \text{H}_2\text{O}_2 \quad (4.22)$$

The above two reactions increase the amounts of $\cdot$OH and H$_2$O$_2$ thus improving the efficiency of photocatalytic process. In BiOCl, when Fe$^{3+}$ concentration is in excess of 120 mgL$^{-1}$, the photodegradation efficiency decreased gradually due to the deposition of
Fe\textsuperscript{3+} ions on the semiconductor particles. Active sites of the catalyst are covered with Fe\textsuperscript{3+} ions and hence of the photon absorption by the catalyst decreases [15].

Table 4.7: Effect of FeCl\textsubscript{3}: [MG] = 25 mgL\textsuperscript{-1}, BiOCl = 0.7 gmL\textsuperscript{-1}, Irradiation intensity = 20 \times 10\textsuperscript{3} lux, pH = 8.0, Temperature = 30 \pm 0.3 \textdegree C

<table>
<thead>
<tr>
<th>FeCl\textsubscript{3} (mgL\textsuperscript{-1})</th>
<th>k (min\textsuperscript{-1})</th>
<th>t\textsubscript{1/2} (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.024</td>
<td>28.66</td>
</tr>
<tr>
<td>20</td>
<td>0.025</td>
<td>27.11</td>
</tr>
<tr>
<td>40</td>
<td>0.028</td>
<td>24.67</td>
</tr>
<tr>
<td>60</td>
<td>0.030</td>
<td>23.00</td>
</tr>
<tr>
<td>80</td>
<td>0.025</td>
<td>26.67</td>
</tr>
<tr>
<td>100</td>
<td>0.018</td>
<td>37.37</td>
</tr>
<tr>
<td>120</td>
<td>0.016</td>
<td>41.25</td>
</tr>
</tbody>
</table>

In BiOCl/ FeCl\textsubscript{3}/Vis addition of FeCl\textsubscript{3} caused an increase in decolorization rate (0.030 min\textsuperscript{-1}) upto 60 mgL\textsuperscript{-1}. Photoactivation of surface adsorbed complex ion (Fe\textsuperscript{3+}OH\textsuperscript{-}) results in formation of Fe\textsuperscript{2+} OH species, which inject electrons to conduction band of BiOCl shown in eqs. (4.24 to 4.25). Increased rate of decolorization in case of FeCl\textsubscript{3} is explicable due to rapid scavenging of conduction band electrons by molecular oxygen leading to formation of superoxide and hydroperoxide radicals (eq. 4.26). Higher concentration of FeCl\textsubscript{3} eliminates adsorption of cationic dye on BiOCl surface and also inhibits reaction rate by reducing production of hydroxyl radicals [16-18].

\[
\text{MG} + h\nu_{\text{visible}} \rightarrow \text{MG}^* \text{ or } \text{MG}^* \tag{4.23}
\]

\[
\text{MG}^* \text{ or } \text{MG}^* + \text{BiOCl (Fe}^{3+} \text{OH}) \rightarrow \text{BiOCl (Fe}^{2+} \text{OH}) + \text{MG}^{**} \tag{4.24}
\]

\[
\text{BiOCl (Fe}^{2+} \cdot \text{OH}) \rightarrow \text{BiOCl (e}^-_{\text{CB}}) + \text{BiOCl (Fe}^{3+} \cdot \text{OH}) \tag{4.25}
\]

\[
\text{BiOCl (e}^-_{\text{CB}}) + \text{O}_2 \rightarrow \text{O}_2^- \xrightarrow{H^+} \text{HO}_2^* \tag{4.26}
\]

\[
\text{MG/MG}^{**} + \cdot \text{OH/ O}_2^-/ \text{HO}_2^* \rightarrow \text{Degradation products} \tag{4.27}
\]

The metal ions such as Fe\textsuperscript{3+} could be used as sensitizers during semiconductor photo catalytic degradation of organic pollutants.
4.3.8: Effect of Fe$^{3+}$/H$_2$O$_2$:

Among AOPs, catalytic oxidation using Fenton and Fenton like reagent is an attractive treatment for the effective decolorization and degradation of dyes because of its low cost and lack of toxicity of the reagents (H$_2$O$_2$ and Fe$^{2+}$ or Fe$^{3+}$) [19]. In recent years, many research workers have reported the degradation of dyes using Fenton and visible/solar light system [20,21]. Efficiency of Fe$^{3+}$/H$_2$O$_2$ system has been studied for decolorization of MG in the presence of BiOCl and visible irradiation. The results are given in Table 4.8 and Fig. 4.16.

<table>
<thead>
<tr>
<th>Fe$^{3+}$/H$_2$O$_2$</th>
<th>With BiOCl</th>
<th>Without BiOCl</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>k (min$^{-1}$)</td>
<td>t$_{1/2}$ (min)</td>
</tr>
<tr>
<td>1:2</td>
<td>0.025</td>
<td>27.36</td>
</tr>
<tr>
<td>1.2:2</td>
<td>0.029</td>
<td>23.81</td>
</tr>
<tr>
<td>2:3</td>
<td>0.036</td>
<td>19.05</td>
</tr>
<tr>
<td>2.3:3</td>
<td>0.032</td>
<td>21.07</td>
</tr>
<tr>
<td>3:4</td>
<td>0.028</td>
<td>23.91</td>
</tr>
</tbody>
</table>

Table 4.8: Effect of Fe$^{3+}$/H$_2$O$_2$: [MG] = 25 mgL$^{-1}$, BiOCl = 0.7 gmL$^{-1}$, Irradiation intensity = 20 $\times$ 10$^3$ lux, pH = 8.0, Temperature = 30 $\pm$ 0.3 $^0$C.
Rate constant has a value of 0.025 min\(^{-1}\) on the addition of \((\text{Fe}^{3+} : \text{H}_2\text{O}_2)\) in molar ratio (1:2). In the presence of \((\text{Fe}^{3+} : \text{H}_2\text{O}_2)\) in molar ratio (1:2:2), rate constant has been found 0.029 min\(^{-1}\). Upon irradiation of \(\text{Fe}^{3+}/\text{H}_2\text{O}_2/\text{BiOCl}/\text{MG}\) system with visible light, production of \(\cdot\text{OH}\) radicals increases involving a very complex mechanism. Dye absorbs visible irradiation and is excited into high-energy state. These excited dye molecules reduce the ferric ion complex to ferrous ion complex followed by the transfer to ferric ion [22]. The reduced ferrous ions react with hydrogen peroxide to decompose and produce hydroxyl radical (eq. (4.30)). \(\cdot\text{OH}\) radicals also decompose \(\text{H}_2\text{O}_2\) to \(\text{HO}_2\). A similar mechanism has been reported by Amiri, Wu and Herrara et al [23-25].

\[
\begin{align*}
\text{MG} + \text{hv}_{\text{visible}} & \longrightarrow 1\text{MG}^* \text{ or } 3\text{MG}^* \quad (4.28) \\
1\text{MG}^* \text{ or } 3\text{MG}^* + \text{BiOCl(Fe}^{3+}\text{OH}) & \longrightarrow \text{BiOCl(Fe}^{2+}\text{OH}^\cdot) + \text{MG}^{++} \quad (4.29) \\
\text{BiOCl(Fe}^{2+}\text{OH}^\cdot) + \text{H}_2\text{O}_2 & \xrightarrow{\text{hv}} \text{BiOCl(Fe}^{3+}\text{OH}^\cdot) + \text{OH}^- + \cdot\text{OH} \quad (4.30) \\
\text{BiOCl(Fe}^{3+}\text{OH}^\cdot) + \text{H}_2\text{O}_2 & \xrightarrow{\text{hv}} \text{BiOCl(Fe}^{2+}\text{OH}^\cdot) + \text{HO}_2^\cdot + \text{H}^+ \quad (4.31) \\
\text{BiOCl(Fe}^{2+}\text{OH}^\cdot) & \longrightarrow \text{BiOCl(Fe}^{3+}\text{OH}^\cdot) + \text{BiOCl(e}_{\text{CB}}^-) \quad (4.32) \\
\text{BiOCl(e}_{\text{CB}}^-) + \text{O}_2 & \longrightarrow \text{O}_2^\cdot \xrightarrow{\text{H}^+} \text{HO}_2^\cdot \quad (4.33)
\end{align*}
\]
\[ \text{H}_2\text{O}_2 + \text{O}_2^- \rightarrow \cdot\text{OH} + \text{OH}^- + \text{O}_2 \]  
(4.34)

\[ \text{H}_2\text{O}_2 + \text{BiOCl}(e_{\text{CB}}^-) \rightarrow \cdot\text{OH} + \text{OH}^- \]  
(4.35)

\[ \text{OH}^- + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HO}_2^- \]  
(4.36)

\[ \text{MG/MG}^{4+} + \cdot\text{OH} / \text{O}_2^- / \text{HO}_2^- \rightarrow \text{Degradation products} \]  
(4.37)

### 4.3.9: Effect of temperature:

A series of experiments were carried out under the same operating conditions but varying reaction temperatures and the results are shown in Fig. 4.17 for comparison. It is clear from the Fig. 4.17 that the dye decomposition rate increased with the reaction temperature. Higher temperature will give a faster decomposition rate; so we can utilize the heat generated by the visible light radiation to heat the reaction solution in practice. The influence of temperature has been studied in the range 30 °C to 55 °C (Table 4.9 and Fig. 4.17). Rate constant increased from 0.024 min\(^{-1}\) to 0.028 min\(^{-1}\) with increase in temperature from 30 to 35 °C. However, further increase in temperature reduces the value of rate constant. Increased temperature tends to reduced electron-hole recombination. However, an increment in temperature also decreases the solubility of oxygen in water [15]. Both above mentioned conflicting factors have been equipoise at 35 °C. Significant amount of solution was evaporated at higher temperature.

**Table 4.9: Effect of temperature:** [MG] = 25 mgL\(^{-1}\), BiOCl = 0.7 gmL\(^{-1}\), Irradiation intensity = \(20 \times 10^3\) lux, pH = 8.0.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>k (min(^{-1}))</th>
<th>(t_{\text{½}}) (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>0.024</td>
<td>28.66</td>
</tr>
<tr>
<td>35</td>
<td>0.028</td>
<td>23.91</td>
</tr>
<tr>
<td>40</td>
<td>0.026</td>
<td>25.78</td>
</tr>
<tr>
<td>45</td>
<td>0.023</td>
<td>29.92</td>
</tr>
<tr>
<td>50</td>
<td>0.016</td>
<td>43.09</td>
</tr>
<tr>
<td>55</td>
<td>0.009</td>
<td>69.57</td>
</tr>
</tbody>
</table>
4.3.10: Effect of $N_2$ and $O_2$ purging:

The existence of oxygen in the suspension plays an important role in the photocatalytic degradation of organic pollutants. The oxygen molecule acts as an electron acceptor and decreases the electron–hole pair recombination [26]. In order to determine the effect of dissolved oxygen on the degradation of MG, the suspension purged with nitrogen and oxygen. The experimental results (Fig. 4.18) showed that the degradation of MG has been severely retarded by bubbling of pure $N_2$ (decrease in rate constant from 0.024 min$^{-1}$ to 0.0064 min$^{-1}$ but increases rapidly on bubbling oxygen through the dye solution (increase in rate constant from 0.024 min$^{-1}$ to 0.028 min$^{-1}$). The photocatalytic mechanism shows that the surface redox reactions initiated by photogenerated electrons and holes start the photocatalytic degradation of organics. If the surface chemical reactions of conduction band (CB) electrons are blocked by $N_2$ purging, the valence band (VB) holes would have a tendency to be consumed by the accumulated electrons via the electron–hole recombination inside the catalyst, hence, the photocatalytic degradation process would be significantly suppressed [27]. In the aerated condition, the oxygen accepts the conduction band electron and gives rise to a superoxide radical anion which further reacts with the hydrogen ion to form a hydroxyl radical in the system which in turn increases the degradation rate [28, 29]
Fig. 4.18: Decolorization of MG under various photocatalytic systems: \[ [MG] = 25 \text{ mgL}^{-1}, \text{BiOCl} = 0.7 \text{ gmL}^{-1}, \text{Irradiation intensity} = 20 \times 10^3 \text{ lux}, \text{pH} = 8.0, \text{Solar light intensity} = 14 \times 10^3 \pm 5 \text{ lux}, \text{Temperature} = 30 \pm 0.3 ^0\text{C}. \]

4.3.11: Comparison of Solar/Visible Light:

The effect of visible light on the degradation of MG dye by photocatalytic process has been investigated. The comparative study has been carried out for the degradation of dye solution in solar/visible light. The aqueous suspension of BiOCl containing MG dye was exposed to solar. Fig. 4.18 shows that the degradation rate as a function of irradiation time on illumination of an aqueous suspension of dye under sunlight and visible respectively. The rate of degradation was found to be much more in the solar light \( (k = 0.027 \text{ min}^{-1}) \). Blank experiments were also carried out under sunlight in absence of BiOCl where no observable loss of dye was observed.

4.3.12: Effect of other photocatalysts:

Experiments have been performed with other photocatalysts as well (see Table 4.10). The influence of three different photocatalysts, BiOCl, TiO\(_2\) and BaCrO\(_4\) on degradation kinetics of MG has been studied and results are shown in Fig. 4.19. The order of photoactivity follows the order: BiOCl > TiO\(_2\) > BaCrO\(_4\).
As a rule, the photocatalytic activity is closely related to the mobility of the photogenerated charge carriers and the positions of the conduction band (CB) and valence band (VB) in the photocatalyst. In metal oxide photocatalysts, the VB is commonly composed of O 2p. However, the VB of materials that contain element Bi mostly consists of O 2p and Bi 6s hybrid orbitals, whereas the CB consists of Bi 6p. It has been found that the broad VB increases the mobility of the photogenerated carriers [30,31]. This phenomenon was obvious for the bismuth-based photocatalysts because the Bi 6s orbital is largely dispersed, which is more beneficial to increasing the mobility of
photogenerated carriers. Moreover, the Bi–O sites in BiOCl acted as electron traps in the photocatalytic reaction. Therefore, materials containing Bi are probably active photocatalysts. It has already been reported that semiconductors such as BiOCl and TiO$_2$ have band gaps larger than 3 eV show strong photocatalytic activity. The conduction band and valence band potentials of both BiOCl and TiO$_2$ are larger than the corresponding redox potentials of H$^+$/H$_2$ and H$_2$O/O$_2$, and the photogenerated electron and hole can be separated efficiently. BaCrO$_4$ with smaller band gap shows less activity since its conduction band is much lower than that of BiOCl and TiO$_2$. Conduction band electron in these semiconductors rapidly falls into the hole thus showing reduced activity.

4.3.13: Effect of light intensity and irradiation time:

The influence of light intensity on the degradation efficiency has been examined at constant dye concentration (25 mgL$^{-1}$) and catalyst loading (0.7 gmL$^{-1}$). It is evident that the rate constant increases with increase in the light intensity as shown in Table 4.11 and Fig. 4.20. The visible light irradiation generates the photons required for the electron transfer from the valence band to the conduction band of a semiconductor photocatalyst and the energy of a photon is related to its wavelength and the overall energy input to a photocatalytic process is dependent on light intensity. The rate of degradation increases when more radiations fall on the catalyst surface and hence more hydroxyl radicals are produced [32,33].

Table 4.11: Effect of light intensity: [MG] = 25 mgL$^{-1}$, BiOCl = 0.7 gmL$^{-1}$, pH = 8.0, Temperature = 30 ± 0.3 °C.

<table>
<thead>
<tr>
<th>Light intensity × 10$^3$ lux</th>
<th>k (min$^{-1}$)</th>
<th>$t_{1/2}$ (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.024</td>
<td>28.66</td>
</tr>
<tr>
<td>16</td>
<td>0.028</td>
<td>23.91</td>
</tr>
<tr>
<td>20</td>
<td>0.032</td>
<td>21.07</td>
</tr>
<tr>
<td>25</td>
<td>0.035</td>
<td>19.70</td>
</tr>
<tr>
<td>30</td>
<td>0.037</td>
<td>18.39</td>
</tr>
</tbody>
</table>
4.3.14: Stability test for BiOCl activity:

To assess the stability of the BiOCl in the photocatalytic reaction, BiOCl was re-examined for two extra cycles. As shown in Fig. 4.21 (II), (III), the high photocatalytic performance of the as-prepared BiOCl for MG degradation was effectively maintained for 120 min of testing. After three cycles of repetition tests for photodegradation of MG, catalyst did not exhibit any significant loss of activity. This indicates that BiOCl is more stable and has good photocatalytic performance on degradation of MG [34, 35].

Fig. 4.21: MG degradation by BiOCl: (I) the first cycle; (II) the second cycle; (III) the third cycle; [MG] = 25 mgL\(^{-1}\), BiOCl = 0.7 gmL\(^{-1}\), Irradiation intensity = 20 \(\times\) 10\(^3\) lux, pH = 8.0, Temperature = 30 ± 0.3 °C.
4.3.15: COD and CO\textsubscript{2} measurements during mineralization of MG:

The chemical oxygen demand (COD) test is widely used as an effective technique to measure the organic strength of wastewater. The test allows the measurement of waste in terms of the total quantity of oxygen required for the oxidation of organic matter to CO\textsubscript{2} and water. In the present work results of chemical oxygen demand were taken as one of the parameter to judge the feasibility of the photochemical process for the degradation of MG dye solution [36].

The COD of the dye solution was estimated before and after treatment. The reduction in the COD values of the treated dye solution indicates the mineralization of dye molecules along with color removal. From Table 4.12 and Fig. 4.22, we can see that there is a substantial decrease of the COD of the solution, which continuously decreases with time. For instance, after a period of 2 h, the COD was reduced to about 52% of its initial value while at the end of the experiment (8 h) more than 98% of the COD has been removed (Fig. 4.22). Consequently, the complete mineralization of MG was achieved after 8 h of visible light irradiation in the presence of BiOCl because of the formation of more stable intermediates towards oxidation. The result implies that both mechanisms of degradation and mineralization play important roles for the photocatalytic effects under visible light irradiation.

Table 4.12: Mineralization of MG: [MG] = 25 mgL\textsuperscript{-1}, BiOCl = 0.7 gmL\textsuperscript{-1}, Irradiation intensity = 20 x 10\textsuperscript{3} lux, pH = 8.0 and Temperature = 30 ± 0.3 °C.

<table>
<thead>
<tr>
<th>Irradiation time (h)</th>
<th>COD (mgL\textsuperscript{-1})</th>
<th>CO\textsubscript{2} (mgL\textsuperscript{-1})</th>
<th>% Efficiency</th>
<th>NO\textsubscript{3}\textsuperscript{-} (mgL\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>99</td>
<td>13</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>64</td>
<td>36</td>
<td>35</td>
<td>10</td>
</tr>
<tr>
<td>4</td>
<td>47</td>
<td>67</td>
<td>52</td>
<td>14</td>
</tr>
<tr>
<td>6</td>
<td>18</td>
<td>88</td>
<td>81</td>
<td>22</td>
</tr>
<tr>
<td>8</td>
<td>1</td>
<td>121</td>
<td>98</td>
<td>28</td>
</tr>
</tbody>
</table>
Analysis of inorganic ions revealed as expected the formation of NO$_3^-$ in solution. As depicted in Table 4.12 and Fig. 4.22(C), the amount of NO$_3^-$ ions increased with increasing irradiation time. 28 mgL$^{-1}$ of NO$_3^-$ has been found after 8 h of irradiation time. The nitrogen atoms with -3 oxidation state produced NH$_4^+$ cations, subsequently NH$_4^+$ cations were converted into NO$_3^-$ ions. It was obvious that aqueous MG was mainly mineralized rather than being bleached [37].

### 4.3.16: UV-Vis spectra of MG Dye:

Primary absorption peaks of MG dye was at 420 nm and 617 nm. As the reaction proceeds, the two peaks disappear gradually as shown in Fig. 4.23 and the full scanning spectrum pattern changes obviously after 8 hrs. This may be the evidence of the intermediate by-product. At the end of the 8 hrs of reaction time, there is no evident absorption peak observed. This indicates that the pollutants are destroyed with the photocatalytic reaction and proves that wastewater is fully decomposed [38,39].
Fig. 4.23: UV-Vis spectrum of MG: [MG] = 25 mgL⁻¹, BiOCl = 0.7 gmL⁻¹, Irradiation intensity = 20 × 10³ lux, pH = 8.0, Temperature = 30 ± 0.3 °C.

4.3.17: Mechanism of MG degradation:

A mechanism of a chemical reaction is a mental model envisaged on the sound basis of experimental findings and mathematical modeling. Numerous mechanisms have been proposed by various workers for many different photocatalytic systems. Difference in substrate, nature of photocatalyst and type of radiation lead to a particular mechanism. A pertinent/mechanism helps in optimizing most plausible reaction condition.

BiOCl oxidizes in two ways, photogenerated holes h⁺ in the valence band and the •OH radicals, which are strongly active and degrading non-selective agents [40, 41]. Valence band holes (h_{VB}⁺) and conduction band electrons (e_{CB}⁻) are generated when aqueous BiOCl suspension is irradiated with visible light. These electron-hole pairs interact separately with the substrate. Valence band holes (h_{VB}⁺) react with surface bound H₂O or OH⁻ to produce hydroxyl radical (•OH). Valence band holes can also oxidize organic molecule. Conduction band electrons (e_{CB}⁻) reduce molecular oxygen to generate superoxide radicals as shown in eqs. (4.38) to eqs. (4.47) [42, 5].
Secondly, sensitization of dye molecule 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 (MG*) that undergoes degradation to yield products as follows [43, 41].

\[
\begin{align*}
\text{MG} + h\nu_{\text{Vis}} & \rightarrow \, 1\text{MG}^* \text{or } 3\text{MG}^* \\
1\text{MG}^* \text{or } 3\text{MG}^* + \text{BiOCl} & \rightarrow \, \text{MG}^{**} + \text{BiOCl} (e^-_{CB}) \\
\text{BiOCl} (e^-_{CB}) + \text{O}_2 & \rightarrow \, \text{O}_2^- + \text{BiOCl} \\
\text{MG}^{**} & \rightarrow \, \text{degradation products}
\end{align*}
\]
From estimated value of COD and CO$_2$, it is evident that 98% of COD removal has been achieved in 8 h of irradiation under chosen reaction condition. A decrease in COD and increase in CO$_2$ confirm the degradation of dye (Fig. 4.22(a), (b)). Significant amount of NO$_3^-$ released during the mineralization of dye (Fig. 4.22(c)). Complete disappearance of peaks in UV-Vis region indicates the absence of any organic moiety (see Fig. 4.23). COD and CO$_2$ estimations are in agreement with UV-vis spectral analysis during mineralization.

### 4.3.18: Kinetic studies:

Due to practical applications, the degradation kinetics of MG was investigated under the conditions of the appropriate optimum catalyst concentrations, natural pH and temperature of 30 ºC. From the results, it becomes clear that the degradation process proceeds in two parallel branches of only visible light degradation and when visible light is assisted with catalyst particles:

$$R = \frac{d[MG]}{dt} = R_1 + R_2$$

where R, R$_1$ and R$_2$ are the net degradation, the photocatalysis and the photolysis rates, respectively. The difference between the net rate and photolysis rate obtained experimentally, can be considered as the photocatalysis branch rate using the power law kinetic models in the forms:
\[ R_1 = k_1 [\text{MG}]^{n_1} \]  
(4.59)

\[ R_2 = k_2 [\text{MG}]^{n_2} \]  
(4.60)

Where, \( n_1, n_2, k_1 \) and \( k_2 \) are the appropriate order and rate constant of the reaction respectively. In this work, to obtain the appropriate parameters of eq. (4.59) and eq. (4.60), the differential method of analysis, based on the data of concentration vs. time, was used.

Fig. 4.24 (a), (b) presents the goodness of fit of the rate eq. (4.59) and eq. (4.60) to the data.

**Fig. 4.24(a):** The variation of MG degradation rate versus its concentration for photocatalysis: BiOCl = 0.7 gmL\(^{-1}\), Irradiation intensity = 20 \( \times 10^3 \) lux, pH = 8.0, Temperature = 30 ± 0.3 \(^0\)C.

**Fig. 4.24(b):** The variation of MG degradation rate versus its concentration for photolysis: BiOCl = 0.7 gmL\(^{-1}\), Irradiation intensity = 20 \( \times 10^3 \) lux, pH = 8.0, Temperature = 30 ± 0.3 \(^0\)C.
Our results are in agreement with other studies reported in literature [44-46]. Under chosen experimental conditions, the rate of degradation of MG for photodegradation and photolysis has been found to be 3.33 mgL$^{-1}$min$^{-1}$ and 2.46 mgL$^{-1}$min$^{-1}$ respectively.
Nile Blue

Nile blue belongs to phenoxazine class having basic nature. It is used for dyeing wool, cotton and leather. It is a water soluble dye with sharp adsorption peaks at 630 nm in visible region. NB is used in calico printing for tannin discharge effects and cellulose acetate dye.
4.3 (B): Effects of various experimental parameters on the degradation rate of Nile Blue (NB)

4.3.1: Photocatalytic degradation of nile blue (NB):
In Langmuir–Hinshelwood treatment of heterogeneous surface reactions, the photochemical degradation rate is described by pseudo first order kinetics which is rationalized in terms of the modified model to accommodate reactions occurring at a solid-liquid interface as [1, 2]

\[
\frac{dC}{dt} = \frac{-k_{L-H} K_{ad} C}{(1 + K_{ad} C)}
\]

where \(k_{L-H}\) is the reaction rate constant, \(K_{ad}\) is the adsorption coefficient of dye on the surface of BiOCl, 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. (4.11). So for simplification the denominator becomes 1. Integrating eq. (4.11), 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 nile blue (NB) on the BiOCl surface can be calculated by using eq. (4.13)

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

The photocatalytic degradation of NB dye follows pseudo first kinetics. The detection was realized at 630 nm. The results for typical run are given in Fig. 4.25(a) and (b). The absorbance of NB dye decreases with an increase in irradiation time.
Fig. 4.25 (a): Decolorization of NB: [NB] = 60 mgL\(^{-1}\), BiOCl = 4.0 gmL\(^{-1}\), Irradiation intensity = 76 \times 10^2\ lux, pH = 6.1, Temperature = 30 ± 0.3 °C.

While in dark and during photolysis, no significant changes have been observed (see Fig. 4.25(a)). The reaction rate constant (k) for the photocatalytic degradation reaction of NB dye, by BiOCl catalyst, was obtained from the slope of the linear relationship of the natural logarithm of the ratio between the initial concentration of NB and the
concentration after photocatalytic degradation $\ln(C_0/C)$ versus the corresponding irradiation time as shown in Fig. 4.25(b). The value of $k$ gives an indication for the activity of the photocatalyst. The plot of $\ln(C_0/C)$ versus time follows pseudo first order kinetics with regression co-efficient of 0.969, rate constant of 0.021 min$^{-1}$ and half life time of 31.55 min (Fig. 4.25(b)).

**4.3.2: Influence of initial pH:**

We have studied the degradation of nile blue dye by varying pH from 2.2 to 12.3. The results of pH effect is shown in Table 4.13 and Fig. 4.26. It is quite evident from the graph (Fig. 4.26) that variation in pH from 2.2 to 6.1 greatly influenced the photodegradation of NB in aqueous BiOCl suspension. The photodegradation efficiency increased with the increase in pH value. Since NB dye is cationic it is obvious that their adsorption on the photocatalyst surface is not possible in acidic medium due to repulsive forces between BiOCl surface and dye. But, it is possible to formation of hydroxyl radicals which react with dye molecules in acidic medium. Therefore degradation efficiency of dye was observed in acidic solution. The prevailing pH of the solutions affects the mode and extent of adsorption of NB on the BiOCl surface and thus, indirectly, photodegradation rate of NB [3].

<table>
<thead>
<tr>
<th>pH</th>
<th>$k(\text{min}^{-1})$</th>
<th>$t_{1/2}$(min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.2</td>
<td>0.008</td>
<td>86.19</td>
</tr>
<tr>
<td>4.3</td>
<td>0.009</td>
<td>70.00</td>
</tr>
<tr>
<td>6.1</td>
<td>0.018</td>
<td>38.11</td>
</tr>
<tr>
<td>8.0</td>
<td>0.015</td>
<td>44.25</td>
</tr>
<tr>
<td>10.5</td>
<td>0.012</td>
<td>53.97</td>
</tr>
<tr>
<td>12.3</td>
<td>0.006</td>
<td>112.13</td>
</tr>
</tbody>
</table>

**Table 4.13: Effect of pH:** [NB] = 20 mgL$^{-1}$, BiOCl = 2.0 gmL$^{-1}$, Irradiation intensity = $76 \times 10^2$ lux, Temperature = 30 ± 0.3 °C.
4.3.3: **Effect of catalyst weight:**

Heterogeneous photocatalytic reactions are known to show proportional increase in photodegradation with catalyst loading. In order to avoid excess catalyst and ensure total absorption of efficient photons optimum catalyst concentration has to be determined [4]. Thus the effect of photocatalyst weight for BiOCl on the photodegradation of the dye was studied in the range of 1.0 to 7.0 gmL$^{-1}$ and results are presented in Table 4.14 and plotted in Fig. 4.27. The graph depicts that as the concentration of catalyst increases from 1.0 to 4.0 gmL$^{-1}$, the degradation rate constant increases from 0.015 to 0.023 min$^{-1}$ but further increase in the catalyst concentration upto 7.0 gmL$^{-1}$, the rate constant decreases to 0.012 min$^{-1}$ respectively. The optimum weight of catalyst loading was found to be 4.0 gmL$^{-1}$. The increased degradation rate that follows the increase in the catalyst weight can be attributed to the fact that the total active surface area increases with increasing catalyst weight, thus accelerating the process. When all the dye molecules are adsorbed on catalyst (BiOCl) no improvement is achieved by adding more catalyst. The decrease in efficiency may be due to an increasing opacity of the suspension and to an enhancement of the light reflectance, because of the excess of BiOCl particles [5]. Additionally, in the case of high catalyst loads we observed agglomeration and sedimentation of BiOCl which
makes a significant fraction of catalyst to be inaccessible to either absorbing the dye or absorbing the radiation, with consequent decrease in active sites available to the catalytic reaction [4].

**Table 4.14: Effect of catalyst weight:** [NB] = 20 mgL⁻¹, Irradiation intensity=76×10² lux, pH=6.1, Temperature= 30±0.3 °C

<table>
<thead>
<tr>
<th>BiOCl gmL⁻¹</th>
<th>k (min⁻¹)</th>
<th>t½ (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>0.015</td>
<td>44.25</td>
</tr>
<tr>
<td>2.0</td>
<td>0.017</td>
<td>40.24</td>
</tr>
<tr>
<td>3.0</td>
<td>0.019</td>
<td>35.98</td>
</tr>
<tr>
<td>4.0</td>
<td>0.023</td>
<td>29.84</td>
</tr>
<tr>
<td>5.0</td>
<td>0.018</td>
<td>36.66</td>
</tr>
<tr>
<td>6.0</td>
<td>0.015</td>
<td>45.83</td>
</tr>
<tr>
<td>7.0</td>
<td>0.012</td>
<td>54.73</td>
</tr>
</tbody>
</table>

**Fig. 4.27:** Effect of catalyst weight.
4.3.4: Effect of initial dye concentration:

By taking different concentrations of dye, the effect of variation of dye concentration was also studied. In order to optimize the initial dye concentrations was varied from 20 to 80 mgL$^{-1}$. The results are shown in Table 4.15 and in Fig. 4.28. It has been observed from the graph that the increase in dye concentration from 20 mgL$^{-1}$ to 60 mgL$^{-1}$, the rate constant was found to be increased from 0.011 to 0.021 min$^{-1}$. Thereafter, rate constant decreased to 0.018 min$^{-1}$ with increase in dye concentration up to 80 mgL$^{-1}$. Rate constant was found to be maximal at 60 mgL$^{-1}$ of dye concentration. This may be attributed to the fact that as the concentration of dye increases, more dye molecules available for excitation followed by inter system crossing and hence, there was an increase in the rate [5]. Further increase in dye concentration, the equilibrium adsorption of dye on catalyst surface active sites increases, which hinders the competitive adsorption of OH$^-$ on the same sites, which means a lower formation rate of $^\cdot$OH radical. The increase in dye concentration also decreases the path length of photon entering the dye solution. At high dye concentration a significant amount of visible light may be absorbed by the dye molecules rather than the catalyst and this may also reduce the catalytic efficiency. Consequently, the degradation rate decreased as the dye concentration increases [3].

Table 4.15: Effect of initial dye concentration: BiOCl = 2.0 gmL$^{-1}$, Irradiation intensity = 76 × 10$^2$ lux, pH = 6.1, Temperature = 30 ± 0.3 $^0$C.

<table>
<thead>
<tr>
<th>NB (mgL$^{-1}$)</th>
<th>k (min$^{-1}$)</th>
<th>$t_{1/2}$ (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.011</td>
<td>59.23</td>
</tr>
<tr>
<td>30</td>
<td>0.013</td>
<td>51.56</td>
</tr>
<tr>
<td>40</td>
<td>0.015</td>
<td>45.65</td>
</tr>
<tr>
<td>50</td>
<td>0.020</td>
<td>34.17</td>
</tr>
<tr>
<td>60</td>
<td>0.021</td>
<td>31.55</td>
</tr>
<tr>
<td>70</td>
<td>0.019</td>
<td>35.86</td>
</tr>
<tr>
<td>80</td>
<td>0.018</td>
<td>38.50</td>
</tr>
</tbody>
</table>
4.3.5: Effect of varying oxidant concentration:

In this section we have studied the effect of concentration of H$_2$O$_2$ on the initial reaction rate of nile blue degradation is shown in Table 4.16 and Fig. 4.29(a). The photocatalytic efficiency found to increase as the concentration of H$_2$O$_2$ increased from 15 to 30 mgL$^{-1}$ and it reached the optimum at 30 mgL$^{-1}$. Consequently the rate decreased as the concentration of the H$_2$O$_2$ increased beyond the optimum. H$_2$O$_2$ is considered to have two functions in the process of photocatalytic degradation. It accepts a photogenerated electron from the conduction band and thus promotes the charge separation and it also forms 'OH radicals according to eq. (4.14) and (4.15) [6-9]

\[
\begin{align*}
H_2O_2 + e^- & \rightarrow OH^- + \cdot OH \\
H_2O_2 + O_2^- & \rightarrow \cdot OH + OH^- + O_2
\end{align*}
\]  

(4.14) (4.15)

Excess H$_2$O$_2$ may act as a hole or an 'OH scavenger or react with photocatalyst and form peroxocompounds, which are detrimental to the photocatalytic action. This explains the need for an optimal concentration of H$_2$O$_2$ for the maximum effect.
K$_2$S$_2$O$_8$ can also trap the photogenerated conduction band electron results in the formation of sulphate ion (SO$_4^{2-}$), a strong oxidizing agent (standard oxidation potential = 2.6 eV), which can participate in degradation process.

\[
S_2O_8^{2-} + e^- \rightarrow SO_4^{2-} + SO_4^{2-}
\]  

(4.16)

Table 4.16: Effect of oxidant: Decolorization of NB: [NB] = 60 mgL$^{-1}$, BiOCl = 4.0 gmL$^{-1}$, Irradiation intensity = $76 \times 10^2$ lux, pH = 6.1, Temperature = 30 ± 0.3 $^0$C.

<table>
<thead>
<tr>
<th>Oxidant (mgL$^{-1}$)</th>
<th>H$_2$O$_2$</th>
<th>K$_2$S$_2$O$_8$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>k (min$^{-1}$)</td>
<td>t$_{1/2}$ (min)</td>
</tr>
<tr>
<td>0</td>
<td>0.021</td>
<td>31.55</td>
</tr>
<tr>
<td>15</td>
<td>0.024</td>
<td>28.10</td>
</tr>
<tr>
<td>30</td>
<td>0.028</td>
<td>24.67</td>
</tr>
<tr>
<td>45</td>
<td>0.025</td>
<td>26.92</td>
</tr>
<tr>
<td>60</td>
<td>0.024</td>
<td>28.73</td>
</tr>
<tr>
<td>75</td>
<td>0.021</td>
<td>32.90</td>
</tr>
<tr>
<td>90</td>
<td>0.018</td>
<td>37.74</td>
</tr>
<tr>
<td>105</td>
<td>0.015</td>
<td>46.01</td>
</tr>
</tbody>
</table>

Fig. 4.29: Effect of oxidant: (a) H$_2$O$_2$ and (b) K$_2$S$_2$O$_8$.  

}
From Fig. 4.29(b), with increase in K\textsubscript{2}S\textsubscript{2}O\textsubscript{8} concentration from 15 to 45 mgL\textsuperscript{-1}, rate constant increased from 0.023 to 0.029 min\textsuperscript{-1}. At optimal concentration of K\textsubscript{2}S\textsubscript{2}O\textsubscript{8}, rate constant has been found to be 0.029 min\textsuperscript{-1}. Consequently degradation rate decreases as the concentration of the K\textsubscript{2}S\textsubscript{2}O\textsubscript{8} increases beyond the optimum [8]. A possible explanation of this behavior may be the light absorption from dye molecule leads to the photo-sensitization of the molecule, which is accompanied by the excitation of an electron from the lower to the upper energy level. Following this, the excited dye molecule injects electrons to the S\textsubscript{2}O\textsubscript{8}\textsuperscript{2\textendash} according to eq. (4.16). The resulting SO\textsubscript{4}\textsuperscript{\textendash} radicals, strong oxidizing agents, attack the chromophore group in dye leading to the decolorization of the solution. The decrease in rate constant above optimum concentration is due to the adsorption of sulphate ions formed during the reaction on surface of catalyst deactivating a section of photocatalyst [10,11][8,9].

4.3.6: **Effect of varying salt concentration:**

Normally with the addition of either sodium chloride (NaCl) or sodium carbonate (Na\textsubscript{2}CO\textsubscript{3}), at or near boiling point, the direct or substantive dyeing is carried out in a neutral or slightly alkaline dye bath. The effect of presence of NaCl and Na\textsubscript{2}CO\textsubscript{3} is shown in Table 4.17 and Fig. 4.30.

*Table 4.17: Effect of salt: Decolorization of NB: [NB] = 60 mgL\textsuperscript{-1}, BiOCl = 4.0 gmL\textsuperscript{-1}, Irradiation intensity = 76 × 10\textsuperscript{2} lux, pH = 6.1, Temperature = 30 ± 0.3 °C.*

<table>
<thead>
<tr>
<th>Salt (mgL\textsuperscript{-1})</th>
<th>Na\textsubscript{2}CO\textsubscript{3}</th>
<th>NaCl</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>k (min\textsuperscript{-1})</td>
<td>t\textsubscript{1/2} (min)</td>
</tr>
<tr>
<td>0</td>
<td>0.021</td>
<td>31.55</td>
</tr>
<tr>
<td>20</td>
<td>0.018</td>
<td>36.55</td>
</tr>
<tr>
<td>40</td>
<td>0.014</td>
<td>47.53</td>
</tr>
<tr>
<td>60</td>
<td>0.012</td>
<td>54.22</td>
</tr>
<tr>
<td>80</td>
<td>0.010</td>
<td>65.62</td>
</tr>
<tr>
<td>100</td>
<td>0.008</td>
<td>79.10</td>
</tr>
<tr>
<td>120</td>
<td>0.006</td>
<td>100.43</td>
</tr>
<tr>
<td>140</td>
<td>0.006</td>
<td>114.35</td>
</tr>
</tbody>
</table>
As can be seen from Fig. 4.30, an increment in concentration of CO$_3^{2-}$ from 20 mgL$^{-1}$ to 140 mgL$^{-1}$, results in decrease of rate constant 0.018 to 0.006 min$^{-1}$, while with same Cl$^-$ ion concentration variation, the rate constant decreased from 0.020 to 0.006 min$^{-1}$. Half life time increases from 36.55 to 114.35 min and 33.77 to 110.0 min with an increase in concentration from 20 mgL$^{-1}$ to 140 mgL$^{-1}$ for CO$_3^{2-}$ and Cl$^-$ ions respectively. The inhibition is undoubtedly due to their ability to act as hydroxyl radical (OH) scavengers. The observed mechanism of hydroxyl radical scavenging is given by eqs. (4.17) to (4.20) [12,13].

\[
\begin{align*}
\text{Cl}^- + \cdot \text{OH} & \rightarrow \text{Cl} + \text{OH}^- \quad \text{(4.17)} \\
\text{Cl}^- + h_{vb}^+ & \rightarrow \cdot \text{Cl} \quad \text{(4.18)} \\
\text{Cl}^- + \cdot \text{Cl} & \rightarrow \text{Cl}_2^* \quad \text{(4.19)} \\
\text{CO}_3^{2-} + \cdot \text{OH} & \rightarrow \text{CO}_3^- + \text{H}_2\text{O} \quad \text{(4.20)}
\end{align*}
\]

These ions may also block the active sites on the photocatalyst surface thus deactivating the catalysts towards the dye and intermediate molecules. Although, the generated radical anions have been shown to be an oxidant itself, but its oxidation potential is less than that of the hydroxyl radicals [14].
4.3.7: Effect of FeCl₃:

Here, we have studied the effect of FeCl₃ on the photodegradation of NB has been studied by varying the concentration from 15 mgL⁻¹ to 105 mgL⁻¹ (Table 4.18 and Fig. 4.31). FeCl₃ behaves as an electron scavenger (Fe³⁺ + e⁻ → Fe²⁺) thus preventing the recombination of electron hole pairs. Under the experimental conditions the following reactions become significant.

\[
\begin{align*}
\text{Fe}^{2+} + \text{H}_2\text{O}_2 + \text{H}^+ & \rightarrow \text{Fe}^{3+} + \cdot\text{OH} + \text{H}_2\text{O} \quad (4.21) \\
\text{Fe}^{2+} + \text{HO}_2^- + \text{H}^+ & \rightarrow \text{Fe}^{3+} + \text{H}_2\text{O}_2 \quad (4.22)
\end{align*}
\]

In BiOCl/FeCl₃/Vis addition of FeCl₃ caused an increase in rate constant (0.032 min⁻¹) up to concentration 60 mgL⁻¹. Photoactivation of surface adsorbed complex ion (Fe³⁺ OH⁻) results in formation of Fe²⁺•OH species, which inject electrons to conduction band of BiOCl (eqs. 4.24 to 4.25). Increased rate of degradation in case of FeCl₃ is explicable due to rapid scavenging of conduction band electrons by molecular oxygen leading to formation of superoxide and hydroperoxide radicals (eq. 4.26). Higher concentration of FeCl₃ eliminates adsorption of cationic dye on BiOCl surface and also inhibits reaction rate by reducing production of hydroxyl radicals [15-18].

\[
\begin{align*}
\text{NB} + h\nu_{\text{visible}} & \rightarrow \text{NB}^* \text{ or } \text{3NB}^* \quad (4.23) \\
\text{1NB}^* \text{ or } \text{3NB}^* + \text{BiOCl (Fe}^{3+} \text{OH}^-) & \rightarrow \text{BiOCl (Fe}^{2+} \cdot\text{OH}) + \text{NB}^{++} \quad (4.24) \\
\text{BiOCl (Fe}^{2+} \cdot\text{OH}) & \rightarrow \text{BiOCl (e}^-_{\text{CB}}) + \text{BiOCl (Fe}^{3+} \cdot\text{OH}) \quad (4.25) \\
\text{BiOCl (e}^-_{\text{CB}}) + \text{O}_2 & \rightarrow \text{O}_2^- + \text{H}^+ \rightarrow \text{HO}_2^* \quad (4.26) \\
\text{NB/NB}^{++} + \cdot\text{OH/ O}_2^- / \text{HO}_2^* & \rightarrow \text{Degradation products} \quad (4.27)
\end{align*}
\]

The metal ions such as Fe³⁺ could be used as sensitizers during semiconductor photocatalytic degradation of organic pollutants.
Table 4.18: Effect of FeCl₃: [NB] = 60 mgL⁻¹, BiOCl = 4.0 gmL⁻¹, Irradiation intensity = 76 × 10² lux, pH = 6.1, Temperature = 30 ± 0.3 °C.

<table>
<thead>
<tr>
<th>FeCl₃ (mgL⁻¹)</th>
<th>k (min⁻¹)</th>
<th>t₁/₂ (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.021</td>
<td>41.25</td>
</tr>
<tr>
<td>15</td>
<td>0.023</td>
<td>38.11</td>
</tr>
<tr>
<td>30</td>
<td>0.026</td>
<td>34.89</td>
</tr>
<tr>
<td>45</td>
<td>0.028</td>
<td>30.96</td>
</tr>
<tr>
<td>60</td>
<td>0.032</td>
<td>36.32</td>
</tr>
<tr>
<td>75</td>
<td>0.030</td>
<td>40.24</td>
</tr>
<tr>
<td>90</td>
<td>0.025</td>
<td>43.42</td>
</tr>
<tr>
<td>105</td>
<td>0.019</td>
<td>67.54</td>
</tr>
</tbody>
</table>

Fig. 4.31: Effect of FeCl₃.

4.3.8: Effect of Fe³⁺/H₂O₂:

For the treatment of the effective decolorization and degradation of dyes under laboratory conditions, the oxidation system based on Fenton reaction has been used. The process is based on the formation of reactive oxidizing species, able to efficiently degrade the pollutants of the wastewater stream. Fenton’s reagent is a mixture of H₂O₂ and Fe²⁺ or Fe³⁺ iron [19-21]. Efficiency of Fe³⁺/H₂O₂ system has been studied for decolorization of
NB in the presence of BiOCl and visible light irradiation. The results are displayed in Table 4.19 and plotted in Fig. 4.32.

Table 4.19: Effect of Fe\(^{3+}/\)H\(_2\)O\(_2\): [NB] = 60 mgL\(^{-1}\), BiOCl = 4.0 gmL\(^{-1}\), Irradiation intensity = 76 \times 10\(^2\) lux, pH = 6.1, Temperature = 30 \pm 0.3 \degree C.

<table>
<thead>
<tr>
<th>Fe(^{3+}:) H(_2)O(_2)</th>
<th>With BiOCl</th>
<th>Without BiOCl</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(k) (min(^{-1}))</td>
<td>(t_{1/2}) (min)</td>
</tr>
<tr>
<td>3:1</td>
<td>0.045</td>
<td>15.07</td>
</tr>
<tr>
<td>1.4:1</td>
<td>0.054</td>
<td>12.79</td>
</tr>
<tr>
<td>1:1.4</td>
<td>0.058</td>
<td>11.76</td>
</tr>
<tr>
<td>1:3</td>
<td>0.040</td>
<td>17.06</td>
</tr>
<tr>
<td>11:1</td>
<td>0.028</td>
<td>23.91</td>
</tr>
</tbody>
</table>

Fig. 4.32: Effect of Fe\(^{3+}/\)H\(_2\)O\(_2\).

Rate constant has a value of 0.045 min\(^{-1}\) on the addition of (Fe\(^{3+}:\) H\(_2\)O\(_2\)) in molar ratio (3:1). In the presence of (Fe\(^{3+}:\) H\(_2\)O\(_2\)) in molar ratio (1.4:1), rate constant has been found 0.054 min\(^{-1}\). Upon irradiation of Fe\(^{3+}/\)H\(_2\)O\(_2\)/BiOCl/NB system with visible light, production of \(^{•}\)OH radicals increases involving a very complex mechanism. Dye absorbs
visible irradiation and is excited into high-energy state. This excited dye molecules reduce the ferric ion complex to ferrous ion complex followed by the transfer to ferric ion [22]. The reduced ferrous ions react with hydrogen peroxide to decompose and produce hydroxyl radical (eq. (4.30)). "OH radicals also decompose H$_2$O$_2$ to HO$_2^\cdot$. A similar mechanism has been reported by Amiri, Wu and Herrara et al [23-25].

$$\text{NB} + h\nu_{\text{visible}} \rightarrow \text{NB}^* \text{ or } \text{NB}^*$$  \hspace{1cm} (4.28)

$$\text{NB}^* \text{ or } \text{NB}^* + \text{BiOCl(Fe}^{3+}\text{OH}^-) \rightarrow \text{BiOCl(Fe}^{2+}\text{OH}^\cdot) + \text{NB}^{4+}$$  \hspace{1cm} (4.29)

$$\text{BiOCl(Fe}^{2+}\text{OH}^\cdot) + \text{H}_2\text{O}_2 \xrightarrow{\text{hv}} \text{BiOCl(Fe}^{3+}\text{OH}^\cdot) + \text{OH}^- + \cdot\text{OH}$$  \hspace{1cm} (4.30)

$$\text{BiOCl(Fe}^{3+}\text{OH}^\cdot) + \text{H}_2\text{O}_2 \xrightarrow{\text{hv}} \text{BiOCl(Fe}^{2+}\text{OH}^\cdot) + \text{HO}_2^\cdot + \text{H}^+$$  \hspace{1cm} (4.31)

$$\text{BiOCl(Fe}^{2+}\text{OH}^\cdot) \rightarrow \text{BiOCl(Fe}^{3+}\text{OH}^\cdot) + \text{BiOCl(e}^-_{\text{CB}})$$  \hspace{1cm} (4.32)

$$\text{BiOCl(e}^-_{\text{CB}}) + \text{O}_2 \rightarrow \text{O}_2^- \xrightarrow{\text{H}^+} \text{HO}_2^-$$  \hspace{1cm} (4.33)

$$\text{H}_2\text{O}_2 + \text{O}_2^- \rightarrow \cdot\text{OH} + \text{OH}^- + \text{O}_2$$  \hspace{1cm} (4.34)

$$\text{H}_2\text{O}_2 + \text{BiOCl(e}^-_{\text{CB}}) \rightarrow \cdot\text{OH} + \text{OH}^-$$  \hspace{1cm} (4.35)

$$\cdot\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HO}_2^-$$  \hspace{1cm} (4.36)

$$\text{NB} / \text{NB}^{4+} + \cdot\text{OH} / \text{O}_2^- / \text{HO}_2^- \rightarrow \text{Degradation products}$$  \hspace{1cm} (4.37)

**4.3.9: Effect of temperature:**

The effect of temperature has been studied by varying the range from 30 to 55 °C (see Table 4.20 and Fig. 4.33). Rate constant increases from 0.019 to 0.027 min$^{-1}$ with increase in temperature from 30 to 40 °C. However, further increase in temperature reduces the value of rate constant. Increased temperature tends to reduced electron-hole recombination. However, an increment in temperature also decreases the solubility of oxygen in water [15]. Both above mentioned conflicting factors have been equipoise at 35 °C. Significant amount of solution was evaporated at higher temperature.
Table 4.20: Effect of temperature: [NB] = 60 mgL⁻¹, BiOCl = 4.0 gmL⁻¹, Irradiation intensity = $76 \times 10^2$ lux, pH = 6.1.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>k (min⁻¹)</th>
<th>$t_{1/2}$ (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>0.019</td>
<td>35.75</td>
</tr>
<tr>
<td>35</td>
<td>0.022</td>
<td>30.71</td>
</tr>
<tr>
<td>40</td>
<td>0.027</td>
<td>25.21</td>
</tr>
<tr>
<td>45</td>
<td>0.024</td>
<td>28.66</td>
</tr>
<tr>
<td>50</td>
<td>0.020</td>
<td>33.57</td>
</tr>
<tr>
<td>55</td>
<td>0.012</td>
<td>55.52</td>
</tr>
</tbody>
</table>

Fig. 4.33: Effect of temperature.

4.3.10: Effect of $N_2$ and $O_2$ purging:

Dissolved gases in the suspension plays an important role in the photocatalytic degradation of organic pollutants. Fig. 4.34 shows that the degradation of NB has been severely retarded by bubbling of pure N₂ (decrease in rate constant from 0.021 min⁻¹ to 0.0046 min⁻¹) but increases rapidly on bubbling of oxygen through the dye solution (increase in rate constant from 0.021 min⁻¹ to 0.036 min⁻¹). The photocatalytic
mechanism shows that the surface redox reactions initiated by photogenerated electrons and holes start the photocatalytic degradation of organics. If the surface chemical reactions of conduction band (CB) electrons are blocked by \( \text{N}_2 \) purging, the valance band (VB) holes would have a tendency to be consumed by the accumulated electrons via the electron–hole recombination inside the catalyst, hence, the photocatalytic degradation process would be significantly suppressed [26, 27]. According to photocatalytic mechanism, in the aerated condition, the oxygen accepts the conduction band electron and gives rise to a superoxide radical anion which further reacts with the hydrogen ion to form a hydroxyl radical in the system which in turn increases the degradation rate [28, 29].

![Decolorization of NB under various photocatalytic systems](image)

**Fig. 4.34: Decolorization of NB under various photocatalytic systems:**

\([\text{NB}] = 60 \, \text{mgL}^{-1}, \, \text{BiOCl} = 4.0 \, \text{gml}^{-1}, \, \text{Irradiation intensity} = 76 \times 10^2 \, \text{lux}, \, \text{pH} = 6.1, \, \text{Solar light intensity} = 152 \times 10^3 \pm 5 \, \text{lux} , \text{Temperature} = 30 \pm 0.3 \, \text{°C}.

### 4.3.11: Comparison of Solar/Visible Light:

For the degradation of dye, the comparative study has been carried out under solar/visible light. Fig. 4.34 shows that the degradation rate as a function of irradiation time on illumination of an aqueous suspension of NB under sunlight and visible respectively. The rate of degradation was found to be much more in the solar light \((k = 0.0432 \, \text{min}^{-1})\). Blank experiments also were carried out under sunlight in the absence of BiOCl where no observable loss of dye was observed.
4.3.12: Effect of other photocatalysts:

The influence of three different photocatalysts, BiOCl, TiO₂ and BaCrO₄ has been used to study the effect on degradation kinetics of NB and results are shown in Table 4.21 and Fig. 4.35. The order of photoactivity was found to be: BiOCl > TiO₂ > BaCrO₄.

Table 4.21: Effect of other photocatalysts: [NB] = 60 mgL⁻¹, [Photocatalyst] = 4.0 gmL⁻¹, Irradiation intensity = 76 × 10² lux, pH = 6.1, Temperature = 30 ± 0.3 °C.

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Bandgap(eV)</th>
<th>k (min⁻¹)</th>
<th>t₁/₂ (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BiOCl</td>
<td>3.2</td>
<td>0.021</td>
<td>31.55</td>
</tr>
<tr>
<td>TiO₂</td>
<td>3.1</td>
<td>0.018</td>
<td>37.13</td>
</tr>
<tr>
<td>BaCrO₄</td>
<td>2.6</td>
<td>0.011</td>
<td>58.33</td>
</tr>
</tbody>
</table>

Fig. 4.35: Effect of other photocatalysts.

As a rule, the photocatalytic activity is closely related to the mobility of the photogenerated charge carriers and the positions of the conduction band (CB) and valence band (VB) in the photocatalyst. In metal oxide photocatalysts, the VB is commonly composed of O 2p. However, the VB of materials that contain element Bi mostly consists of O 2p and Bi 6s hybrid orbitals, whereas the CB consists of Bi 6p. It has been found that the broad VB increases the mobility of the photogenerated carriers [30,31]. This phenomenon was obvious for the bismuth-based photocatalysts because the
Bi 6s orbital is largely dispersed, which is more beneficial to increasing the mobility of photogenerated carriers. Moreover, the Bi–O sites in BiOCl acted as electron traps in the photocatalytic reaction. Therefore, materials containing Bi are probably active photocatalysts. It has already been reported that semiconductors such as BiOCl and TiO$_2$ have band gaps larger than 3 eV show strong photocatalytic activity. The conduction band and valence band potentials of both BiOCl and TiO$_2$ are larger than the corresponding redox potentials of H$^+$/H$_2$ and H$_2$O/O$_2$, and the photogenerated electron and hole can be separated efficiently. BaCrO$_4$ with smaller band gap shows less activity since its conduction band is much lower than that of BiOCl and TiO$_2$. Conduction band electron in these semiconductors rapidly falls into the hole thus showing reduced activity.

### 4.3.13: Effect of light intensity and irradiation time:

Here, we have studied the influence of light intensity on the degradation efficiency at constant dye concentration (60 mgL$^{-1}$) and catalyst loading (4.0 mgL$^{-1}$). It is evident that the rate constant increases with increase in the light intensity as shown in Table 4.22 and Fig. 4.36. The visible light irradiation generates the photons required for the electron transfer from the valence band to the conduction band of a semiconductor photocatalyst. The energy of a photon is related to its wavelength and the overall energy input to a photocatalytic process is dependent on light intensity. The rate of degradation increases when more radiations fall on the catalyst surface and hence more hydroxyl radicals are produced [32,33].

**Table 4.22: Effect of light intensity:** [NB] = 60 mgL$^{-1}$, BiOCl = 4.0 gmL$^{-1}$, pH = 6.1, Temperature = 30 ± 0.3 °C.

<table>
<thead>
<tr>
<th>Light intensity $\times 10^2$ lux</th>
<th>k (min$^{-1}$)</th>
<th>$t_{1/2}$ (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>0.014</td>
<td>48.94</td>
</tr>
<tr>
<td>52</td>
<td>0.016</td>
<td>41.25</td>
</tr>
<tr>
<td>76</td>
<td>0.021</td>
<td>31.55</td>
</tr>
<tr>
<td>100</td>
<td>0.025</td>
<td>27.43</td>
</tr>
<tr>
<td>134</td>
<td>0.028</td>
<td>24.16</td>
</tr>
</tbody>
</table>
4.3.14: Stability test for BiOCl activity:

To assess the stability of the BiOCl in the photocatalytic reaction, BiOCl was re-examined for two extra cycles. Results are shown in Fig. 4.37:

---

**Fig. 4.37:** NB degradation by BiOCl: (I) the first cycle; (II) the second cycle; (III) the third cycle; [NB] = 60 mgL⁻¹, BiOCl = 4.0 gmL⁻¹, Irradiation intensity=76×10² lux, pH = 6.1, Temperature = 30 ± 0.3 °C.
As shown in Fig. 4.37 (II), (III), the high photocatalytic performance of the as-prepared BiOCl for NB degradation was effectively maintained for 160 min of testing. After three cycles of repetition tests for photodegradation of NB, catalyst did not exhibit any significant loss of activity. This indicated that BiOCl is more stable and has good photocatalytic performance on degradation of NB [34, 35].

**4.3.15: COD and CO₂ measurements during mineralization of NB:**

To judge the feasibility of the photochemical process for degradation and mineralization of NB dye solution, the results of chemical oxygen demand (COD) were taken as one of the parameter [36]. From Table 4.23 and Fig. 4.38, there is a substantial decrease of the COD of the solution from 221 mgL\(^{-1}\) to 4 mg/L\(^{-1}\) and increase in CO\(_2\) value from 80 mgL\(^{-1}\) to 310 mgL\(^{-1}\) in 6 h of irradiation. Consequently, the complete mineralization of NB was achieved after 6 h of visible light irradiation in the presence of BiOCl because of the formation of more stable intermediates towards oxidation. The result implies that both mechanisms of degradation and mineralization play important roles for the photocatalytic effects under visible light irradiation.

**Table 4.23: Mineralization of NB:** \([\text{NB}] = 60 \text{ mgL}^{-1}, \text{BiOCl} = 4.0 \text{ gmL}^{-1},\) Irradiation intensity = 76 × 10\(^2\) lux, pH = 6.1, Temperature = 30 ± 0.3 \(^0\)C.

<table>
<thead>
<tr>
<th>Irradiation time (h)</th>
<th>COD (mgL(^{-1}))</th>
<th>CO(_2) (mgL(^{-1}))</th>
<th>% Efficiency</th>
<th>NO(_3)^- (mgL(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>221</td>
<td>80</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>192</td>
<td>141</td>
<td>13</td>
<td>8</td>
</tr>
<tr>
<td>2</td>
<td>93</td>
<td>185</td>
<td>58</td>
<td>12</td>
</tr>
<tr>
<td>3</td>
<td>20</td>
<td>210</td>
<td>90.</td>
<td>15</td>
</tr>
<tr>
<td>4</td>
<td>14</td>
<td>242</td>
<td>93</td>
<td>20</td>
</tr>
<tr>
<td>5</td>
<td>8</td>
<td>273</td>
<td>96</td>
<td>27</td>
</tr>
<tr>
<td>6</td>
<td>4</td>
<td>310</td>
<td>98</td>
<td>28</td>
</tr>
</tbody>
</table>
Analysis of inorganic ions revealed as expected the formation of \( \text{NO}_3^- \) in solution. As depicted in Table 4.23, the amount of \( \text{NO}_3^- \) ions increased with increasing irradiation time. 28 mgL\(^{-1}\) of \( \text{NO}_3^- \) has been found after 6 h of irradiation time. The nitrogen atoms with \(-3\) oxidation state produced \( \text{NH}_4^+ \) cations, subsequently \( \text{NH}_4^+ \) cations were converted into \( \text{NO}_3^- \) ions. It was obvious that aqueous NB was mainly mineralized rather than being bleached [37].

After 6 h of irradiation, 98 % efficiency has been observed for the process. 28 mgL\(^{-1}\) of \( \text{NO}_3^- \) have been found after 6 h of irradiation time.

4.3.16: UV-Vis spectra of NB Dye:

Primary absorption peaks of NB dye was at 275 nm and 630 nm. As the reaction proceeds, the two peaks disappear gradually as shown in Fig. 4.39 and the full scanning spectrum pattern changes obviously after 8 h. This may be the evidence of the intermediate by-product. At the end of the 8 h of reaction time, there is no evident absorption peak observed. It indicates that the pollutants are destroyed with the photocatalytic reaction and proves that wastewater is fully decomposed [38,39].
**Fig. 4.39:** UV-Vis spectrum of NB: \([NB] = 60 \text{ mg}\text{L}^{-1}, \text{BiOCl} = 4.0 \text{ g}\text{m}\text{L}^{-1}, \text{Irradiation intensity} = 76 \times 10^2 \text{ lux}, \text{pH} = 6.1, \text{Temperature} = 30 \pm 0.3 ^\circ \text{C}.

### 4.3.17: Mechanism of NB degradation:

The degradation mechanism of NB is as follows: BiOCl oxidizes in two ways, photogenerated holes \(h^+\) in the valence band and the \(^{•}\text{OH}\) radicals, which are strongly active and degrading non-selective agents \([40,41]\). Valence band holes (\(h_{VB}^+\)) and conduction band electrons (\(e_{CB}^-\)) are generated when aqueous BiOCl suspension was irradiated with visible light. These electron-hole pairs interact separately with the substrate. Valence band holes (\(h_{VB}^+\)) react with surface bound \(H_2O\) or \(OH^-\) to produce hydroxyl radical (\(^{•}\text{OH}\)). Valence band holes can also oxidize organic molecules. Conduction band electrons (\(e_{CB}^-\)) reduce molecular oxygen to generate superoxide radicals as shown in eqs. (4.38) to (4.47) \([42, 5]\).

\[
\begin{align*}
\text{BiOCl} + h_{\text{Visible}}^+ & \rightarrow \text{BiOCl} (h_{VB}^+ + e_{CB}^-) \quad (4.38) \\
\text{BiOCl} (h_{VB}^+) + H_2O & \rightarrow \text{BiOCl} + H^+ + ^{•}\text{OH} \quad (4.39) \\
\text{BiOCl} (h_{VB}^+) + OH^- & \rightarrow \text{BiOCl} + ^{•}\text{OH} \quad (4.40) \\
\text{BiOCl} (e_{CB}^-) + O_2 & \rightarrow \text{BiOCl} + O_2^- \quad (4.41)
\end{align*}
\]
\[
\begin{align*}
O_2^- + H^+ & \rightarrow HO_2^* \\
HO_2^* + H^+ + BiOCl (e^-_{CB}) & \rightarrow H_2O_2 + BiOCl \\
H_2O_2 + BiOCl (e^-_{CB}) & \rightarrow HO^- + OH^- + BiOCl \\
NB + h^+_{VB} & \text{ Oxidation products} \\
NB + e^-_{CB} & \text{ Reduction products} \\
NB + OH^- & \text{ Degradation products}
\end{align*}
\]

Secondly, sensitization of dye molecule 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 (NB\(^{+}\)) that undergoes degradation to yield products as follows [43, 41]

\[
\begin{align*}
NB + h v (Vis) & \rightarrow 1NB^* \text{ or } 3NB^* \\
1NB^* \text{ or } 3NB^* + BiOCl & \rightarrow NB^{+} + BiOCl (e^-_{CB}) \\
BiOCl (e^-_{CB}) + O_2 & \rightarrow O_2^- + BiOCl \\
NB^{++} & \rightarrow \text{ degradation products}
\end{align*}
\]

Cationic dye radicals reacts with hydroxyl ions undergoing oxidation via eqs. 4.52 to 4.53 or interacts with O\(_2^\cdot\), HO\(_2^\cdot\) or HO\(^-\) species to generate intermediates that finally lead to degradation products (eqs. 4.54 to 4.57).

\[
\begin{align*}
NB^{++} + OH^- & \rightarrow NB + OH^- \\
NB + 2HO^\cdot & \rightarrow H_2O + \text{ oxidation products} \\
O_2^- + H^+ & \rightarrow HO_2^* \\
HO_2^\cdot + H^+ + BiOCl (e^-_{CB}) & \rightarrow H_2O_2 + BiOCl \\
H_2O_2 + BiOCl (e^-_{CB}) & \rightarrow HO^- + OH^- + BiOCl \\
NB^{+} + O_2^- & \rightarrow \text{ degradation products}
\end{align*}
\]

From estimated value of COD and CO\(_2\), it is evident that 98 % of COD removal has been achieved in 6 h of irradiation under chosen reaction condition. A decrease in COD (Fig. 4.38(A)) and increase in CO\(_2\) confirm the degradation of dye (see Fig. 4.38(B)).
Significant amount of NO$_3^-$ released during the mineralization of dye (Fig. 4.38(B)). Complete disappearance of peaks in UV-vis region indicates the absence of any organic moiety (Fig. 4.39). COD and CO$_2$ estimations are in agreement with UV-Vis spectral analysis during mineralization.

### 4.3.18: Kinetic Studies:

Due to the practical applications, the degradation kinetics of NB was investigated under the conditions of the appropriate optimum catalyst concentrations, natural pH and temperature of 30 °C. From the results, it becomes clear that the degradation process proceeds in two parallel branches of only visible light degradation and when visible light is assisted with catalyst particles:

$$R = \frac{d[\text{NB}]}{dt} = R_1 + R_2$$

(4.58)

where $R$, $R_1$ and $R_2$ are the net degradation, the photocatalysis and the photolysis rates, respectively. The difference between the net rate and photolysis rate obtained experimentally, can be considered as the photocatalysis branch rate. Using the power law kinetic models in the forms:

$$R_1 = k_1[\text{NB}]^{n_1}$$

(4.59)

$$R_2 = k_2[\text{NB}]^{n_2}$$

(4.60)

where, $n_1$, $n_2$, $k_1$ and $k_2$ are the appropriate order and rate constant of the reaction respectively. In this work, to obtain the appropriate parameters of eq. (4.59) and eq. (4.60), the differential method of analysis, based on the data of concentration vs. time, has been used.

Fig. 4.40(a) and Fig. 4.40(b) present the goodness of fit of the rate eq. (4.59) and eq. (4.60) to the data.
Fig. 4.40(a): The variation of NB degradation rate versus its concentration for photocatalysis: $[\text{NB}] = 60 \text{ mgL}^{-1}$, BiOCl = 4.0 gmL$^{-1}$, Irradiation intensity = $76 \times 10^2$ lux, pH = 6.1, Temperature = $30 \pm 0.3$ °C.

Our results are in agreement with other studies reported in literature [44-46]. Under chosen experimental conditions, the rate of degradation of NB for photodegradation and photolysis has been found to be $3.22 \text{ mgL}^{-1}\text{min}^{-1}$ and $2.59 \text{ mgL}^{-1}\text{min}^{-1}$ respectively.
**Methylene Blue**

Methylene blue; CI Basic blue 9 was discovered by Caro in 1876. It is tinctorially strong greenish-blue dye with rather poor light fastness. Methylene blue is nowadays used as a pH indicator and biological stain. It is also used in calico printing and in medicines. The zinc double chloride salt of methylene blue is used to dye tannin-mordanted cotton.
4.3 (C): Effects of various experimental parameters on the degradation rate of Methylene Blue (MB)

4.3.1: Photocatalytic degradation of methylene blue (MB):
In Langmuir–Hinshelwood treatment of heterogeneous surface reactions, the photochemical degradation rate is described by pseudo first order kinetics which is rationalized in terms of the modified model to accommodate reactions occurring at a solid-liquid interface as [1, 2]

\[ R = -\frac{dc}{dt} = \frac{k_{L-H} K_{ad} C}{(1 + K_{ad} C)} \]  \hspace{1cm} (4.11)

where \( k_{L-H} \) is the reaction rate constant, \( K_{ad} \) is the adsorption coefficient of dye on the surface of BiOCl, 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. (4.11). So for simplification the denominator becomes 1. Integrating eq. (4.11), we obtain

\[ \ln \left( \frac{C_0}{C} \right) = k_{L-H} K_{ad} t = kt \]  \hspace{1cm} (4.12)

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 methylene blue (MB) on the BiOCl surface can be calculated by using eq. (4.13)

\[ t_{(1/2)} = \frac{0.693}{k} \]  \hspace{1cm} (4.13)

The photocatalytic degradation of MB dye follows pseudo first kinetics. The detection was realized at 660 nm. The results for typical run are given in Fig. 4.41(a) and (b). The absorbance of MB dye decreases with an increase in irradiation time.
Fig. 4.41 (a): Decolorization of MB: [MB] = 40 mgL\(^{-1}\), BiOCl = 3.0 gmL\(^{-1}\), Irradiation intensity = 10 \times 10^3\ lux, pH = 9.0, Temperature = 30 ± 0.3 °C.

Fig. 4.41(b): Pseudo first order kinetics: [MB] = 40 mgL\(^{-1}\), BiOCl = 3.0 gmL\(^{-1}\), Irradiation intensity = 10 \times 10^3\ lux, pH = 9.0, Temperature = 30 ± 0.3 °C.

While in dark and during photolysis, no significant changes have been observed (see Fig. 4.41(a)). The reaction rate constant (k) for the photocatalytic degradation reaction of MB dye, by BiOCl catalyst, was obtained from the slope of the linear relationship of the natural logarithm of the ratio between the initial concentration of MB and the
concentration after photocatalytic degradation $\ln(C_0/C)$ versus the corresponding irradiation time as shown in Fig. 4.41(b). The value of $k$ gives an indication for the activity of the photocatalyst. The plot of $\ln(C_0/C)$ versus time follows pseudo first order kinetics with regression co-efficient of 0.984, rate constant of 0.031 min$^{-1}$ and half life time of 22 min (Fig. 4.41(b)).

4.3.2: Influence of initial pH:
Degradation of methylene blue dye studied by varying pH from 3.3 to 13.7. The results of pH effect are shown in Table 4.24 and Fig. 4.42.

<table>
<thead>
<tr>
<th>pH</th>
<th>$k$ (min$^{-1}$)</th>
<th>$t_{1/2}$ (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.3</td>
<td>0.014</td>
<td>48.94</td>
</tr>
<tr>
<td>5.1</td>
<td>0.018</td>
<td>36.90</td>
</tr>
<tr>
<td>7.0</td>
<td>0.022</td>
<td>31.47</td>
</tr>
<tr>
<td>9.0</td>
<td>0.026</td>
<td>26.07</td>
</tr>
<tr>
<td>11.5</td>
<td>0.024</td>
<td>28.66</td>
</tr>
<tr>
<td>13.7</td>
<td>0.020</td>
<td>33.87</td>
</tr>
</tbody>
</table>

Fig. 4.42: Influence of initial pH.
It is quite evident from the Fig. 4.42 that as the pH of dye solution increased from 3.3 to 9.0 the photocatalytic reaction rate increased and the further increase in pH up to 13.7 resulted into decrease in rate of degradation. The maximum degradation has been found at pH 9.0. The increase in rate of photocatalytic degradation might be due to the more availability of OH$^-$ ions in basic medium which will generate more \( \cdot \text{OH} \) radicals by combining with holes which are formed due to the electronic excitation in catalyst. In acidic condition, electrostatic interactions between the positively charged active sites on catalyst surface and cationic dye molecules led to strong repulsion consequently made it difficult for dye molecules to get adsorbed on the catalyst surface [3].

\textbf{4.3.3: Effect of catalyst weight:}

In order to avoid excess catalyst and ensure total absorption of efficient photons optimum catalyst concentration has to be determined [4]. Thus the effect of photocatalyst weight for BiOCl on the photodegradation of the MB was studied in the range of 1.0 to 6.0 gmL$^{-1}$ and results are presented in Table 4.25 and Fig. 4.43. The graph depicts that as the concentration of catalyst increases from 1.0 to 3.0 gmL$^{-1}$, the degradation rate constant increases from 0.021 to 0.031 min$^{-1}$ but further increase in the catalyst concentration up to 6.0 gmL$^{-1}$, the rate constant decreases to 0.010 min$^{-1}$ respectively. The optimum weight of catalyst loading was found to be 3.0 gmL$^{-1}$.

\textbf{Table 4.25: Effect of catalyst weight:} [MB] = 20 mgL$^{-1}$, Irradiation intensity =10×10$^3$ lux, pH = 9.0, Temperature =30 ±0.3 °C.

\begin{tabular}{|c|c|c|}
\hline
BiOCl gmL$^{-1}$ & k (min$^{-1}$) & t$_{1/2}$ (min) \\
\hline
1.0 & 0.021 & 32.44 \\
2.0 & 0.026 & 26.19 \\
3.0 & 0.031 & 22.00 \\
4.0 & 0.025 & 27.04 \\
5.0 & 0.021 & 32.53 \\
6.0 & 0.010 & 65.62 \\
\hline
\end{tabular}
The increased degradation rate that follows the increase in the catalyst weight can be attributed to the fact that the total active surface area increases with increasing catalyst weight, thus accelerating the process. When all the dye molecules are adsorbed on catalyst (BiOCl) no improvement is achieved by adding more catalyst. The decrease in efficiency may be due to an increasing opacity of the suspension and to an enhancement of the light reflectance, because of the excess of BiOCl particles [5]. Additionally, in the case of high catalyst loads we observed agglomeration and sedimentation of BiOCl which makes a significant fraction of catalyst to be inaccessible to either absorbing the dye or absorbing the radiation, with consequent decrease in active sites available to the catalytic reaction [4].

4.3.4: Effect of initial dye concentration:
Effect of variation of dye concentration was also studied by taking different concentrations of dyes. In order to optimize the initial dye concentrations, it was varied from 10 to 60 mgL$^{-1}$. The results are shown in Table 4.26 and plotted in Fig. 4.44. It has been observed from the graph that the increased in dye concentration from 10 mgL$^{-1}$ to 40 mgL$^{-1}$, the rate constant increased from 0.022 to 0.031 min$^{-1}$. Thereafter, rate constant decreased to 0.027 min$^{-1}$ with increased dye concentration up to 60 mgL$^{-1}$. Rate constant was found to be maximal at 40 mgL$^{-1}$ of dye concentration. This may be attributed to the fact that as the concentration of dye increases, more dye molecules available for
excitation followed by inter system crossing and hence, there was an increase in the rate [5]. Further increase in dye concentration, the equilibrium adsorption of dye on catalyst surface active sites increases, which hinders the competitive adsorption of OH$^-\,$ on the same sites, which means a lower formation rate of $\cdot$OH radical. The increase in dye concentration also decreases the path length of photon entering the dye solution. At high dye concentration a significant amount of visible light may be absorbed by the dye molecules rather than the catalyst and this may also reduce the catalytic efficiency. Consequently, the degradation rate decreased as the dye concentration increases [3].

**Table 4.26: Effect of initial dye concentration:** BiOCl = 3.0 gmL$^{-1}$, Irradiation intensity = 10 $\times$ 10$^3$ lux, pH = 9.0, Temperature = 30 ± 0.3 0°C

<table>
<thead>
<tr>
<th>MB (mgL$^{-1}$)</th>
<th>k (min$^{-1}$)</th>
<th>t$_{1/2}$ (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.022</td>
<td>31.38</td>
</tr>
<tr>
<td>20</td>
<td>0.023</td>
<td>29.53</td>
</tr>
<tr>
<td>30</td>
<td>0.025</td>
<td>26.98</td>
</tr>
<tr>
<td>40</td>
<td>0.031</td>
<td>22.00</td>
</tr>
<tr>
<td>50</td>
<td>0.028</td>
<td>24.75</td>
</tr>
<tr>
<td>60</td>
<td>0.027</td>
<td>25.66</td>
</tr>
</tbody>
</table>

**Fig. 4.44:** Effect of initial dye concentration.
4.3.5: Effect of varying oxidant concentration:

The effect of the concentration of H$_2$O$_2$ on the initial reaction rate of methylene blue degradation is shown in Table 4.27 and Fig. 4.45(a). The photocatalytic efficiency found to increase as the concentration of H$_2$O$_2$ increased from 20 to 40 mgL$^{-1}$ and it reached the optimum at 40 mgL$^{-1}$. Consequently the rate decreased as the concentration of the H$_2$O$_2$ increased beyond the optimum. H$_2$O$_2$ is considered to have two functions in the process of photocatalytic degradation. It accepts a photogenerated electron from the conduction band and thus promotes the charge separation and it also forms $^\cdot$OH radicals according to eq. (4.14) and eq. (4.15) [6-9]

\[
\begin{align*}
\text{H}_2\text{O}_2 + e^- & \rightarrow \text{OH}^- + ^\cdot\text{OH} \quad (4.14) \\
\text{H}_2\text{O}_2 + \text{O}_2^- & \rightarrow ^\cdot\text{OH} + \text{OH}^- + \text{O}_2 \quad (4.15)
\end{align*}
\]

Excess H$_2$O$_2$ may act as a hole or an $^\cdot$OH scavenger or react with photocatalyst and form peroxocompounds, which are detrimental to the photocatalytic action. This explains the need for an optimal concentration of H$_2$O$_2$ for the maximum effect. K$_2$S$_2$O$_8$ can also trap the photogenerated conduction band electron results in the formation of sulphate ion (SO$_4^{2-}$), a strong oxidizing agent (standard oxidation potential = 2.6 eV), which can participate in degradation process.

\[
\text{S}_2\text{O}_8^{2-} + e^- \rightarrow \text{SO}_4^{2-} + \text{SO}_4^{2-} \quad (4.16)
\]

From Fig. 4.45(b), we can see that with increase in K$_2$S$_2$O$_8$ concentration from 20 to 40 mgL$^{-1}$, rate constant increased from 0.034 to 0.036 min$^{-1}$. At optimal concentration of K$_2$S$_2$O$_8$, rate constant has been found to be 0.036 min$^{-1}$. Consequently degradation rate decreases as the concentration of the K$_2$S$_2$O$_8$ increases beyond the optimum [8]. A possible explanation of this behavior may be the light absorption from dye molecule leads to the photo-sensitization of the molecule, which is accompanied by the excitation of an electron from the lower to the upper energy level. Following this, the excited dye molecule injects electrons to the S$_2$O$_8^{2-}$ according to eq. (4.16). The resulting SO$_4^{2-}$ radicals, strong oxidizing agents, attack the chromophore group in dye leading to the decolorization of the solution. The decrease in rate constant above optimum
concentration is due to the adsorption of sulphate ions formed during the reaction on surface of catalyst deactivating a section of photocatalyst [10,11][8,9].

Table 4.27: Effect of oxidant: Decolorization of MB: [MB] = 40 mgL⁻¹, BiOCl = 3.0 gmL⁻¹, Irradiation intensity = 10×10³ lux, pH = 9.0, Temperature = 30 ± 0.3 °C.

<table>
<thead>
<tr>
<th>Oxidant (mgL⁻¹)</th>
<th>H₂O₂</th>
<th>K₂S₂O₈</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>k (min⁻¹)</td>
<td>t½ (min)</td>
</tr>
<tr>
<td>0</td>
<td>0.031</td>
<td>22.00</td>
</tr>
<tr>
<td>20</td>
<td>0.032</td>
<td>21.15</td>
</tr>
<tr>
<td>40</td>
<td>0.037</td>
<td>18.65</td>
</tr>
<tr>
<td>60</td>
<td>0.031</td>
<td>22.08</td>
</tr>
<tr>
<td>80</td>
<td>0.025</td>
<td>26.86</td>
</tr>
<tr>
<td>100</td>
<td>0.019</td>
<td>34.68</td>
</tr>
</tbody>
</table>

Fig. 4.45: Effect of oxidant: (a) H₂O₂ and (b) K₂S₂O₈.

4.3.6: Effect of varying salt concentration:
The effect of presence of NaCl and Na₂CO₃ is shown in Table 4.28 and Fig. 4.46. As can be seen from Table 4.28 and Fig. 4.46, an increment in concentration of CO₃²⁻ from 20 mgL⁻¹ to 100 mgL⁻¹, results in decrease of rate constant 0.024 to 0.008 min⁻¹, while with same Cl⁻ ion concentration variation, the rate constant decreased from 0.026 to 0.007 min⁻¹.
Half life time increases from 27.96 to 77.51 min and 26.13 to 79.65 min with an increase in concentration from 20 mgL$^{-1}$ to 100 mgL$^{-1}$ for CO$_3^{2-}$ and Cl$^{-}$ ions respectively.

Table 4.28: Effect of Salt: [MB] = 40 mgL$^{-1}$, BiOCl = 3.0 gmL$^{-1}$, Irradiation intensity = $10 \times 10^3$ lux, pH = 9.0, Temperature = 30 ± 0.3 $^0$C

<table>
<thead>
<tr>
<th>Salt (mgL$^{-1}$)</th>
<th>Na$_2$CO$_3$</th>
<th>NaCl</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>k (min$^{-1}$)</td>
<td>$t_{1/2}$ (min)</td>
</tr>
<tr>
<td>0</td>
<td>0.031</td>
<td>22.00</td>
</tr>
<tr>
<td>20</td>
<td>0.024</td>
<td>27.96</td>
</tr>
<tr>
<td>40</td>
<td>0.021</td>
<td>31.73</td>
</tr>
<tr>
<td>60</td>
<td>0.018</td>
<td>37.86</td>
</tr>
<tr>
<td>80</td>
<td>0.015</td>
<td>45.29</td>
</tr>
<tr>
<td>100</td>
<td>0.008</td>
<td>77.51</td>
</tr>
</tbody>
</table>

Fig. 4.46: Effect of Salt: (a) Na$_2$CO$_3$ and (b) NaCl.

The inhibition is undoubtedly due to their ability to act as hydroxyl radical (·OH) scavengers. The observed mechanism of hydroxyl radical scavenging is given by eq. (4.17) to eq. (4.20) [12,13].
\[
\begin{align*}
\text{Cl}^- + \cdot\text{OH} & \rightarrow \text{Cl} + \text{OH}^- \\
\text{Cl}^- + h_{\text{VB}}^+ & \rightarrow \cdot\text{Cl} \\
\text{Cl}^- + \text{Cl}^\cdot & \rightarrow \text{Cl}_2^\cdot \\
\text{CO}_3^{2-} + \cdot\text{OH} & \rightarrow \text{CO}_3^- + \text{H}_2\text{O} \\
\end{align*}
\]  

\((4.17)\) \hspace{1cm} \((4.18)\) \hspace{1cm} \((4.19)\) \hspace{1cm} \((4.20)\)

These ions may also block the active sites on the photocatalyst surface thus deactivating the catalysts towards the dye and intermediate molecules. Although, the generated radical anions have been shown to be an oxidant itself, but its oxidation potential is less than that of the hydroxyl radicals \([14]\).

**4.3.7: Effect of FeCl\(_3\):**

In present case, effect of FeCl\(_3\) on the photodegradation of MB has been studied by varying the concentration from 10 mgL\(^{-1}\) to 70 mgL\(^{-1}\) as shown in Table 4.29 and Fig. 4.47. FeCl\(_3\) behaves as an electron scavenger (\(\text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+}\)) thus preventing the recombination of electron hole pairs. Under the experimental conditions the following reactions become significant.

\[
\begin{align*}
\text{Fe}^{2+} + \text{H}_2\text{O}_2 + H^+ & \rightarrow \text{Fe}^{3+} + \cdot\text{OH} + \text{H}_2\text{O} \\
\text{Fe}^{2+} + \text{HO}_2^- + H^+ & \rightarrow \text{Fe}^{3+} + \text{H}_2\text{O}_2 \\
\end{align*}
\]  

\((4.21)\) \hspace{1cm} \((4.22)\)

In BiOCl/ FeCl\(_3\)/Vis addition of FeCl\(_3\) caused an increase in decolorization rate (0.041 min\(^{-1}\)) upto concentration 30 mgL\(^{-1}\). Photoactivation of surface adsorbed complex ion (Fe\(^{3+}\) OH\(^-\)) results in formation of Fe\(^{2+}\)•OH species, which inject electrons to conduction band of BiOCl (eqs. 4.24 to 4.25). Increased rate of decolorization in case of FeCl\(_3\) is explicable due to rapid scavenging of conduction band electrons by molecular oxygen leading to formation of superoxide and hydroperoxide radicals (eq. 4.26). Higher concentration of FeCl\(_3\) eliminates adsorption of cationic dye on BiOCl surface and also inhibits reaction rate by reducing production of hydroxyl radicals \([15-18]\).
\[ MB + h\nu_{\text{visible}} \rightarrow_1 MB^* \text{ or }_3 MB^* \quad (4.23) \]

\[ _1MB^* \text{ or }_3 MB^* + \text{BiOCl (Fe}^{3+} \cdot \text{OH}^-) \rightarrow \text{BiOCl (Fe}^{2+} \cdot \text{OH}) + MB^{++} \quad (4.24) \]

\[ \text{BiOCl (Fe}^{2+} \cdot \text{OH}) \rightarrow \text{BiOCl (} \cdot e_{CB}^-) + \text{BiOCl (Fe}^{3+} \cdot \text{OH}) \quad (4.25) \]

\[ \text{BiOCl (} \cdot e_{CB}^-) + O_2 \rightarrow O_2^- + H^+ \rightarrow HO_2^- \quad (4.26) \]

\[ \text{MB/MB}^{3+} + \cdot OH/ O_2^-/ HO_2^- \rightarrow \text{Degradation products} \quad (4.27) \]

The metal ions such as Fe\(^{3+}\) could be used as sensitizers during semiconductor photocatalytic degradation of organic pollutants.

**Table 4.29: Effect of FeCl\(_3\):** [MB] = 40 mgL\(^{-1}\), BiOCl = 3.0 gmL\(^{-1}\), Irradiation intensity = 10 \(\times\) 10\(^3\) lux, pH = 9.0, Temperature = 30 ± 0.3 °C

<table>
<thead>
<tr>
<th>FeCl(_3) (mgL(^{-1}))</th>
<th>k (min(^{-1}))</th>
<th>(t_{\frac{1}{2}}) (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.031</td>
<td>22.00</td>
</tr>
<tr>
<td>10</td>
<td>0.035</td>
<td>19.67</td>
</tr>
<tr>
<td>20</td>
<td>0.040</td>
<td>17.06</td>
</tr>
<tr>
<td>30</td>
<td>0.041</td>
<td>16.64</td>
</tr>
<tr>
<td>40</td>
<td>0.037</td>
<td>18.50</td>
</tr>
<tr>
<td>50</td>
<td>0.033</td>
<td>20.40</td>
</tr>
<tr>
<td>60</td>
<td>0.024</td>
<td>27.83</td>
</tr>
<tr>
<td>70</td>
<td>0.020</td>
<td>33.47</td>
</tr>
</tbody>
</table>

**Fig. 4.47:** Effect of FeCl\(_3\).
4.3.8: Effect of Fe$^{3+}$/H$_2$O$_2$:

The oxidation system based on Fenton reaction has been used for the treatment of the effective decolorization and degradation of dyes under laboratory conditions. The process is based on the formation of reactive oxidizing species, able to efficiently degrade the pollutants of the wastewater stream. Fenton’s reagent is a mixture of H$_2$O$_2$ and Fe$^{2+}$ or Fe$^{3+}$ iron [19-21]. Efficiency of Fe$^{3+}$/H$_2$O$_2$ system has been studied for decolorization of MB in the presence of BiOCl and visible light irradiation. The results are displayed in Table 4.30 and plotted in Fig. 4.48.

Table 4.30: Effect of Fe$^{3+}$/H$_2$O$_2$: [MB] = 40 mgL$^{-1}$, BiOCl = 3.0 gmL$^{-1}$, Irradiation intensity = 10 × 10$^3$ lux, pH = 9.0, Temperature = 30 ± 0.3 °C.

<table>
<thead>
<tr>
<th>Fe$^{3+}$: H$_2$O$_2$</th>
<th>With BiOCl</th>
<th>Without BiOCl</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$k$ (min$^{-1}$)</td>
<td>$t_{1/2}$ (min)</td>
</tr>
<tr>
<td>3:1</td>
<td>0.035</td>
<td>19.64</td>
</tr>
<tr>
<td>1:4:1</td>
<td>0.057</td>
<td>12.11</td>
</tr>
<tr>
<td>1:1:4</td>
<td>0.047</td>
<td>14.73</td>
</tr>
<tr>
<td>1:3</td>
<td>0.035</td>
<td>19.67</td>
</tr>
<tr>
<td>11:1</td>
<td>0.019</td>
<td>34.68</td>
</tr>
</tbody>
</table>

Fig. 4.48: Effect of Fe$^{3+}$/H$_2$O$_2$. 
Rate constant has a value of 0.035 min\(^{-1}\) on the addition of (Fe\(^{3+}\): H\(_2\)O\(_2\)) in molar ratio (3:1). In the presence of (Fe\(^{3+}\): H\(_2\)O\(_2\)) in molar ratio (1.4:1), rate constant has been found 0.057 min\(^{-1}\). Upon irradiation of Fe\(^{3+}/H_2O_2/BiOCl/MB\) system with visible light, production of OH radicals increases involving a very complex mechanism. Dye absorbs visible irradiation and is excited into high-energy state. These excited dye molecules reduce the ferric ion complex to ferrous ion complex followed by the transfer to ferric ion [22]. The reduced ferrous ions react with hydrogen peroxide to decompose and produce hydroxyl radical (eq. (4.30)). OH radicals also decompose H\(_2\)O\(_2\) to HO\(_2\). A similar mechanism has been reported by Amiri, Wu and Herrara et al [23-25].

\[
\begin{align*}
\text{MB} + h\nu_{\text{visible}} & \rightarrow _1\text{MB}^* \text{ or } _3\text{MB}^* \\
_{1}\text{MB}^* \text{ or } _3\text{MB}^* + \text{BiOCl}(\text{Fe}^{3+}\text{OH}^-) & \rightarrow \text{BiOCl}(\text{Fe}^{2+}\text{OH}^+) + \text{MB}^{4+} \\
\text{BiOCl}(\text{Fe}^{2+}\text{OH}^+) + \text{H}_2\text{O}_2 & \xrightarrow{h\nu} \text{BiOCl}(\text{Fe}^{2+}\text{OH}^+) + \text{OH}^- + \cdot\text{OH} \\
\text{BiOCl}(\text{Fe}^{3+}\text{OH}^+) + \text{H}_2\text{O}_2 & \xrightarrow{h\nu} \text{BiOCl}(\text{Fe}^{2+}\text{OH}^+) + \text{HO}_2^* + \text{H}^+ \\
\text{BiOCl}(\text{e}_{\text{CB}}^-) + \text{O}_2 & \rightarrow \text{O}_2^- \xrightarrow{\text{H}^+} \text{HO}_2^* \\
\text{H}_2\text{O}_2 + \text{O}_2^- & \rightarrow \cdot\text{OH} + \text{OH}^- + \text{O}_2 \\
\text{H}_2\text{O}_2 + \text{BiOCl}(\text{e}_{\text{CB}}^-) & \rightarrow \cdot\text{OH} + \text{OH}^- \\
\cdot\text{OH} + \text{H}_2\text{O}_2 & \rightarrow \text{H}_2\text{O} + \text{HO}_2^* \\
\text{MB}/\text{MB}^{4+} + \cdot\text{OH}/\text{O}_2^-/\text{HO}_2^* & \rightarrow \text{Degradation products}
\end{align*}
\]

\(4.3.9: \text{Effect of temperature:}\)

The influence of temperature has been studied in the range from 30\(^{\circ}\)C to 55\(^{\circ}\)C (see Table 4.31 and Fig. 4.49). Rate constant increased from 0.025 to 0.037 min\(^{-1}\) with increase in temperature from 30 to 45\(^{\circ}\)C. However, further increase in temperature reduces the value of rate constant. Increased temperature tends to reduced electron-hole recombination. However, an increment in temperature also decreases the solubility of oxygen in water [15]. Both above mentioned conflicting factors have been equipoise at 35\(^{\circ}\)C. Significant amount of solution was evaporated at higher temperature.
Table 4.31: Effect of temperature: [MB] = 40 mgL\(^{-1}\), BiOCl = 3.0 gmL\(^{-1}\), Irradiation intensity = \(10 \times 10^3\) lux, pH = 9.0.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>k (min(^{-1}))</th>
<th>(t_{\frac{1}{2}}) (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>0.025</td>
<td>27.36</td>
</tr>
<tr>
<td>35</td>
<td>0.029</td>
<td>23.71</td>
</tr>
<tr>
<td>40</td>
<td>0.034</td>
<td>20.33</td>
</tr>
<tr>
<td>45</td>
<td>0.037</td>
<td>18.53</td>
</tr>
<tr>
<td>50</td>
<td>0.034</td>
<td>20.01</td>
</tr>
<tr>
<td>55</td>
<td>0.030</td>
<td>22.64</td>
</tr>
</tbody>
</table>

Fig. 4.49: Effect of temperature.

4.3.10: Effect of \(N_2\) and \(O_2\) purging:

Dissolved gases in the suspension plays an important role in the photocatalytic degradation of organic pollutants. Fig. 4.50 shows that the degradation of MB has been severely retarded by bubbling of pure \(N_2\) (decrease in rate constant from 0.031 min\(^{-1}\) to 0.008 min\(^{-1}\)) but increased rapidly on oxygen bubbling through the dye solution (increase in rate constant from 0.031 min\(^{-1}\) to 0.0437 min\(^{-1}\)). The photocatalytic mechanism shows that the surface redox reactions initiated by
photogenerated electrons and holes start the photocatalytic degradation of organics. If the surface chemical reactions of conduction band (CB) electrons are blocked by N₂ purging, the valance band (VB) holes would have a tendency to be consumed by the accumulated electrons via the electron–hole recombination inside the catalyst, hence, the photocatalytic degradation process would be significantly suppressed [26, 27]. In the aerated condition, the oxygen accepts the conduction band electron and gives rise to a superoxide radical anion which further reacts with the hydrogen ion to form a hydroxyl radical in the system which in turn increases the degradation rate [28, 29].

![Graph showing decolorization of MB under various photocatalytic systems](image)

**Fig. 4.50: Decolorization of MB under various photocatalytic systems:**

[MB] = 40 mgL⁻¹, BiOCl = 3.0 gmL⁻¹, Irradiation intensity = 10 × 10³ lux, pH = 9.0, Solar light intensity = 110 ×10³ ± 5 lux, Temperature = 30 ± 0.3 °C.

### 4.3.11: Comparison of Solar/Visible Light:

The comparative study has been carried out for the degradation of dye solution in solar/visible light. Fig. 4.50 shows the degradation rate as a function of irradiation time on illumination of an aqueous suspension of MB under sunlight and visible light respectively. The rate of degradation was found to be much more in the solar light (k = 0.065 min⁻¹). Blank experiments were also carried out under sunlight in the absence of BiOCl where no observable loss of dye was observed.
4.3.12: Effect of other photocatalysts:

The influence of three different photocatalysts, BiOCl, TiO$_2$ and BaCrO$_4$ on degradation kinetics of MB has been studied and results are shown in Table 4.32 and Fig. 4.51. The order of photoactivity is as follows: BiOCl > TiO$_2$ > BaCrO$_4$.

Table 4.32: Effect of other photocatalysts: [MB] = 40 mgL$^{-1}$, [Photocatalyst] = 3.0 gmL$^{-1}$, Irradiation intensity = 10 $\times$ 10$^3$ lux, pH = 9.0, Temperature = 30 ± 0.3$^0$C.

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Bandgap(eV)</th>
<th>k (min$^{-1}$)</th>
<th>$t_{1/2}$ (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BiOCl</td>
<td>3.2</td>
<td>0.031</td>
<td>22.00</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>3.1</td>
<td>0.022</td>
<td>31.47</td>
</tr>
<tr>
<td>BaCrO$_4$</td>
<td>2.6</td>
<td>0.013</td>
<td>50.65</td>
</tr>
</tbody>
</table>

Fig. 4.51: Effect of other photocatalysts.

As it is known that the photocatalytic activity is closely related to the mobility of the photogenerated charge carriers and the positions of the conduction band (CB) and valence band (VB) in the photocatalyst. In metal oxide photocatalysts, the VB is commonly composed of O 2p. However, the VB of materials that contain element Bi mostly consists of O 2p and Bi 6s hybrid orbitals, whereas the CB consists of Bi 6p. It has been found that the broad VB increases the mobility of the photogenerated carriers.
[30,31]. This phenomenon was obvious for the bismuth-based photocatalysts because the Bi 6s orbital is largely dispersed, which is more beneficial to increasing the mobility of photogenerated carriers. Moreover, the Bi-O sites in BiOCl acted as electron traps in the photocatalytic reaction. Therefore, materials containing Bi are probably active photocatalysts. It has already been reported that semiconductors such as BiOCl and TiO₂ have band gaps larger than 3.0 eV show strong photocatalytic activity. The conduction band and valence band potentials of both BiOCl and TiO₂ are larger than the corresponding redox potentials of H⁺/H₂ and H₂O/O₂, and the photogenerated electron and hole can be separated efficiently. BaCrO₄ with smaller band gap shows less activity since its conduction band is much lower than that of BiOCl and TiO₂. Electron (CB) in these semiconductors rapidly falls into the hole thus showing reduced activity.

4.3.13: Effect of light intensity and irradiation time:

The influence of light intensity on the degradation efficiency has been examined at constant dye concentration (40 mgL⁻¹) and catalyst loading (3.0 mgL⁻¹). It is evident that the rate constant increases with increase in the light intensity as shown in Table 4.33 and Fig. 4.52. The visible light irradiation generates the photons required for the electron transfer from the valence band to the conduction band of a semiconductor photocatalyst. The energy of a photon is related to its wavelength and the overall energy input to a photocatalytic process is dependent on light intensity. The rate of degradation increases when more radiations fall on the catalyst surface and hence more hydroxyl radicals are produced [32,33].

Table 4.33: Effect of light intensity: [MB] = 40 mgL⁻¹, BiOCl = 3.0 gmL⁻¹, pH = 9.0, Temperature = 30 ± 0.3 °C.

<table>
<thead>
<tr>
<th>Light intensity × 10³ lux</th>
<th>k (min⁻¹)</th>
<th>t½ (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.031</td>
<td>22.00</td>
</tr>
<tr>
<td>14</td>
<td>0.038</td>
<td>18.13</td>
</tr>
<tr>
<td>20</td>
<td>0.041</td>
<td>16.78</td>
</tr>
<tr>
<td>28</td>
<td>0.045</td>
<td>15.33</td>
</tr>
<tr>
<td>35</td>
<td>0.049</td>
<td>14.00</td>
</tr>
</tbody>
</table>
4.3.14: Stability test for BiOCl activity:

To assess the stability of the BiOCl in the photocatalytic reaction, BiOCl was re-examined for two extra cycles. As shown in Fig. 4.53 (II), (III), the high photocatalytic performance of the as-prepared BiOCl for MB degradation was effectively maintained for 80 min of testing. After three cycles of repetition tests for photodegradation of MB, catalyst did not exhibit any significant loss of activity. This experimental result indicated that BiOCl is more stable and has good photocatalytic performance on degradation of MB [34, 35].

Fig. 4.53: MB degradation by BiOCl: (I) the first cycle; (II) the second cycle; (III) the third cycle; [MB] = 40 mgL\(^{-1}\), BiOCl = 3.0 gmL\(^{-1}\), Irradiation intensity = 10 \times 10^3\ lux, pH = 9.0, Temperature = 30 ± 0.3 °C.
4.3.15: COD and CO$_2$ measurements during mineralization of MB:

In the present work results of chemical oxygen demand (COD) are taken as one of the parameter to judge the feasibility of the photochemical process for degradation and mineralization of MB dye solution [36].

**Table 4.34: Mineralization of MB:** [MB] = 40 mgL$^{-1}$, BiOCl = 3.0 gmL$^{-1}$, Irradiation intensity = $10 \times 10^3$ lux, pH = 9.0, Temperature = $30 \pm 0.3$ $^0$C.

<table>
<thead>
<tr>
<th>Irradiation time (h)</th>
<th>COD (mgL$^{-1}$)</th>
<th>CO$_2$ (mgL$^{-1}$)</th>
<th>% Efficiency</th>
<th>NO$_3^-$ (mgL$^{-1}$)</th>
<th>SO$_4^{2-}$ (mgL$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>240</td>
<td>4</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>201</td>
<td>11</td>
<td>13</td>
<td>8</td>
<td>7</td>
</tr>
<tr>
<td>2</td>
<td>164</td>
<td>24</td>
<td>58</td>
<td>12</td>
<td>16</td>
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<td>15</td>
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<td>22</td>
<td>54</td>
<td>93</td>
<td>20</td>
<td>32</td>
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<tr>
<td>5</td>
<td>16</td>
<td>71</td>
<td>96</td>
<td>27</td>
<td>33</td>
</tr>
<tr>
<td>6</td>
<td>4</td>
<td>80</td>
<td>98</td>
<td>28</td>
<td>36</td>
</tr>
</tbody>
</table>

**Fig. 4.54:** (a) COD and CO$_2$ trend and (b) formation of NO$_3^-$ and SO$_4^{2-}$ during mineralization of MB: [MB] = 40 mgL$^{-1}$, BiOCl = 3.0 gmL$^{-1}$, Irradiation intensity = $10 \times 10^3$ lux, pH = 9.0, Temperature = $30 \pm 0.3$ $^0$C.
From Table 4.34 and Fig. 4.54, there is a substantial decrease of the COD of the solution from 240 mgL$^{-1}$ to 4 mgL$^{-1}$ and increase in CO$_2$ value from 4 mgL$^{-1}$ to 80 mgL$^{-1}$ in 6 h of irradiation. Consequently, the complete mineralization of MB was achieved after 6 h of visible light irradiation in the presence of BiOCl because of the formation of more stable intermediates towards oxidation. The result implies that both mechanisms of degradation and mineralization play important role for the photocatalytic effects under visible light irradiation.

Analysis of inorganic ions revealed as expected the formation of NO$_3^-$ and SO$_4^{2-}$ in solution. As depicted in Table 4.34, the amount of SO$_4^{2-}$ and NO$_3^-$ ions increased with increasing irradiation time. Note that the amount of SO$_4^{2-}$ ions released into the solution is lower than that expected from stoicheometry. It was observed that the concentration of sulphate ions increased rapidly at the first 3 h and tends to reach a plateau of ca. 32 mgL$^{-1}$ within 4 h. This can be attributed to the fast elimination of the SO$_3^-$ moiety in solution. This behavior can be ascribed to a partially irreversible adsorption of sulphate ions on photocatalyst surface, as it has been already reported for the degradation of other sulfur containing dyes [35–37]. The nitrogen atoms with −3 oxidation state produced NH$_4^+$ cations, subsequently NH$_4^+$ cations were converted into NO$_3^-$ ions. It was obvious that aqueous MB was mainly mineralized rather than being bleached [37].

After 6 h of irradiation, 98% efficiency has been observed for the process. 28 mgL$^{-1}$ of NO$_3^-$ and 36 mgL$^{-1}$ of SO$_4^{2-}$ have been found after 6 h of irradiation time.

**4.3.16: UV-Vis spectra of MB Dye:**

Primary absorption peaks of MB dye was at 290 nm and 660 nm. As the reaction proceeds, the two peaks disappear gradually as shown in Fig. 4.55 and the full scanning spectrum pattern changes obviously after 8 h. This may be the evidence of the intermediate by-product. At the end of the 8 h of reaction time, there is no evident absorption peak observed. It indicates that the pollutants are destroyed with the photocatalytic reaction and proves that wastewater is fully decomposed [38,39].
Fig. 4.55: UV-Vis spectrum of MB: [MB] = 40 mgL$^{-1}$, BiOCl = 3.0 gmL$^{-1}$, Irradiation intensity = $10 \times 10^3$ lux, pH = 9.0, Temperature = 30 ± 0.3 °C.

4.3.17: Mechanism of MB degradation:

BiOCl oxidizes in two ways, photogenerated holes h$^+$ in the valence band and the •OH radicals, which are strongly active and degrading non-selective agents [40,41]. Valence band holes (h$_{VB}^+$) and conduction band electrons (e$_{CB}^-$) are generated when aqueous BiOCl suspension was irradiated with visible light. These electron-hole pairs interact separately with the substrate. Valence band holes (h$_{VB}^+$) react with surface bound H$_2$O or OH$^-$ to produce hydroxyl radical (•OH). Valence band holes can also oxidize organic molecule. Conduction band electrons (e$_{CB}^-$) reduce molecular oxygen to generate superoxide radicals as shown in eq. (4.38) - eq. (4.47) [42, 5].

\[
\begin{align*}
\text{BiOCl} + h\nu_{\text{Visible}} &\rightarrow \text{BiOCl} (h_{\text{VB}}^+ + e_{\text{CB}}^-) \\
\text{BiOCl} (h_{\text{VB}}^+ ) + \text{H}_2\text{O} &\rightarrow \text{BiOCl} + \text{H}^+ + \text{•OH} \\
\text{BiOCl} (h_{\text{VB}}^+ ) + \text{OH}^- &\rightarrow \text{BiOCl} + \text{•OH} \\
\text{BiOCl} (e_{\text{CB}}^-) + \text{O}_2 &\rightarrow \text{BiOCl} + \text{O}_2^- \\
\text{O}_2^- + \text{H}^+ &\rightarrow \text{HO}_2^- \\
\text{HO}_2^- + \text{H}^+ + \text{BiOCl} (e_{\text{CB}}^-) &\rightarrow \text{H}_2\text{O}_2 + \text{BiOCl}
\end{align*}
\]
\[
\begin{align*}
\text{H}_2\text{O}_2 + \text{BiOCl} (e^-_{\text{CB}}) & \rightarrow \cdot\text{OH} + \cdot\text{OH}^- + \text{BiOCl} \quad (4.44) \\
\text{MB} + h^+_{\text{VB}} & \rightarrow \text{Oxidation products} \quad (4.45) \\
\text{MB} + e^-_{\text{CB}} & \rightarrow \text{Reduction products} \quad (4.46) \\
\text{MB} + \cdot\text{OH} & \rightarrow \text{Degradation products} \quad (4.47)
\end{align*}
\]

Secondly, sensitization of dye molecule 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 was converted to the cationic dye radicals (MB\(^{+\ast}\)) that undergoes degradation to yield products as follows [43, 41]:

\[
\begin{align*}
\text{MB} + h^\nu (\text{Vis}) & \rightarrow 1\text{MB}^{+\ast} \text{or } 3\text{MB}^{+\ast} \quad (4.48) \\
1\text{MB}^{+\ast} \text{or } 3\text{MB}^{+\ast} + \text{BiOCl} & \rightarrow \text{MB}^{++} + \text{BiOCl} (e^-_{\text{CB}}) \quad (4.49) \\
\text{BiOCl} (e^-_{\text{CB}}) + \text{O}_2 & \rightarrow \text{O}_2^{--} + \text{BiOCl} \quad (4.50) \\
\text{MB}^{++} & \rightarrow \text{degradation products} \quad (4.51)
\end{align*}
\]

Cationic dye radicals reacts with hydroxyl ions undergoing oxidation via eq. 4.52 to eq. 4.53 or interacts with O\(_2^{--}\), HO\(_2^{+}\) or HO\(_2^{-}\) species to generate intermediates that finally lead to degradation products (eqs. 4.54 to 4.57)

\[
\begin{align*}
\text{MB}^{+\ast} + \cdot\text{OH}^- & \rightarrow \text{MB} + \cdot\text{OH} \quad (4.52) \\
\text{MB} + 2\cdot\text{HO}^- & \rightarrow \text{H}_2\text{O} + \text{oxidation products} \quad (4.53) \\
\text{O}_2^{--} + \text{H}^+ & \rightarrow \text{HO}_2^{+} \quad (4.54) \\
\text{HO}_2^{+} + \text{H}^+ + \text{BiOCl} (e^-_{\text{CB}}) & \rightarrow \text{H}_2\text{O}_2 + \text{BiOCl} \quad (4.55) \\
\text{H}_2\text{O}_2 + \text{BiOCl} (e^-_{\text{CB}}) & \rightarrow \text{HO}^{+} + \cdot\text{OH}^- + \text{BiOCl} \quad (4.56) \\
\text{MB}^{+\ast} + \text{O}_2^{--} & \rightarrow \text{degradation products} \quad (4.57)
\end{align*}
\]

From estimated value of COD and CO\(_2\), it is evident that 100 % of COD removal has been achieved in 8 h of irradiation under chosen reaction condition. A decrease in COD and increase in CO\(_2\) confirm the degradation of dye (see Fig. 4.54(a)). Significant amount of NO\(_3^{-}\) and SO\(_4^{2-}\) released during the mineralization of dye (Fig. 4.54(b)). Complete
disappearance of peaks in UV-vis region indicates the absence of any organic moiety (Fig. 4.55). COD and CO$_2$ estimations are in agreement with UV-Vis spectral analysis during mineralization.

4.3.18: Kinetic Studies:
Due to the practical applications, the degradation kinetics of MB was investigated under the conditions of the appropriate optimum catalyst concentrations, natural pH and temperature of 30 ºC. From the results, it becomes clear that the degradation process proceeds in two parallel branches of only visible light degradation and when visible light is assisted with catalyst particles:

$$ R = -\frac{d[MB]}{dt} = R_1 + R_2 $$

where $R$, $R_1$ and $R_2$ are the net degradation, the photocatalysis and the photolysis rates, respectively. Under chosen experimental condition, photolysis has no significant effect on degradation process. Therefore, eq. (4.58) reduces to following eq.

$$ R = -\frac{d[MB]}{dt} = R_1 $$

(4.59)

Here, simple power law model has been examined to find the rate of the photocatalytic degradation [44-46]

$$ R_1 = k_1[MB]^{n_1} $$

(4.60)

where, $n_1$, $n_2$, $k_1$ and $k_2$ are the appropriate order and rate constant of the reaction respectively. In this work, to obtain the appropriate parameters of eq. (4.60), the differential method of analysis, based on the data of concentration vs. time, was used. Fig. 4.56 presents the goodness of fit of the rate eq. (4.60) to the data.
Fig.: 4.56: The variation of MB degradation rate versus its concentration for photocatalysis: BiOCl = 3.0 gmL$^{-1}$, Irradiation intensity = $10 \times 10^3$ lux, pH = 9.0, Temperature = $30 \pm 0.3 \degree C$.

Our results are in agreement with other studies reported in literature [44-46]. Under chosen experimental conditions, the rate of degradation of MB for photodegradation has been found to be 2.66 mgL$^{-1}$min$^{-1}$. 
Methylene Green

Methylene green, a methylated homologue of basic dye, is a cationic thiazine dye showing deep greenish-blue color in the oxidized state. It is a highly hygroscopic, dark green crystalline powder having a bronze-like luster. It stains nuclei green and is sometimes used as counter stain to red purple primary stains. It is also used for coloring paper, tannin, mordant cotton and silk.
4.3 (D): Effects of various experimental parameters on the degradation rate of Methylene Green (MG)

4.3.1: Photocatalytic degradation of methylene green (MG):

In Langmuir–Hinshelwood treatment of heterogeneous surface reactions, the photochemical degradation rate is described by pseudo first order kinetics which is rationalized in terms of the modified model to accommodate reactions occurring at a solid-liquid interface as [1, 2].

\[
R = \frac{-dc}{dt} = \frac{k_{L-H} K_{ad} C}{(1 + K_{ad} C)}
\]

(4.11)

where \(k_{L-H}\) is the reaction rate constant, \(K_{ad}\) is the adsorption coefficient of dye on the surface of BiOCl, 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. (4.11). So for simplification the denominator becomes 1. Integrating eq. (4.11), we obtain

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

(4.12)

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 methylene green dye (MG) on the BiOCl surface can be calculated by using eq. (4.13)

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

(4.13)

The photocatalytic degradation of MG dye follows pseudo first kinetics. The detection was realized at 600 nm. The results for typical run are given in Fig. 4.57 (a), (b). The absorbance of MG dye decreases with an increase in irradiation time. While in dark and during photolysis, no significant changes have been observed (Fig. 4.57(a)).
Fig. 4.57 (a): Decolorization of MG: \([\text{MG}] = 50 \text{ mgL}^{-1}, \text{BiOCl} = 1.5 \text{ gmL}^{-1}, \text{Irradiation intensity} = 86 \times 10^2 \text{ lux}, \text{pH} = 8.3, \text{Temperature} = 30 \pm 0.3 ^\circ \text{C}.\]

The reaction rate constant \((k)\) for the photocatalytic degradation reaction of MG dye, by BiOCl catalyst, was obtained from the slope of the linear relationship of the natural logarithm of the ratio between the initial concentration of MG and the concentration after photocatalytic degradation \(\ln(C_0/C)\) versus the corresponding irradiation time as shown in Fig. 4.57(b). The value of \(k\) gives an indication for the activity of the photocatalyst. The plot of \(\ln(C_0/C)\) versus time follows pseudo first order kinetics with regression coefficient of 0.9968, rate constant of 0.017 min\(^{-1}\) and half life time of 39.69 min (see Fig. 4.57(b)).

Fig. 4.57(b): Pseudo first order kinetics: \([\text{MG}] = 50 \text{ mgL}^{-1}, \text{BiOCl} = 1.5 \text{ gmL}^{-1}, \text{Irradiation intensity} = 86 \times 10^2 \text{ lux}, \text{pH} = 8.3, \text{Temperature} = 30 \pm 0.3 ^\circ \text{C}.\)
4.3.2: **Influence of initial pH:**

We have studied the degradation of methylene green dye studied by varying pH from 4.5 to 14.4. The results of pH effect were shown in Table 4.35 and Fig. 4.58. It is quite evident from the graph (Fig. 4.58) that as the pH of dye solution was increased from 4.5 to 8.3, the photocatalytic reaction rate increased and the further increase in pH up to 14.4 result in decrease in rate of degradation. The maximum degradation has been found at pH 8.3. The increase in rate of photocatalytic degradation might be due to the more availability of OH$^-$ ions in basic medium which will generate more •OH radicals by combining with holes which are formed due to the electronic excitation in catalyst. In acidic condition, electrostatic interactions between the positively charged active sites on catalyst surface and cationic dye molecules led to strong repulsion consequently made it difficult for dye molecules to get adsorbed on the catalyst surface [3].

**Table 4.35: Effect of pH:** [MG] = 50 mgL$^{-1}$, BiOCl = 1.5 gmL$^{-1}$, Irradiation intensity = $86 \times 10^2$ lux, Temperature = 30 ± 0.3 °C.

<table>
<thead>
<tr>
<th>pH</th>
<th>k(min$^{-1}$)</th>
<th>t$_{1/2}$ (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.5</td>
<td>0.014</td>
<td>48.52</td>
</tr>
<tr>
<td>6.3</td>
<td>0.016</td>
<td>43.25</td>
</tr>
<tr>
<td>8.3</td>
<td>0.017</td>
<td>39.69</td>
</tr>
<tr>
<td>10</td>
<td>0.016</td>
<td>42.15</td>
</tr>
<tr>
<td>12</td>
<td>0.015</td>
<td>46.01</td>
</tr>
<tr>
<td>14.4</td>
<td>0.011</td>
<td>58.33</td>
</tr>
</tbody>
</table>

**Fig. 4.58:** Influence of initial pH.
4.3.3: **Effect of catalyst weight:**

In order to avoid excess catalyst and ensure total absorption of efficient photons optimum catalyst concentration has to be determined [4]. Thus the effect of photocatalyst weight for BiOCl on the photodegradation of the MG was studied in the range of 0.5 to 3.0 gmL\(^{-1}\) and results are presented in Table 4.36 and plotted in Fig. 4.59. The graph depicts that as the concentration of catalyst increases from 0.5 to 1.5 gmL\(^{-1}\), the degradation rate constant increases from 0.010 to 0.017 min\(^{-1}\) but increasing the catalyst concentration up to 3.0 gmL\(^{-1}\), the rate constant decreases to 0.009 min\(^{-1}\) respectively. The optimum weight of catalyst loading was found to be 1.5 gmL\(^{-1}\).

Table 4.36: **Effect of catalyst weight:** [MG] = 50 mgL\(^{-1}\), Irradiation intensity = 86 × 10\(^{2}\) lux, pH = 8.3, Temperature = 30 ± 0.3 °C

<table>
<thead>
<tr>
<th>BiOCl gmL(^{-1})</th>
<th>k (min(^{-1}))</th>
<th>(t_{1/2}) (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.010</td>
<td>67.15</td>
</tr>
<tr>
<td>1.0</td>
<td>0.014</td>
<td>46.57</td>
</tr>
<tr>
<td>1.5</td>
<td>0.017</td>
<td>39.69</td>
</tr>
<tr>
<td>2.0</td>
<td>0.014</td>
<td>48.73</td>
</tr>
<tr>
<td>2.5</td>
<td>0.012</td>
<td>57.46</td>
</tr>
<tr>
<td>3.0</td>
<td>0.009</td>
<td>72.64</td>
</tr>
</tbody>
</table>

Fig. 4.59: Effect of catalyst weight.
The increased degradation rate that follows the increase in the catalyst weight can be attributed to the fact that the total active surface area increases with increasing catalyst weight, thus accelerating the process. When all the dye molecules are adsorbed on catalyst (BiOCl) no improvement is achieved by adding more catalyst. The decrease in efficiency may be due to an increasing opacity of the suspension and to an enhancement of the light reflectance, because of the excess of BiOCl particles [5] Additionally, in the case of high catalyst loads we observed agglomeration and sedimentation of BiOCl which makes a significant fraction of catalyst to be inaccessible to either absorbing the dye or absorbing the radiation, with consequent decrease in active sites available to the catalytic reaction [4].

4.3.4: Effect of initial dye concentration:

By taking different concentrations of dye, the effect of variation of dye concentration was also studied. In order to optimize the initial dye concentrations was varied from 20 to 70 mgL\(^{-1}\). The results are shown in Table 4.37 and graph (Fig. 4.60). It has been observed from the graph that the increased in dye concentration from 20 mgL\(^{-1}\) to 50 mgL\(^{-1}\), the rate constant increased from 0.008 min\(^{-1}\) to 0.017 min\(^{-1}\). Thereafter, rate constant decreased to 0.012 min\(^{-1}\) with increase in dye concentration up to 70 mgL\(^{-1}\). Rate constant was maximal at 50 mgL\(^{-1}\) of dye concentration. This may be attributed to the fact that as the concentration of dyes increases, more dye molecules available for excitation followed by inter system crossing and hence, there was an increase in the rate [5]. Further increase in dye concentration, the equilibrium adsorption of dye on catalyst surface active sites increases, which hinders the competitive adsorption of OH\(^{-}\) on the same sites, which means a lower formation rate of •OH radical. The increase in dye concentration also decreases the path length of photon entering the dye solution. At high dye concentration a significant amount of visible light may be absorbed by the dye molecules rather than the catalyst and this may also reduce the catalytic efficiency. Consequently, the degradation rate decreased as the dye concentration increases [3].
Table 4.37: Effect of initial dye concentration: BiOCl = 1.5 $\text{gmL}^{-1}$, Irradiation intensity = $86 \times 10^2 \text{lux}$, pH = 8.3, Temperature = $30 \pm 0.3^0 \text{C}$

<table>
<thead>
<tr>
<th>MG (mgL$^{-1}$)</th>
<th>k (min$^{-1}$)</th>
<th>$t_\frac{1}{2}$ (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.008</td>
<td>78.0</td>
</tr>
<tr>
<td>30</td>
<td>0.011</td>
<td>58.0</td>
</tr>
<tr>
<td>40</td>
<td>0.015</td>
<td>44.9</td>
</tr>
<tr>
<td>50</td>
<td>0.017</td>
<td>39.6</td>
</tr>
<tr>
<td>60</td>
<td>0.014</td>
<td>48.3</td>
</tr>
<tr>
<td>70</td>
<td>0.012</td>
<td>56.0</td>
</tr>
</tbody>
</table>

Fig. 4.60: Effect of initial dye concentration.

4.3.5: Effect of varying oxidant concentration:

In this section we have studied the effect of concentration of H$_2$O$_2$ on the initial reaction rate of methylene green degradation is shown in Table 4.38 and Fig. 4.61(a). The photocatalytic efficiency found to increase as the concentration of H$_2$O$_2$ increased from 15 to 45 mgL$^{-1}$ and it reached the optimum at 45 mgL$^{-1}$. Consequently it decreased as the concentration of the H$_2$O$_2$ increased beyond the optimum. H$_2$O$_2$ is considered to have two functions in the process of photocatalytic degradation. It accepts a photogenerated electron from the conduction band and thus promotes the charge separation and it also forms 'OH radicals according to eq. (4.14) and (4.15) [6-9].
\[
\begin{align*}
H_2O_2 + e^- & \rightarrow OH^- + \cdot OH \quad (4.14) \\
H_2O_2 + O_2^- & \rightarrow \cdot OH + OH^- + O_2 \quad (4.15)
\end{align*}
\]

Excess H₂O₂ may act as a hole or an \( \cdot OH \) scavenger or react with photocatalyst and form peroxocompounds, which are detrimental to the photocatalytic action. This explains the need for an optimal concentration of H₂O₂ for the maximum effect.

**Table 4.38: Effect of oxidant:** [MG] = 50 mg L⁻¹, BiOCl = 1.5 gm L⁻¹, Irradiation intensity = \( 86 \times 10^2 \) lux, pH = 8.3, Temperature = 30 ± 0.3 °C.

<table>
<thead>
<tr>
<th>Oxidant (mg L⁻¹)</th>
<th>H₂O₂</th>
<th></th>
<th></th>
<th>K₂S₂O₈</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( k ) (min⁻¹)</td>
<td>( t_\frac{1}{2} ) (min)</td>
<td>( k ) (min⁻¹)</td>
<td>( t_\frac{1}{2} ) (min)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>0.017</td>
<td>39.69</td>
<td>0.017</td>
<td>39.69</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>0.019</td>
<td>35.75</td>
<td>0.018</td>
<td>38.11</td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>0.022</td>
<td>31.47</td>
<td>0.020</td>
<td>33.28</td>
<td></td>
<td></td>
</tr>
<tr>
<td>45</td>
<td>0.023</td>
<td>29.02</td>
<td>0.022</td>
<td>30.55</td>
<td></td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>0.020</td>
<td>33.38</td>
<td>0.018</td>
<td>37.74</td>
<td></td>
<td></td>
</tr>
<tr>
<td>75</td>
<td>0.017</td>
<td>39.55</td>
<td>0.014</td>
<td>47.72</td>
<td></td>
<td></td>
</tr>
<tr>
<td>90</td>
<td>0.015</td>
<td>46.20</td>
<td>0.011</td>
<td>62.77</td>
<td></td>
<td></td>
</tr>
<tr>
<td>105</td>
<td>0.011</td>
<td>61.76</td>
<td>0.009</td>
<td>74.03</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Fig. 4.61: Effect of oxidant:** (a) H₂O₂ and (b) K₂S₂O₈.

K₂S₂O₈ can also trap the photogenerated conduction band electron results in the formation of sulphate ion \( (SO₄^{2-}) \), a strong oxidizing agent (standard oxidation potential = 2.6 eV), which can participate in degradation process.
\[ \text{S}_2\text{O}_8^{2-} + e^- \rightarrow \text{SO}_4^{2-} + \text{SO}_4^{-} \] (4.16)

From Fig. 4.61(b), with increase in $K_2\text{S}_2\text{O}_8$ concentration from 15 to 45 mgL$^{-1}$, rate constant increased from 0.018 min$^{-1}$ to 0.022 min$^{-1}$. At optimal concentration of $K_2\text{S}_2\text{O}_8$, rate constant has been found to be 0.022 min$^{-1}$. Consequently degradation rate decreases as the concentration of the $K_2\text{S}_2\text{O}_8$ increases beyond the optimum [8]. A possible explanation of this behavior may be the light absorption from dye molecule leads to the photo-sensitization of the molecule, which is accompanied by the excitation of an electron from the lower to the upper energy level. Following this, the excited dye molecule injects electrons to the $\text{S}_2\text{O}_8^{2-}$ according to eq. (4.16). The resulting $\text{SO}_4^{-}$ radicals, strong oxidizing agents, attack the chromophore group in dye leading to the decolorization of the solution. The decrease in rate constant above optimum concentration is due to the adsorption of sulphate ions formed during the reaction on surface of catalyst deactivating a section of photocatalyst [10,11,8,9].

4.3.6: Effect of varying salt concentration:

Normally with the addition of either sodium chloride (NaCl) or sodium carbonate (Na$_2$CO$_3$), at or near boiling point, the direct or substantive dyeing is carried out in a neutral or slightly alkaline dye bath. The effect of presence of NaCl and Na$_2$CO$_3$ is shown in Table 4.39 and Fig. 4.62.

**Table 4.39: Effect of Salt**: [MG] = 50 mgL$^{-1}$, BiOCl = 1.5 gmL$^{-1}$, Irradiation intensity = $86 \times 10^2$ lux, pH = 8.3, Temperature = $30 \pm 0.3 \degree$C

<table>
<thead>
<tr>
<th>Salt (mgL$^{-1}$)</th>
<th>Na$_2$CO$_3$</th>
<th>NaCl</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$k$ (min$^{-1}$)</td>
<td>$t_{1/2}$ (min)</td>
</tr>
<tr>
<td>0</td>
<td>0.017</td>
<td>39.69</td>
</tr>
<tr>
<td>15</td>
<td>0.016</td>
<td>42.15</td>
</tr>
<tr>
<td>30</td>
<td>0.015</td>
<td>44.42</td>
</tr>
<tr>
<td>45</td>
<td>0.014</td>
<td>46.95</td>
</tr>
<tr>
<td>60</td>
<td>0.013</td>
<td>50.43</td>
</tr>
<tr>
<td>75</td>
<td>0.011</td>
<td>58.62</td>
</tr>
<tr>
<td>90</td>
<td>0.010</td>
<td>65.62</td>
</tr>
<tr>
<td>105</td>
<td>0.009</td>
<td>70.42</td>
</tr>
</tbody>
</table>
As can be seen from Table 4.39 and Fig. 4.62, an increment in concentration of CO$_3^{2-}$ from 15 mgL$^{-1}$ to 105 mgL$^{-1}$, results in decrease of rate constant 0.016 to 0.009 min$^{-1}$, while with same Cl$^-\_i$on concentration variation, the rate constant decreases from 0.014 to 0.006 min$^{-1}$. Half life time increases from 42.15 to 70.42 min and 47.33 to 101.31 min with an increase in concentration from 15 mgL$^{-1}$ to 105 mgL$^{-1}$ for CO$_3^{2-}$ and Cl$^-$ ions respectively. The inhibition is undoubtedly due to their ability to act as hydroxyl radical (’OH) scavengers. The observed mechanism of hydroxyl radical scavenging is given by eq. (4.17) – eq. (4.20) [12,13].

\[ \text{Cl}^- + \cdot \text{OH} \rightarrow \text{Cl} + \text{OH}^- \]  \hspace{1cm} (4.17)
\[ \text{Cl}^- + h^+_{\text{VB}} \rightarrow \cdot \text{Cl} \]  \hspace{1cm} (4.18)
\[ \text{Cl}^- + \cdot \text{Cl} \rightarrow \text{Cl}_2 \]  \hspace{1cm} (4.19)
\[ \text{CO}^{2-} + \cdot \text{OH} \rightarrow \text{CO}_3^- + \text{H}_2\text{O} \]  \hspace{1cm} (4.20)

These ions may also block the active sites on the photocatalyst surface thus deactivating the catalysts towards the dye and intermediate molecules. Although, the generated radical anions have been shown to be an oxidant itself, but its oxidation potential is less than that of the hydroxyl radicals [14].
4.3.7: Effect of FeCl₃:

Here, we have studied the effect of FeCl₃ on the photodegradation of MG has been studied by varying the concentration from 15 mgL⁻¹ to 90 mgL⁻¹ (see Table 4.40 and Fig. 4.63). FeCl₃ behaves as an electron scavenger \((\text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{3+})\) thus preventing the recombination of electron hole pairs. Under the experimental conditions the following reactions become significant.

\[
\begin{align*}
\text{Fe}^{2+} + \text{H}_2\text{O}_2 + \text{H}^+ & \rightarrow \text{Fe}^{3+} + \cdot\text{OH} + \text{H}_2\text{O} \quad (4.21) \\
\text{Fe}^{2+} + \text{HO}_2^- + \text{H}^+ & \rightarrow \text{Fe}^{3+} + \text{H}_2\text{O}_2 \quad (4.22)
\end{align*}
\]

In BiOCl/ FeCl₃/Vis addition of FeCl₃ caused an increase in decolorization rate (0.023 min⁻¹) up to concentration 30 mgL⁻¹. Photoactivation of surface adsorbed complex ion (Fe³⁺ OH⁻) results in formation of Fe²⁺•OH species, which inject electrons to conduction band of BiOCl (eqs. 4.24 to 4.25). Increased rate of degradation in case of FeCl₃ is explicable due to rapid scavenging of conduction band electrons by molecular oxygen leading to formation of superoxide and hydroperoxide radicals (eq. 4.26). Higher concentration of FeCl₃ eliminates adsorption of cationic dye on BiOCl surface and also inhibits reaction rate by reducing production of hydroxyl radicals [15-18].

\[
\begin{align*}
\text{MG} + h\nu_{\text{visible}} & \rightarrow \text{iMG}^* \text{ or } \text{3MG}^* \\
\text{iMG}^* \text{ or } \text{3MG}^* + \text{BiOCl} (\text{Fe}^{3+} \text{ OH}^-) & \rightarrow \text{BiOCl} (\text{Fe}^{2+} \cdot \text{OH}) + \text{MG}^{++} \quad (4.24) \\
\text{BiOCl} (\text{Fe}^{2+} \cdot \text{OH}) & \rightarrow \text{BiOCl} (e_{\text{CB}}^-) + \text{BiOCl} (\text{Fe}^{3+} \cdot \text{OH}) \quad (4.25) \\
\text{BiOCl} (e_{\text{CB}}^-) + \text{O}_2 & \rightarrow \text{O}_2^- \xrightarrow{\text{H}^+} \text{HO}_2^* \quad (4.26) \\
\text{MG/MG}^{++} + \cdot\text{OH}/ \text{O}_2^-/\text{HO}_2^* & \rightarrow \text{Degradation products} \quad (4.27)
\end{align*}
\]

The metal ions such as Fe³⁺ could be used as sensitizers during semiconductor photocatalytic degradation of organic pollutants.
Table 4.40: Effect of FeCl₃: [MG] = 50 mgL⁻¹, BiOCl = 1.5 gmL⁻¹, Irradiation intensity = 86 ×10² lux, pH = 8.3, Temperature = 30 ± 0.3 °C

<table>
<thead>
<tr>
<th>FeCl₃ (mgL⁻¹)</th>
<th>k (min⁻¹)</th>
<th>t₁/₂ (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.017</td>
<td>39.69</td>
</tr>
<tr>
<td>15</td>
<td>0.020</td>
<td>34.27</td>
</tr>
<tr>
<td>30</td>
<td>0.023</td>
<td>29.76</td>
</tr>
<tr>
<td>45</td>
<td>0.021</td>
<td>32.71</td>
</tr>
<tr>
<td>60</td>
<td>0.019</td>
<td>35.98</td>
</tr>
<tr>
<td>75</td>
<td>0.016</td>
<td>41.69</td>
</tr>
<tr>
<td>90</td>
<td>0.014</td>
<td>47.92</td>
</tr>
</tbody>
</table>

4.3.8: Effect of Fe³⁺/H₂O₂:
For the treatment of the effective decolorization and degradation of dyes under laboratory conditions, the oxidation system based on Fenton reaction has been used. The process is based on the formation of reactive oxidizing species, able to efficiently degrade the pollutants of the wastewater stream. Fenton’s reagent is a mixture of H₂O₂ and Fe²⁺ or Fe³⁺ iron [19-21]. Efficiency of Fe³⁺/H₂O₂ system has been studied for decolorization of
MG in the presence of BiOCl and visible light irradiation. The results are displayed in Table 4.41 and plotted in Fig. 4.64.

**Table 4.41: Effect of Fe\(^{3+}/H_2O_2\):** [MG] = 50 mgL\(^{-1}\), BiOCl = 1.5 gmL\(^{-1}\), Irradiation intensity = 86 \times 10^2 lux, pH = 8.3, Temperature = 30 ± 0.3 \(^{0}\)C.

<table>
<thead>
<tr>
<th>Fe(^{3+}): H(_2)O(_2)</th>
<th>With BiOCl</th>
<th>Without BiOCl</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>k (min(^{-1}))</td>
<td>t(_{1/2}) (min)</td>
</tr>
<tr>
<td>3:1</td>
<td>0.032</td>
<td>21.54</td>
</tr>
<tr>
<td>1.4:1</td>
<td>0.050</td>
<td>13.73</td>
</tr>
<tr>
<td>1:1.4</td>
<td>0.048</td>
<td>14.40</td>
</tr>
<tr>
<td>1:3</td>
<td>0.031</td>
<td>21.91</td>
</tr>
<tr>
<td>11:1</td>
<td>0.026</td>
<td>26.49</td>
</tr>
</tbody>
</table>

**Fig. 4.64:** Effect of Fe\(^{3+}/H_2O_2\).

Rate constant has a value of 0.032 min\(^{-1}\) on the addition of (Fe\(^{3+}\): H\(_2\)O\(_2\)) in molar ratio (3:1). In the presence of (Fe\(^{3+}\): H\(_2\)O\(_2\)) in molar ratio (1.4:1), rate constant has been found 0.050 min\(^{-1}\). Upon irradiation of Fe\(^{3+}/H_2O_2/BiOCl/MG\) system with visible light, production of \(^{1}\)OH radicals increases involving a very complex mechanism. Dye absorbs
visible irradiation and is excited into high-energy state. This excited dye molecules reduce the ferric ion complex to ferrous ion complex followed by the transfer to ferric ion [22]. The reduced ferrous ions react with hydrogen peroxide to decompose and produce hydroxyl radical (eq. 4.30). \( \cdot \)OH radicals also decompose \( \text{H}_2\text{O}_2 \) to \( \text{HO}_2^* \). A similar mechanism has been reported by Amiri, Wu and Herrara et al [23-25].

\[
\text{MG} + \text{hv}_{\text{visible}} \rightarrow _1\text{MG}^* \text{ or } _3\text{MG}^* \tag{4.28}
\]
\[
_1\text{MG}^* \text{ or } _3\text{MG}^* + \text{BiOCl}(\text{Fe}^{3+}\text{OH}^-) \rightarrow \text{BiOCl}(\text{Fe}^{2+}\text{OH}^+) + \text{MG}^{2+} \tag{4.29}
\]
\[
\text{BiOCl}(\text{Fe}^{2+}\text{OH}^+) + \text{H}_2\text{O}_2 \xrightarrow{\text{hv}} \text{BiOCl}(\text{Fe}^{3+}\text{OH}^+) + \text{OH}^- + \cdot \text{OH} \tag{4.30}
\]
\[
\text{BiOCl}(\text{Fe}^{3+}\text{OH}^+) + \text{H}_2\text{O}_2 \xrightarrow{\text{hv}} \text{BiOCl}(\text{Fe}^{2+}\text{OH}^+) + \text{HO}_2^- + \text{H}^+ \tag{4.31}
\]
\[
\text{BiOCl}(\text{e}^-_{\text{CB}}) + \text{O}_2 \rightarrow \text{O}_2^- + \text{H}^+ \rightarrow \text{HO}_2^* \tag{4.32}
\]
\[
\text{H}_2\text{O}_2 + \text{O}_2^- \rightarrow \cdot \text{OH} + \text{OH}^- + \text{O}_2 \tag{4.33}
\]
\[
\text{H}_2\text{O}_2 + \text{BiOCl}(\text{e}^-_{\text{CB}}) \rightarrow \cdot \text{OH} + \text{OH}^- \tag{4.34}
\]
\[
\cdot \text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HO}_2^* \tag{4.35}
\]
\[
\text{MG/MG}^{2+} + \cdot \text{OH} / \text{O}_2^- / \text{HO}_2^* \rightarrow \text{Degradation products} \tag{4.36}
\]

### 4.3.9: Effect of temperature:

The effect of temperature has been studied in the range from 30 \(^\circ\)C to 55 \(^\circ\)C (Table 4.42 and Fig. 4.65). Rate constant increases from 0.017 min\(^{-1}\) to 0.020 min\(^{-1}\) with increase in temperature from 30 to 40 \(^\circ\)C. However, further increased in temperature reduces the value of rate constant. Increased temperature tends to reduced electron-hole recombination. However, an increment in temperature also decreases the solubility of oxygen in water [15]. Both above mentioned conflicting factors have been equipoise at 35 \(^\circ\)C. Significant amount of solution was evaporated at higher temperature.
Table 4.42: Effect of temperature: [MG] = 50 mgL\(^{-1}\), BiOCl = 1.5 gmL\(^{-1}\), Irradiation intensity = 86 \times 10^2 lux, pH = 8.3.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>k (min(^{-1}))</th>
<th>t(_{1/2}) (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>0.017</td>
<td>39.69</td>
</tr>
<tr>
<td>35</td>
<td>0.018</td>
<td>36.90</td>
</tr>
<tr>
<td>40</td>
<td>0.020</td>
<td>34.37</td>
</tr>
<tr>
<td>45</td>
<td>0.019</td>
<td>36.47</td>
</tr>
<tr>
<td>50</td>
<td>0.016</td>
<td>41.54</td>
</tr>
<tr>
<td>55</td>
<td>0.011</td>
<td>62.09</td>
</tr>
</tbody>
</table>

**Fig. 4.65:** Effect of temperature.

4.3.10: Effect of N\(_2\) and O\(_2\) purging:

Dissolved gases in the suspension plays an important role in the photocatalytic degradation of organic pollutants. Fig. 4.66 show that the degradation of MG has been severely retarded by bubbling of pure N\(_2\) (decrease in rate constant from 0.017 min\(^{-1}\) to 0.0059 min\(^{-1}\)) but increases rapidly on bubbling of oxygen through the dye solution (increase in rate constant from 0.017 min\(^{-1}\) to 0.026 min\(^{-1}\)). The photocatalytic mechanism shows that the surface redox reactions initiated by photogenerated electrons and holes start the photocatalytic degradation of organics. If the surface chemical reactions of conduction band (CB) electrons are blocked by N\(_2\) purging, the valance band
(VB) holes would have a tendency to be consumed by the accumulated electrons via the electron–hole recombination inside the catalyst, hence, the photocatalytic degradation process would be significantly suppressed [26, 27]. In the aerated condition, the oxygen accepts the conduction band electron and gives rise to a superoxide radical anion which further reacts with the hydrogen ion to form a hydroxyl radical in the system which in turn increases the degradation rate [28, 29].

![Graph showing degradation rate](image)

**Fig. 4.66: Decolorization of MG under various photocatalytic systems:** [MG] = 50 mgL\(^{-1}\), BiOCl = 1.5 gmL\(^{-1}\), Irradiation intensity = \(86 \times 10^2\) lux, pH = 8.3, Solar light intensity = \(13 \times 10^3 \pm 5\) lux, Temperature = 30 ± 0.3 \(^0\)C.

**4.3.11: Comparison of Solar/Visible Light:**

For the degradation of dye, the comparative study has been carried out under solar/visible light. Fig. 4.66 shows the degradation rate as a function of irradiation time on illumination of an aqueous suspension of MG under sunlight and visible respectively. The rate of degradation was found to be much more in the solar light (k = 0.020 min\(^{-1}\)). Blank experiments were also carried out under sunlight in absence of BiOCl where no observable loss of dye was observed.

**4.3.12: Effect of other photocatalysts:**

The influence of three different photocatalysts, BiOCl, TiO\(_2\) and BaCrO\(_4\) has been used to study the effect on degradation kinetics of MG has been studied and results are shown
in Table 4.43 and Fig. 4.67. The order of photoactivity follows the order: BiOCl > TiO$_2$ > BaCrO$_4$. As it is known that the photocatalytic activity is closely related to the mobility of the photogenerated charge carriers and the positions of the conduction band (CB) and valence band (VB) in the photocatalyst. In metal oxide photocatalysts, the VB is commonly composed of O 2p. However, the VB of materials that contain element Bi mostly consists of O 2p and Bi 6s hybrid orbitals, whereas the CB consists of Bi 6p. It has been found that the broad VB increases the mobility of the photogenerated carriers [30,31]. This phenomenon was obvious for the bismuth-based photocatalysts because the Bi 6s orbital is largely dispersed, which is more beneficial to increasing the mobility of photogenerated carriers. Moreover, the Bi-O sites in BiOCl acted as electron traps in the photocatalytic reaction. Therefore, materials containing Bi are probably active photocatalysts. It has already been reported that semiconductors such as BiOCl and TiO$_2$ have band gaps larger than 3 eV show strong photocatalytic activity. The conduction band and valence band potentials of both BiOCl and TiO$_2$ are larger than the corresponding redox potentials of H$^+/\text{H}_2$ and H$_2\text{O}/\text{O}_2$, and the photogenerated electron and hole can be separated efficiently. BaCrO$_4$ with smaller band gap shows less activity since its conduction band is much lower than that of BiOCl and TiO$_2$. Electron (CB) in these semiconductors rapidly falls into the hole thus showing reduced activity.

Table 4.43: Effect of other photocatalysts: [MG] = 50 mgL$^{-1}$, [Photocatalyst] = 1.5 gmL$^{-1}$, Irradiation intensity = $86 \times 10^2$ lux, pH = 8.3, Temperature = 30 ± 0.3 °C.

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Bandgap(eV)</th>
<th>k (min$^{-1}$)</th>
<th>$t_{1/2}$ (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BiOCl</td>
<td>3.2</td>
<td>0.017</td>
<td>28.6</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>3.1</td>
<td>0.021</td>
<td>31.90</td>
</tr>
<tr>
<td>BaCrO$_4$</td>
<td>2.6</td>
<td>0.012</td>
<td>54.73</td>
</tr>
</tbody>
</table>
Here, we have studied the influence of light intensity on the degradation efficiency has been examined at constant dye concentration (50 mgL$^{-1}$) and catalyst loading (1.5 mgL$^{-1}$). It is evident that the rate constant increases with increase in the light intensity as shown in and Table 4.44 and Fig. 4.68. The visible light irradiation generates the photons required for the electron transfer from the valence band to the conduction band of a semiconductor photocatalyst and the energy of a photon is related to its wavelength and the overall energy input to a photocatalytic process is dependent on light intensity. The rate of degradation increases when more radiations fall on the catalyst surface and hence more hydroxyl radicals are produced [32,33].

**Table 4.44: Effect of light intensity:** [MG] = 50 mgL$^{-1}$, BiOCl = 1.5 gmL$^{-1}$, pH = 8.3, Temperature = 30 ± 0.3 $^0$C.

<table>
<thead>
<tr>
<th>Light intensity $\times 10^2$ lux</th>
<th>k (min$^{-1}$)</th>
<th>$t_{1/2}$ (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>74</td>
<td>0.016</td>
<td>42.46</td>
</tr>
<tr>
<td>86</td>
<td>0.017</td>
<td>39.69</td>
</tr>
<tr>
<td>105</td>
<td>0.018</td>
<td>36.55</td>
</tr>
<tr>
<td>124</td>
<td>0.022</td>
<td>31.47</td>
</tr>
<tr>
<td>140</td>
<td>0.023</td>
<td>29.09</td>
</tr>
</tbody>
</table>
4.3.14: Stability test for BiOCl activity:
To assess the stability of the BiOCl in the photocatalytic reaction, BiOCl was re-examined for two extra cycles. As shown in Fig. 4.69 (II), (III), the high photocatalytic performance of the as-prepared BiOCl for MG degradation was effectively maintained for 120 min of testing. After three cycles of repetition tests for photodegradation of MG, catalyst did not exhibit any significant loss of activity. This experimental result indicated that BiOCl is more stable and has good photocatalytic performance on degradation of MG [34, 35].

Fig. 4.69: MG degradation by BiOCl: (I) the first cycle; (II) the second cycle; (III) the third cycle; [MG] = 50 mgL\(^{-1}\), BiOCl = 1.5 gmL\(^{-1}\), Irradiation intensity = 86 × 10\(^2\) lux, pH = 8.3, Temperature = 30 ± 0.3 \(^\circ\)C.
4.3.15: COD and CO$_2$ measurements during mineralization of MG:

To judge the feasibility of the photochemical process for degradation and mineralization of MG dye solution, the results of chemical oxygen demand (COD) were taken as one of the parameter [36].

**Table 4.45: Mineralization of MG:** [MG] = 50 mgL$^{-1}$, BiOCl = 1.5 gmL$^{-1}$, Irradiation intensity = 86 $\times 10^2$ lux, pH = 8.3, Temperature = 30 ± 0.3 0°C.

<table>
<thead>
<tr>
<th>Irradiation time (h)</th>
<th>COD (mgL$^{-1}$)</th>
<th>CO$_2$ (mgL$^{-1}$)</th>
<th>% Efficiency</th>
<th>NO$_3^-$ (mgL$^{-1}$)</th>
<th>SO$_4^{2-}$ (mgL$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>201</td>
<td>7</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>160</td>
<td>85</td>
<td>20</td>
<td>3</td>
<td>10</td>
</tr>
<tr>
<td>4</td>
<td>60</td>
<td>102</td>
<td>70</td>
<td>11</td>
<td>27</td>
</tr>
<tr>
<td>6</td>
<td>32</td>
<td>163</td>
<td>84</td>
<td>20</td>
<td>30</td>
</tr>
<tr>
<td>8</td>
<td>6</td>
<td>225</td>
<td>97</td>
<td>26</td>
<td>32</td>
</tr>
</tbody>
</table>

**Fig. 4.70:** (a) COD and CO$_2$ trend and (b) formation of NO$_3^-$ and SO$_4^{2-}$ during mineralization of MG: [MG] = 50 mgL$^{-1}$, BiOCl = 1.5 gmL$^{-1}$, Irradiation intensity = 86 $\times 10^2$ lux, pH = 8.3, Temperature = 30 ± 0.3 0°C.

From Table 4.45 and Fig. 4.70, there is a substantial decrease of the COD of the solution from 201 mgL$^{-1}$ to 6 mgL$^{-1}$ and increase in CO$_2$ value from 7 mgL$^{-1}$ to 225 mgL$^{-1}$ in 8 h of irradiation. Consequently, the complete mineralization of MG was achieved after 8 h
of visible light irradiation in the presence of BiOCl because of the formation of more stable intermediates towards oxidation. The result implies that both mechanisms of degradation and mineralization play important roles for the photocatalytic effects under visible light irradiation.

Analysis of inorganic ions revealed as expected the formation of NO$_3^-$ and SO$_4^{2-}$ in solution. As depicted in Table 4.45, the amount of SO$_4^{2-}$ and NO$_3^-$ ions increased with increasing irradiation time. Note that the amount of SO$_4^{2-}$ ions released into the solution is lower than that expected from stoicheometry. It was observed that the concentration of sulphate ions increased rapidly at the first 2 h and tends to reach a plateau of ca. 27 mgL$^{-1}$ within 4 h. This can be attributed to the fast elimination of the SO$_3^-$ moiety in solution. This behavior can be ascribed to a partially irreversible adsorption of sulphate ions on photocatalyst surface, as it has been already reported for the degradation of other sulfur containing dyes [35–37]. The nitrogen atoms with $-3$ oxidation state produced NH$_4^+$ cations, subsequently NH$_4^+$ cations were converted into NO$_3^-$ ions. It was obvious that aqueous MG was mainly mineralized rather than being bleached [37]. After 8 h of irradiation, 97% efficiency has been observed for the process. 26 mgL$^{-1}$ of NO$_3^-$ and 32 mgL$^{-1}$ of SO$_4^{2-}$ have been found after 8 h of irradiation time.

4.3.16: UV-Vis spectra of MG Dye:

Primary absorption peaks of MG dye was at 400 nm and 600 nm. As the reaction proceeds, the two peaks disappear gradually as shown in Fig. 4.71 and the full scanning spectrum pattern changes obviously after 8 h. This may be the evidence of the intermediate by-product. At the end of the 8 h of reaction time, there is no evident absorption peak observed. It indicates that the pollutants are destroyed with the photocatalytic reaction and proves that wastewater is fully decomposed [38, 39].
4.3.17: Mechanism of MG degradation:

The degradation mechanism of MG is as follows: BiOCl oxydizes in two ways, photogenerated holes $h^+$ in the valence band and the $'OH$ radicals, which are strongly active and degrading non-selective agents [40, 41]. Valence band holes ($h_{VB}^+$) and conduction band electrons ($e_{CB}$) are generated when aqueous BiOCl suspension is irradiated with visible light. These electron-hole pairs interact separately with the substrate. Valence band holes ($h_{VB}^+$) react with surface bound $H_2O$ or $OH^-$ to produce hydroxyl radical ($'OH$). Valence band holes can also oxidize organic molecule. Conduction band electrons ($e_{CB}$) reduce molecular oxygen to generate superoxide radicals as shown in eq. (4.38) to eq. (4.47) [42, 5].

\[
\begin{align*}
    BiOCl + h_{\text{Visible}} & \rightarrow BiOCl (h_{\text{VB}}^+ + e_{\text{CB}}^-) & (4.38) \\
    BiOCl (h_{\text{VB}}^+) + H_2O & \rightarrow BiOCl + H^+ + 'OH & (4.39) \\
    BiOCl (h_{\text{VB}}^+) + OH^- & \rightarrow BiOCl + 'OH & (4.40) \\
    BiOCl (e_{\text{CB}}^-) + O_2 & \rightarrow BiOCl + O_2^- & (4.41) \\
    O_2^- + H^+ & \rightarrow HO_2^- & (4.42) \\
    HO_2^- + H^+ + BiOCl (e_{\text{CB}}^-) & \rightarrow H_2O_2 + BiOCl & (4.43)
\end{align*}
\]
\[ \begin{align*} 
H_2O_2 + BiOCl (e_{CB}^-) &\rightarrow \cdot OH + OH^- + BiOCl \quad (4.44) \\
MG + h^+_\text{VB} &\rightarrow \text{Oxidation products} \quad (4.45) \\
MG + e^-_{CB} &\rightarrow \text{Reduction products} \quad (4.46) \\
MG + \cdot OH &\rightarrow \text{Degradation products} \quad (4.47)
\end{align*} 

Secondly, sensitization of dye molecule 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 (MG\(^{+}\)) that undergoes degradation to yield products as follows [43, 41]

\[ \begin{align*} 
MG + h_\text{V} \text{(Vis)} &\rightarrow \text{MG}^* \text{or } \text{MG}^* \quad (4.48) \\
1\text{MG}^* \text{or } 3\text{MG}^* + BiOCl &\rightarrow \text{MG}^{+} + BiOCl (e_{CB}^-) \quad (4.49) \\
BiOCl (e_{CB}^-) + O_2 &\rightarrow O_2^- + BiOCl \quad (4.50) \\
\text{MG}^{+} &\rightarrow \text{degradation products} \quad (4.51)
\end{align*} \]

Cationic dye radicals reacts with hydroxyl ions undergoing oxidation via eqs. 4.52 to 4.53 or interacts with O\(_2^-\), HO\(_2^-\) or HO\(^-\) species to generate intermediates that finally lead to degradation products (eqs. 4.54 to 4.57)

\[ \begin{align*} 
\text{MG}^{+} + \text{OH}^- &\rightarrow \text{MG} + \cdot OH \quad (4.52) \\
\text{MG} + 2\text{HO}^- &\rightarrow \text{H}_2\text{O} + \text{oxidation products} \quad (4.53) \\
\text{O}_2^- + \text{H}^+ &\rightarrow \text{HO}_2^+ \quad (4.54) \\
\text{HO}_2^+ + \text{H}^+ + \text{BiOCl (}e_{CB}^-) &\rightarrow \text{H}_2\text{O}_2 + \text{BiOCl} \quad (4.55) \\
\text{H}_2\text{O}_2 + \text{BiOCl (}e_{CB}^-) &\rightarrow \text{HO}^+ + \text{OH}^- + \text{BiOCl} \quad (4.56) \\
\text{MG}^{+} + \text{O}_2^- &\rightarrow \text{degradation products} \quad (4.57)
\end{align*} \]

From estimated value of COD and CO\(_2\), it is evident that 100 % of COD removal has been achieved in 10 h of irradiation under chosen reaction condition. A decrease in COD and increase in CO\(_2\) confirm the degradation of dye (see Fig. 4.70(a)). Significant amount
of NO$_3^-$ and SO$_4^{2-}$ released during the mineralization of dye (see Fig. 4.70 (b)). Complete disappearance of peaks in UV-Vis region indicates the absence of any organic moiety (Fig. 4.71). COD and CO$_2$ estimations are in agreement with UV-Vis spectral analysis during mineralization.

4.3.18: Kinetic Studies:
Due to the practical applications, the degradation kinetics of MG was investigated under the conditions of the appropriate optimum catalyst concentrations, natural pH and temperature of 30 °C. From the results, it becomes clear that the degradation process proceeds in two parallel branches of only visible light degradation and when visible light is assisted with catalyst particles:

$$R = -\frac{d [MG]}{dt} = R_1 + R_2$$

(4.58)

where $R$, $R_1$ and $R_2$ are the net degradation, the photocatalysis and the photolysis rates, respectively. Under chosen experimental condition, photolysis has no significant effect on degradation process. Therefore, eq. (4.58) reduces to following Eq.

$$R = -\frac{d [MG]}{dt} = R_1$$

(4.59)

Here, simple power law model has been examined to find the rate of the photocatalytic degradation [44-46]

$$R_1 = k_1[MG]^{n_1}$$

(4.60)

where, $n_1$, $n_2$, $k_1$ and $k_2$ are the appropriate order and rate constant of the reaction respectively. In this work, to obtain the appropriate parameters of eq. (4.60), the differential method of analysis, based on the data of concentration vs. time, was used.

Fig. 4.72 presents the goodness of fit of the rate eq. (4.60) to the data.
Fig. 4.72: The variation of MG degradation rate versus its concentration for photocatalysis: BiOCl = 1.5 g mL⁻¹, Irradiation intensity = 86 × 10² lux, pH = 8.3, Temperature = 30 ± 0.3 °C.

Our results are in agreement with other studies reported in literature [44-46]. Under chosen experimental conditions, the rate of degradation of MG for photodegradation has been found to be 3.23 mg L⁻¹ min⁻¹.
Neutral Red (or toluylene red, Basic Red 5, or C.I. 50040) is a eurhodin dye used for staining in histology. It is used as a general stain in histology, as a counterstain in combination with other dyes, and for many staining methods. Neutral Red is added to some growth media for bacteria and cell cultures. It usually comes as a chloride salt. Neutral Red acts as a pH indicator, changing from red to yellow between the pH 6.8-8.0.
4.3 (E): Effects of various experimental parameters on the degradation rate of Neutral Red (NR)

4.3.1: Photocatalytic degradation of neutral red (NR):

In Langmuir–Hinshelwood treatment of heterogeneous surface reactions, the photochemical degradation rate is described by pseudo first order kinetics which is rationalized in terms of the modified model to accommodate reactions occurring at a solid-liquid interface as [1, 2]

\[ R = \frac{-dc}{dt} = \frac{k_{L-H} K_{ad} C}{(1 + K_{ad} C)} \]  

(4.11)

where \( k_{L-H} \) is the reaction rate constant, \( K_{ad} \) is the adsorption coefficient of dye on the surface of BiOCl, 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. (4.11). So for simplification the denominator becomes 1. Integrating eq. (4.11), we obtain

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

(4.12)

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 NR on the BiOCl surface can be calculated by using eq. (4.13)

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

(4.13)

The photocatalytic degradation of NR dye follows pseudo first kinetics. The detection was realized at 520 nm. The results for typical run are given in Fig. 4.73 (a), (b). The absorbance of NR dye decreases with an increase in irradiation time. While in dark and during photolysis, no significant changes have been observed (see in Fig. 4.73(a)). The reaction rate constant \( k \) for the photocatalytic degradation reaction of NR dye, by BiOCl catalyst, was obtained from the slope of the linear relationship of the natural logarithm of
the ratio between the initial concentration of NR and the concentration after photocatalytic degradation $\ln(C_0/C)$ versus the corresponding irradiation time as shown in Fig. 4.73(b). The value of $k$ gives an indication for the activity of the photocatalyst. The plot of $\log \ln(C_0/C)$ versus time follows pseudo first order kinetics with regression coefficient of 0.945, rate constant of 0.016 min$^{-1}$ and half life time of 41.25 min (Fig. 4.73(b)).

Fig. 4.73 (a): Decolorization of NR: $[\text{NR}] = 50$ mgL$^{-1}$, BiOCl = 3.0 gmL$^{-1}$, Irradiation intensity = $82 \times 10^2$ lux, pH = 9.0, Temperature = $30 \pm 0.3^0$C.

Fig. 4.73 (b): Pseudo first order kinetics: $[\text{NR}] = 50$ mgL$^{-1}$, BiOCl = 3.0 gmL$^{-1}$, Irradiation intensity = $82 \times 10^2$ lux, pH = 9.0, Temperature = $30 \pm 0.3^0$C.
4.3.2: Influence of initial pH:

Degradation of neutral red dye studied by varying pH from 3.6 to 13.6. The results of pH effect were shown in Table 4.46 and Fig. 4.74.

Table 4.46: Effect of pH: [NR] = 30 mgL⁻¹, BiOCl = 2.0 gmL⁻¹, Irradiation intensity = 82 × 10² lux, , Temperature = 30 ± 0.3 °C.

<table>
<thead>
<tr>
<th>pH</th>
<th>k(min⁻¹)</th>
<th>t₁/₂ (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.6</td>
<td>0.012</td>
<td>56.89</td>
</tr>
<tr>
<td>5.3</td>
<td>0.013</td>
<td>51.33</td>
</tr>
<tr>
<td>7.1</td>
<td>0.014</td>
<td>46.57</td>
</tr>
<tr>
<td>9.0</td>
<td>0.016</td>
<td>41.25</td>
</tr>
<tr>
<td>11.4</td>
<td>0.015</td>
<td>44.94</td>
</tr>
<tr>
<td>13.6</td>
<td>0.013</td>
<td>51.56</td>
</tr>
</tbody>
</table>

Fig. 4.74: Influence of initial pH.

It is quite evident from the graph plotted in Fig. 4.74 that as the pH of dye solution increases from 3.6 to 9.0, the photocatalytic reaction rate increases and the further increase in pH up to 13.6 result in decrease in rate of degradation. The maximum degradation has been found at pH 9.0. The increase in rate of photocatalytic degradation might be due to the more availability of OH⁻ ions in basic medium which will generate more ‘OH radicals by combining with holes which are formed due to the electronic
excitation in catalyst. In acidic condition, electrostatic interactions between the positively charged active sites on catalyst surface and cationic dye molecules led to strong repulsion consequently made it difficult for dye molecules to get adsorbed on the catalyst surface [3].

4.3.3: Effect of catalyst weight:

The effect of photocatalyst weight for BiOCl on the photodegradation of the NR was studied in the range of 1.0 to 6.0 gmL\(^{-1}\) and results are presented in Table 4.47 and plotted in Fig. 4.75.

**Table 4.47: Effect of catalyst weight:** [NR] = 30 mgL\(^{-1}\), Irradiation intensity = \(82 \times 10^2\) lux, pH = 9.0, Temperature = 30 ± 0.3°C

<table>
<thead>
<tr>
<th>BiOCl gmL(^{-1})</th>
<th>k (min(^{-1}))</th>
<th>(t_{1/2}) (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>0.011</td>
<td>61.43</td>
</tr>
<tr>
<td>2.0</td>
<td>0.014</td>
<td>47.92</td>
</tr>
<tr>
<td>3.0</td>
<td>0.016</td>
<td>41.25</td>
</tr>
<tr>
<td>4.0</td>
<td>0.013</td>
<td>52.50</td>
</tr>
<tr>
<td>5.0</td>
<td>0.010</td>
<td>68.75</td>
</tr>
<tr>
<td>6.0</td>
<td>0.008</td>
<td>83.69</td>
</tr>
</tbody>
</table>

**Fig. 4.75:** Effect of catalyst weight.
The graph depicts that as the concentration of catalyst increases from 1.0 - 3.0 gmL⁻¹, the degradation rate constant increases from 0.011 to 0.016 min⁻¹ but further increase in the catalyst concentration up to 6.0 gmL⁻¹, the rate constant decreases to 0.008 min⁻¹ respectively. The optimum weight of catalyst loading was found to be 3.0 gmL⁻¹. The increased degradation rate that follows the increase in the catalyst weight can be attributed to the fact that the total active surface area increases with increasing catalyst weight, thus accelerating the process. When all the dye molecules are adsorbed on catalyst (BiOCl) no improvement is achieved by adding more catalyst. The decrease in efficiency may be due to an increasing opacity of the suspension and to an enhancement of the light reflectance, because of the excess of BiOCl particles [4, 5] Additionally, in the case of high catalyst loads we observed agglomeration and sedimentation of BiOCl which makes a significant fraction of catalyst to be inaccessible to either absorbing the dye or absorbing the radiation, with consequent decrease in active sites available to the catalytic reaction [4].

### 4.3.4: Effect of initial dye concentration:

Effect of variation of dye concentration was also studied by taking different concentrations of dyes. In order to optimize the initial dye concentrations was varied from 10 to 110 mgL⁻¹. The results are shown in Table 4.48 and plotted in Fig. 4.76. It has been observed from the graph that the increased in dye concentration from 10 mgL⁻¹ to 50 mgL⁻¹, the rate constant increased from 0.010 to 0.016 min⁻¹. Thereafter, rate constant decreased to 0.010 min⁻¹ with increased dye concentration up to 110 mgL⁻¹. Rate constant was found to be maximal at 50 mgL⁻¹ of dye concentration. This may be attributed to the fact that as the concentration of dye increases, more dye molecules available for excitation followed by inter system crossing and hence, there was an increase in the rate [5]. Further increase in dye concentration, the equilibrium adsorption of dye on catalyst surface active sites increases, which hinders the competitive adsorption of OH⁻ on the same sites, which means a lower formation rate of ·OH radical. The increase in dye concentration also decreases the path length of photon entering the dye solution. At high
dye concentration a significant amount of visible light may be absorbed by the dye molecules rather than the catalyst and this may also reduce the catalytic efficiency. Consequently, the degradation rate decreased as the dye concentration increases [3].

**Table 4.48: Effect of initial dye concentration:** BiOCl = 3.0 gmL⁻¹, Irradiation intensity = 82 × 10² lux, pH = 9.0, Temperature = 30 ± 0.3 °C.

<table>
<thead>
<tr>
<th>NR (mgL⁻¹)</th>
<th>k (min⁻¹)</th>
<th>t½ (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.010</td>
<td>65.62</td>
</tr>
<tr>
<td>30</td>
<td>0.013</td>
<td>50.00</td>
</tr>
<tr>
<td>50</td>
<td>0.016</td>
<td>41.25</td>
</tr>
<tr>
<td>70</td>
<td>0.012</td>
<td>54.73</td>
</tr>
<tr>
<td>90</td>
<td>0.011</td>
<td>64.52</td>
</tr>
<tr>
<td>110</td>
<td>0.010</td>
<td>86.19</td>
</tr>
</tbody>
</table>

![Fig. 4.76](image) Effect of initial dye concentration.

**4.3.5: Effect of varying oxidant concentration:**

The effect of the concentration of H₂O₂ on the initial reaction rate of neutral red degradation is shown in Table 4.49 and Fig. 4.77(a). The photocatalytic efficiency found to increase initially with increase in H₂O₂ concentration (20 to 140 mgL⁻¹) and it reached
the optimum at 60 mgL\(^{-1}\). Consequently it decreased as the concentration of the H\(_2\)O\(_2\) increased beyond the optimum. H\(_2\)O\(_2\) is considered to have two functions in the process of photocatalytic degradation. It accepts a photogenerated electron from the conduction band and thus promotes the charge separation and it also forms \(^{\cdot}\)OH radicals according to eq. (4.14) and (4.15) [6-9].

\[
\begin{align*}
H_2O_2 + e^- & \rightarrow OH^- + ^{\cdot}\text{OH} \\ H_2O_2 + O_2^- & \rightarrow ^{\cdot}\text{OH} + OH^- + O_2
\end{align*}
\] (4.14) (4.15)

Excess H\(_2\)O\(_2\) may act as a hole or an \(^{\cdot}\)OH scavenger or react with photocatalyst and form peroxocompounds, which are detrimental to the photocatalytic reaction. This explains the need for an optimal concentration of H\(_2\)O\(_2\) for the maximum effect.

K\(_2\)S\(_2\)O\(_8\) can also trap the photogenerated conduction band electron results in the formation of sulphate ion (SO\(_4^{2-}\)), a strong oxidizing agent (standard oxidation potential = 2.6 eV), which can participate in degradation process.

\[
S_2O_8^{2-} + e^- \rightarrow SO_4^{2-} + SO_4^{2-}
\] (4.16)

From Fig. 4.77(b), with increase in K\(_2\)S\(_2\)O\(_8\) concentration from 20 to 60 mgL\(^{-1}\), rate constant increased from 0.016 to 0.020 min\(^{-1}\). At optimal concentration of K\(_2\)S\(_2\)O\(_8\), rate constant has been found to be 0.020 min\(^{-1}\). Consequently degradation rate decreases as the concentration of the K\(_2\)S\(_2\)O\(_8\) increases beyond the optimum [8]. A possible explanation of this behavior may be the light absorption from dye molecule leads to the photo-sensitization of the molecule, which is accompanied by the excitation of an electron from the lower to the upper energy level. Following this, the excited dye molecule injects electrons to the S\(_2\)O\(_8^{2-}\) according to eq. (4.16). The resulting SO\(_4^{2-}\) radicals, strong oxidizing agents, attack the chromophore group in dye leading to the decolorization of the solution. The decrease in rate constant above optimum concentration is due to the adsorption of sulphate ions formed during the reaction on surface of catalyst deactivating a section of photocatslyst [10,11,8,9].
Table 4.49: Effect of oxidant: \([\text{NR}] = 50 \text{ mgL}^{-1}, \text{BiOCl} = 3.0 \text{ gmL}^{-1},\)
Irradiation intensity = \(82 \times 10^2 \text{ lux}, \text{pH} = 9.0, \text{Temperature} = 30 \pm 0.3^\circ \text{C}.

<table>
<thead>
<tr>
<th>Oxidant (mgL(^{-1}))</th>
<th>H(_2)O(_2)</th>
<th>K(_2)S(_2)O(_8)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>k (min(^{-1}))</td>
<td>t(_{1/2}) (min)</td>
</tr>
<tr>
<td>0</td>
<td>0.016</td>
<td>41.25</td>
</tr>
<tr>
<td>20</td>
<td>0.018</td>
<td>37.01</td>
</tr>
<tr>
<td>40</td>
<td>0.020</td>
<td>34.07</td>
</tr>
<tr>
<td>60</td>
<td>0.022</td>
<td>31.04</td>
</tr>
<tr>
<td>80</td>
<td>0.021</td>
<td>32.71</td>
</tr>
<tr>
<td>100</td>
<td>0.019</td>
<td>35.53</td>
</tr>
<tr>
<td>120</td>
<td>0.017</td>
<td>39.15</td>
</tr>
<tr>
<td>140</td>
<td>0.016</td>
<td>42.15</td>
</tr>
</tbody>
</table>

Fig. 4.77: Effect of oxidant: (a) H\(_2\)O\(_2\) and (b) K\(_2\)S\(_2\)O\(_8\).

4.3.6: Effect of varying salt concentration:
The addition of the other oxidizing species such as H\(_2\)O\(_2\) and K\(_2\)S\(_2\)O\(_8\) to catalyst suspensions is a well known procedure and leads to an increase in the rate of photo degradation. The effect of presence of NaCl and Na\(_2\)CO\(_3\) is shown in Table 4.50 and Fig. 4.78.
Table 4.50: Effect of salt: [NR] = 50 mgL\(^{-1}\), BiOCl = 3.0 gmL\(^{-1}\), Irradiation intensity = \(82 \times 10^2\) lux, pH = 9.0, Temperature = 30 ± 0.3 °C.

<table>
<thead>
<tr>
<th>Salt (mgL(^{-1}))</th>
<th>Na(_2)CO(_3)</th>
<th>NaCl</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(k) (min(^{-1}))</td>
<td>(t_\frac{1}{2}) (min)</td>
</tr>
<tr>
<td>0</td>
<td>0.016</td>
<td>41.25</td>
</tr>
<tr>
<td>20</td>
<td>0.015</td>
<td>43.75</td>
</tr>
<tr>
<td>40</td>
<td>0.014</td>
<td>46.38</td>
</tr>
<tr>
<td>60</td>
<td>0.013</td>
<td>49.57</td>
</tr>
<tr>
<td>80</td>
<td>0.012</td>
<td>53.72</td>
</tr>
<tr>
<td>100</td>
<td>0.011</td>
<td>61.43</td>
</tr>
<tr>
<td>120</td>
<td>0.009</td>
<td>75.49</td>
</tr>
<tr>
<td>140</td>
<td>0.008</td>
<td>86.19</td>
</tr>
</tbody>
</table>

Fig. 4.78: Effect of Salt: (a) Na\(_2\)CO\(_3\) and (b) NaCl.

As can be seen from Table 4.50 and Fig. 4.78, an increment in concentration of CO\(_3^{2-}\) from 20 mgL\(^{-1}\) to 140 mgL\(^{-1}\), results in decrease of rate constant 0.015 to 0.008 min\(^{-1}\), while with same Cl\(^-\) ion concentration variation, the rate constant decreased from 0.015 to 0.009 min\(^{-1}\). Half life time increases from 43.75 to 86.19 min and 46.01 to 70.00 min with an increase in concentration from 20 mgL\(^{-1}\) to 140 mgL\(^{-1}\) for CO\(_3^{2-}\) and Cl\(^-\) ions respectively. The inhibition is undoubtedly due to their ability to act as hydroxyl radical.
(OH\(^{-}\)) scavengers. The observed mechanism of hydroxyl radical scavenging is given by eq. (4.17) by eq. (4.20) [12,13].

\[
\begin{align*}
\text{Cl}^{-} + \cdot \text{OH} & \longrightarrow \text{Cl} + \text{OH}^{-} \\
\text{Cl}^{-} + \text{h}^{+}_{\text{VB}} & \longrightarrow \cdot \text{Cl} \\
\text{Cl}^{-} + \cdot \text{Cl} & \longrightarrow \text{Cl}_{2}^{-} \\
\text{CO}_{3}^{2-} + \cdot \text{OH} & \longrightarrow \text{CO}_{3}^{-} + \text{H}_{2}\text{O}
\end{align*}
\] (4.17) (4.18) (4.19) (4.20)

These ions may also block the active sites on the photocatalyst surface thus deactivating the catalysts towards the dye and intermediate molecules. Although, the generated radical anions have been shown to be an oxidant itself, but its oxidation potential is less than that of the hydroxyl radicals [14].

**4.3.7: Effect of FeCl\(_{3}\):**

The effect of FeCl\(_{3}\) on the photodegradation of NR has been studied by varying the concentration from 15 mgL\(^{-1}\) to 105 mgL\(^{-1}\) (see in Table 4.51 and Fig. 4.79). FeCl\(_{3}\) behaves as an electron scavenger \((\text{Fe}^{3+} + \cdot \text{e}^{-} \longrightarrow \text{Fe}^{2+})\) thus preventing the recombination of electron hole pairs. Under the experimental conditions the following reactions become significant.

\[
\begin{align*}
\text{Fe}^{2+} + \text{H}_{2}\text{O}_{2} + \text{H}^{+} & \longrightarrow \text{Fe}^{3+} + \cdot \text{OH} + \text{H}_{2}\text{O} \\
\text{Fe}^{2+} + \text{HO}_{2}^{-} + \text{H}^{+} & \longrightarrow \text{Fe}^{3+} + \text{H}_{2}\text{O}_{2}
\end{align*}
\] (4.21) (4.22)

In BiOCl/FeCl\(_{3}\)/Vis addition of FeCl\(_{3}\) caused an increase in degradation rate (0.022 min\(^{-1}\)) up to concentration 45 mgL\(^{-1}\). Photoactivation of surface adsorbed complex ion \((\text{Fe}^{3+} \cdot \text{OH}^{-})\) results in formation of \(\text{Fe}^{2+} \cdot \text{OH}\) species, which inject electrons to conduction band of BiOCl eqs. (4.24 to 4.25). Increased rate of degradation in case of FeCl\(_{3}\) is explicable due to rapid scavenging of conduction band electrons by molecular oxygen leading to formation of superoxide and hydroperoxide radicals (eq. 4.26). Higher concentration of FeCl\(_{3}\) eliminates adsorption of cationic dye on BiOCl surface and also inhibits reaction rate by reducing production of hydroxyl radicals [15-18].
\[
\text{NR} + h \nu_{\text{visible}} \rightarrow _1\text{NR}^* \text{ or } _3\text{NR}^*
\]  \hspace{1cm} (4.23)

\[
_p\text{NR}^* \text{ or } _3\text{NR}^* + \text{BiOCl (Fe}^{3+} \cdot \text{OH}) \rightarrow \text{BiOCl (Fe}^{2+} \cdot \text{OH}) + \text{NR}^*\]
\hspace{1cm} (4.24)

\[
\text{BiOCl (Fe}^{2+} \cdot \text{OH}) \rightarrow \text{BiOCl (e}^-_{\text{CB}}) + \text{BiOCl (Fe}^{3+} \cdot \text{OH})
\]  \hspace{1cm} (4.25)

\[
\text{BiOCl (e}^-_{\text{CB}}) + \text{O}_2 \rightarrow \text{O}_2^- \rightarrow \text{H}_2\text{O}_2^+
\]  \hspace{1cm} (4.26)

\[
\text{NR/NR}^{3+} + \cdot \text{OH}/\text{O}_2^-/\text{HO}_2^+ \rightarrow \text{Degradation products}
\]  \hspace{1cm} (4.27)

The metal ions such as Fe$^{3+}$ could be used as sensitizers during semiconductor photo catalytic degradation of organic pollutants.

Table 4.51: Effect of FeCl$_3$: [NR] = 50 mgL$^{-1}$, BiOCl = 3.0 gmL$^{-1}$, Irradiation intensity = 82 x 10$^2$ lux, pH = 9.0, Temperature = 30 ± 0.3 $^\circ$C

<table>
<thead>
<tr>
<th>FeCl$_3$ (mgL$^{-1}$)</th>
<th>k (min$^{-1}$)</th>
<th>t$_{1/2}$ (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.016</td>
<td>41.25</td>
</tr>
<tr>
<td>15</td>
<td>0.018</td>
<td>38.11</td>
</tr>
<tr>
<td>30</td>
<td>0.019</td>
<td>34.89</td>
</tr>
<tr>
<td>45</td>
<td>0.022</td>
<td>30.96</td>
</tr>
<tr>
<td>60</td>
<td>0.019</td>
<td>36.32</td>
</tr>
<tr>
<td>75</td>
<td>0.017</td>
<td>40.24</td>
</tr>
<tr>
<td>90</td>
<td>0.015</td>
<td>43.42</td>
</tr>
<tr>
<td>105</td>
<td>0.010</td>
<td>67.54</td>
</tr>
</tbody>
</table>

Fig. 4.79: Effect of FeCl$_3$. 
4.3.8: Effect of Fe$^{3+}$/H$_2$O$_2$:

The oxidation system based on Fenton reaction has been used for the treatment of the effective decolorization and degradation of dyes under laboratory conditions. The process is based on the formation of reactive oxidizing species, able to efficiently degrade the pollutants of the wastewater stream. Fenton’s reagent is a mixture of H$_2$O$_2$ and Fe$^{2+}$ or Fe$^{3+}$ iron [19-21]. Efficiency of Fe$^{3+}$/H$_2$O$_2$ system has been studied for decolorization of NR in the presence of BiOCl and visible light irradiation. The results are displayed in Table 4.52 and plotted in Fig. 4.80.

Table 4.52: Effect of Fe$^{3+}$/H$_2$O$_2$: [NR] = 50 mgL$^{-1}$, BiOCl = 3.0 gmL$^{-1}$, Irradiation intensity = 82 x $10^2$ lux, pH = 9.0, Temperature = 30 ± 0.3 $^\circ$C

<table>
<thead>
<tr>
<th>Fe$^{3+}$: H$_2$O$_2$</th>
<th>With BiOCl</th>
<th>Without BiOCl</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>k (min$^{-1}$)</td>
<td>t$_{1/2}$ (min)</td>
</tr>
<tr>
<td>1:1</td>
<td>0.035</td>
<td>19.70</td>
</tr>
<tr>
<td>1:1.2</td>
<td>0.054</td>
<td>12.67</td>
</tr>
<tr>
<td>1:3</td>
<td>0.058</td>
<td>11.88</td>
</tr>
<tr>
<td>1.3:2</td>
<td>0.034</td>
<td>20.01</td>
</tr>
<tr>
<td>3:3</td>
<td>0.029</td>
<td>23.28</td>
</tr>
</tbody>
</table>

Fig. 4.80: Effect of Fe$^{3+}$/H$_2$O$_2$. 
Rate constant has a value of 0.035 min$^{-1}$ on the addition of (Fe$^{3+}$: H$_2$O$_2$) in molar ratio (1:1). In the presence of (Fe$^{3+}$: H$_2$O$_2$) in molar ratio (1:1.2), rate constant has been found 0.054 min$^{-1}$. Upon irradiation of Fe$^{3+}$/H$_2$O$_2$/BiOCl/NR system with visible light, production of $^{\cdot}$OH radicals increases involving a very complex mechanism. Dye absorbs visible irradiation and is excited into high-energy state. This excited dye molecules reduce the ferric ion complex to ferrous ion complex followed by the transfer to ferric ion [22]. The reduced ferrous ions react with hydrogen peroxide to decompose and produce hydroxyl radical [eq. (4.30)]. $^{\cdot}$OH radicals also decompose H$_2$O$_2$ to HO$_2^\cdot$. A similar mechanism has been reported [23-25].

\[
\text{NR} + h\nu_{\text{visible}} \rightarrow 1\text{NR}^* \text{ or } 3\text{NR}^* \quad (4.28)
\]

\[
1\text{NR}^* \text{ or } 3\text{NR}^* + \text{BiOCl}(\text{Fe}^{3+}\text{OH}^-) \rightarrow \text{BiOCl}(\text{Fe}^{2+}\text{OH}^-) + \text{NR}^{2+} \quad (4.29)
\]

\[
\text{BiOCl}(\text{Fe}^{2+}\text{OH}^-) + \text{H}_2\text{O}_2 \xrightarrow{h\nu} \text{BiOCl}(\text{Fe}^{3+}\text{OH}^-) + \text{OH}^- + ^{\cdot}\text{OH} \quad (4.30)
\]

\[
\text{BiOCl}(\text{Fe}^{2+}\text{OH}^-) + \text{H}_2\text{O}_2 \xrightarrow{h\nu} \text{BiOCl}(\text{Fe}^{2+}\text{OH}^-) + \text{HO}_2^- + \text{H}^+ \quad (4.31)
\]

\[
\text{BiOCl}(\text{Fe}^{2+}\text{OH}^-) \rightarrow \text{BiOCl}(\text{Fe}^{3+}\text{OH}^-) + \text{BiOCl}(e^-_{CB}) \quad (4.32)
\]

\[
\text{H}_2\text{O}_2 + O_2^- \rightarrow ^{\cdot}\text{OH} + \text{OH}^- + \text{O}_2 \quad (4.34)
\]

\[
\text{H}_2\text{O}_2 + \text{BiOCl}(e^-_{CB}) \rightarrow ^{\cdot}\text{OH} + \text{OH}^- \quad (4.35)
\]

\[
^{\cdot}\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HO}_2^\cdot \quad (4.36)
\]

\[
\text{NR} / \text{NR}^{2+} + ^{\cdot}\text{OH} / O_2^- / \text{HO}_2^\cdot \rightarrow \text{Degradation products} \quad (4.37)
\]

**4.3.9: Effect of temperature:**

The influence of temperature has been studied in the range from 30 °C to 55 °C (Table 4.53 and Fig. 4.81). Rate constant increases from 0.016 to 0.026 min$^{-1}$ with increase in temperature from 30 to 45 °C. However, further increase in temperature reduces the value of rate constant. Increased temperature tends to reduce electron-hole recombination. However, an increment in temperature also decreases the solubility of oxygen in water.
Both above mentioned conflicting factors have been equipoise at 35 °C. Significant amount of solution was evaporated at higher temperature.

Table 4.53: Effect of temperature: [NR] = 50 mgL⁻¹, BiOCl = 3.0 gmL⁻¹, Irradiation intensity = 82 × 10² lux, pH = 9.0.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>k (min⁻¹)</th>
<th>t½ (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>0.016</td>
<td>41.25</td>
</tr>
<tr>
<td>35</td>
<td>0.021</td>
<td>54.22</td>
</tr>
<tr>
<td>40</td>
<td>0.023</td>
<td>31.38</td>
</tr>
<tr>
<td>45</td>
<td>0.026</td>
<td>37.74</td>
</tr>
<tr>
<td>50</td>
<td>0.023</td>
<td>50.65</td>
</tr>
<tr>
<td>55</td>
<td>0.020</td>
<td>84.30</td>
</tr>
</tbody>
</table>

Fig. 4.81: Effect of temperature.

4.3.10: Effect of N₂ and O₂ purging:

Dissolved gases in the suspension plays an important role in the photocatalytic degradation of organic pollutants. Fig. 4.82 show that the degradation of NR has been severely retarded by bubbling of pure N₂ (decrease in rate constant from 0.016 min⁻¹ to 0.0059 min⁻¹) but increased rapidly on oxygen bubbling through the dye solution (increase in rate constant from 0.016 min⁻¹ to 0.026 min⁻¹). The photocatalytic mechanism shows that the surface redox reactions initiated by photogenerated electrons
and holes start the photocatalytic degradation of organics. If the surface chemical reactions of CB electrons are blocked by N₂ purging, the VB holes would have a tendency to be consumed by the accumulated electrons via the electron–hole recombination inside the catalyst, hence, the photocatalytic degradation process would be significantly suppressed [26, 27]. In the aerated condition, the oxygen accepts the conduction band electron and gives rise to a superoxide radical anion which further reacts with the hydrogen ion to form a hydroxyl radical in the system which in turn increases the degradation rate [28, 29].

![Graph showing decolorization of NR under various photocatalytic systems.](image)

**Fig. 4.82: Decolorization of NR under various photocatalytic systems:** [NR] = 50 mgL⁻¹, BiOCl = 3.0 gmL⁻¹, Irradiation intensity = 82 × 10² lux, pH = 9.0, Solar light intensity = 165 × 10³ ± 5 lux, Temperature = 30±0.3 ⁰C

### 4.3.11: Comparison of Solar/Visible Light:

The comparative study has been carried out for the degradation of dye solution in solar/visible light. Fig. 4.82 shows the degradation rate as a function of irradiation time on illumination of an aqueous suspension of NR under sunlight and visible light respectively. The rate of degradation was found to be much more in the solar light (k = 0.0204 min⁻¹). Blank experiments were also carried out under sunlight in the absence of BiOCl where no observable loss of dye was observed.
4.3.12: Effect of other photocatalysts:

The influence of three different photocatalysts, BiOCl, TiO\textsubscript{2} and BaCrO\textsubscript{4} on degradation kinetics of NR and results are shown in Table 4.54 and Fig. 4.83. The order of photoactivity is as follows: BiOCl > TiO\textsubscript{2} > BaCrO\textsubscript{4}. As it is known that the photocatalytic activity is closely related to the mobility of the photogenerated charge carriers and the positions of the conduction band (CB) and valence band (VB) in the photocatalyst. In metal oxide photocatalysts, the VB is commonly composed of O 2p. However, the VB of materials that contain element Bi mostly consists of O 2p and Bi 6s hybrid orbitals, whereas the CB consists of Bi 6p. It has been found that the broad VB increases the mobility of the photogenerated carriers [30,31]. This phenomenon was obvious for the bismuth-based photocatalysts because the Bi 6s orbital is largely dispersed, which is more beneficial to increasing the mobility of photogenerated carriers. Moreover, the Bi-O sites in BiOCl acted as electron traps in the photocatalytic reaction. Therefore, materials containing Bi are probably active photocatalysts. It has already been reported that semiconductors such as BiOCl and TiO\textsubscript{2} have band gaps larger than 3.0 eV show strong photocatalytic activity. The conduction band and valence band potentials of both BiOCl and TiO\textsubscript{2} are larger than the corresponding redox potentials of H\textsuperscript{+}/H\textsubscript{2} and H\textsubscript{2}O/O\textsubscript{2}, and the photogenerated electron and hole can be separated efficiently. BaCrO\textsubscript{4} with smaller band gap shows less activity since its conduction band is much lower than that of BiOCl and TiO\textsubscript{2}. Conduction band electron in these semiconductors rapidly falls into the hole thus showing reduced activity.

**Table 4.54: Effect of other photocatalysts:** [NR] = 50 mgL\textsuperscript{-1}, [Photocatalyst] = 3.0 gmL\textsuperscript{-1}, Irradiation intensity = 82 × 10\textsuperscript{2} lux, pH = 9.0, Temperature = 30 ± 0.3 °C.

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Bandgap(eV)</th>
<th>k (min\textsuperscript{-1})</th>
<th>t\textsubscript{1/2} (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BiOCl</td>
<td>3.2</td>
<td>0.016</td>
<td>41.25</td>
</tr>
<tr>
<td>TiO\textsubscript{2}</td>
<td>3.1</td>
<td>0.014</td>
<td>49.35</td>
</tr>
<tr>
<td>BaCrO\textsubscript{4}</td>
<td>2.6</td>
<td>0.009</td>
<td>76.49</td>
</tr>
</tbody>
</table>
4.3.13: Effect of light intensity and irradiation time:
The influence of light intensity on the degradation efficiency has been examined at constant dye concentration (50 mgL<sup>-1</sup>) and catalyst loading (3.0 mgL<sup>-1</sup>). It is evident that the rate constant increases with increase in the light intensity as shown in Table 4.55 and Fig. 4.84. The visible light irradiation generates the photons required for the electron transfer from the valence band to the conduction band of a semiconductor photocatalyst and the energy of a photon is related to its wavelength and the overall energy input to a photocatalytic process is dependent on light intensity. The rate of degradation increases when more radiations fall on the catalyst surface and hence more hydroxyl radicals are produced [32, 33].

Table 4.55: Effect of light intensity: [NR] = 50 mgL<sup>-1</sup>, BiOCl = 3.0 gmL<sup>-1</sup>, pH = 9.0, Temperature = 30 ± 0.3 °C.

<table>
<thead>
<tr>
<th>Light intensity × 10&lt;sup&gt;2&lt;/sup&gt; lux</th>
<th>k (min&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>t&lt;sub&gt;½&lt;/sub&gt; (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>0.014</td>
<td>46.76</td>
</tr>
<tr>
<td>82</td>
<td>0.016</td>
<td>41.25</td>
</tr>
<tr>
<td>100</td>
<td>0.019</td>
<td>35.64</td>
</tr>
<tr>
<td>130</td>
<td>0.021</td>
<td>31.64</td>
</tr>
<tr>
<td>160</td>
<td>0.026</td>
<td>26.01</td>
</tr>
</tbody>
</table>
4.3.14: Stability test for BiOCl activity:

To assess the stability of the BiOCl in the photocatalytic reaction, BiOCl was re-examined for two extra cycles. As shown in Fig. 4.85 (II), (III), the high photocatalytic performance of the as-prepared BiOCl for NR degradation was effectively maintained for initial 90 min of testing. After three cycles of repetition tests for photodegradation of NR, catalyst did not exhibit any significant loss of activity. This indicates that BiOCl is more stable and has good photocatalytic performance on degradation of NR [34, 35].

Fig. 4.84: Effect of light intensity.

Fig. 4.85: NR degradation by BiOCl: (I) the first cycle; (II) the second cycle; (III) the third cycle; [NR] = 50 mgL⁻¹, BiOCl = 3.0 gmL⁻¹, Irradiation intensity = 82 × 10² lux, pH = 9.0, Temperature = 30 ± 0.3 °C.
4.3.15: COD and CO₂ measurements during mineralization of NR:

In the present work results of chemical oxygen demand (COD) are taken as one of the parameter to judge the feasibility of the photochemical process for degradation and mineralization of NR dye solution [36].

Table 4.56: Mineralization of NR: [NR] = 50 mgL⁻¹, BiOCl = 3.0 gmL⁻¹, Irradiation intensity = 82 × 10² lux, pH = 9.0, Temperature = 30 ± 0.3 °C.

<table>
<thead>
<tr>
<th>Irradiation time (h)</th>
<th>COD (mgL⁻¹)</th>
<th>CO₂ (mgL⁻¹)</th>
<th>% Efficiency</th>
<th>NO₃⁻ (mgL⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>360</td>
<td>7</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>171</td>
<td>16</td>
<td>52</td>
<td>16</td>
</tr>
<tr>
<td>4</td>
<td>90</td>
<td>23</td>
<td>75</td>
<td>22</td>
</tr>
<tr>
<td>6</td>
<td>32</td>
<td>54</td>
<td>91</td>
<td>32</td>
</tr>
<tr>
<td>8</td>
<td>14</td>
<td>157</td>
<td>99</td>
<td>34</td>
</tr>
<tr>
<td>10</td>
<td>0</td>
<td>278</td>
<td>100</td>
<td>36</td>
</tr>
</tbody>
</table>
From Table 4.56 and Fig. 4.86, there is a substantial decrease of the COD of the solution from 360 mgL\(^{-1}\) to 0 mgL\(^{-1}\) (Fig. 4.86 (a)) and increase in CO\(_2\) value from 7 mgL\(^{-1}\) to 278 mgL\(^{-1}\) in 10 h of irradiation (Fig. 4.86 (b)). Consequently, the complete mineralization of NR was achieved after 10 h of visible light irradiation in the presence of BiOCl because of the formation of more stable intermediates towards oxidation. The result implies that both mechanisms of degradation and mineralization play important roles for the photocatalytic effects under visible light irradiation.

Analysis of inorganic ions revealed as expected the formation of NO\(_3^-\) in solution. As depicted in Table 4.56 and Fig. 4.86 (b), the amount of NO\(_3^-\) ions increased with increasing irradiation time. 36 mgL\(^{-1}\) of NO\(_3^-\) has been found after 10 h of irradiation time. The nitrogen atoms with −3 oxidation state produced NH\(_4^+\) cations, subsequently NH\(_4^+\) cations were converted into NO\(_3^-\) ions. It was obvious that aqueous NR was mainly mineralized rather than being bleached [37].

After 10 h of irradiation, 100% efficiency has been observed for the process. 36 mgL\(^{-1}\) of NO\(_3^-\) have been found after 10 h of irradiation time.
4.3.16: UV-Vis spectra of NR Dye:

Primary absorption peak of NR dye was at 520 nm. As the reaction proceeds, the two peaks disappear gradually as shown in Fig. 4.87 and the full scanning spectrum pattern changes obviously after 8 h. This may be the evidence of the intermediate by-product. At the end of the 8 h of reaction time, there is no evident absorption peak observed. It indicates that the pollutants are destroyed with the photocatalytic reaction and proves that wastewater is fully decomposed [38,39].

![UV-Vis spectrum of NR](image)

**Fig. 4.87: UV-Vis spectrum of NR:** [NR] = 50 mgL\(^{-1}\), BiOCl = 3.0 gmL\(^{-1}\), Irradiation intensity = 82 \(\times\) 10\(^2\) lux, pH = 9.0, Temperature = 30 ± 0.3 °C.

4.3.17: Mechanism of NR degradation:

BiOCl oxidizes in two ways, photogenerated holes h\(^+\) in the valence band and the \(^\cdot\)OH radicals, which are strongly active and degrading non-selective agents [40,41]. Valence band holes (h\(_{VB}\)) and conduction band electrons (e\(_{CB}\)) are generated when aqueous BiOCl suspension was irradiated with visible light. These electron-hole pairs interact separately with the substrate. Valence band holes (h\(_{VB}\)) react with surface bound H\(_2\)O or OH\(^-\) to produce hydroxyl radical (\(^\cdot\)OH). Valence band holes can also oxidize organic molecule. Conduction band electrons (e\(_{CB}\)) reduce molecular oxygen to generate superoxide radicals as shown in eq. (4.38) to eq. (4.47) [42, 5].
Secondly, sensitization of dye molecule 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 was converted to the cationic dye radicals (NR⁺) that undergoes degradation to yield products as follows [43, 41]:

\[
\text{NR} + \text{hv} \rightarrow \text{NR}^* \\
\text{NR}^* + \text{BiOCl} \rightarrow \text{NR}^{++} + \text{BiOCl} (e^-_{CB}) \\
\text{NR}^{++} \rightarrow \text{degradation products}
\]

Cationic dye radicals reacts with hydroxyl ions undergoing oxidation via eq. 4.52 to 4.53 or interacts with $\cdot$O$_2$ or HO$_2^\cdot$ or HO$^\cdot$ species to generate intermediates that finally lead to degradation products (eqs. 4.54 to 4.57).
\[ \text{NR}^{++} + \text{OH}^- \rightarrow \text{NR} + \cdot\text{OH} \quad (4.52) \]
\[ \text{NR} + \text{2HO}^- \rightarrow \text{H}_2\text{O} + \text{oxidation products} \quad (4.53) \]
\[ \text{O}_2^- + \text{H}^+ \rightarrow \text{HO}_2^- \quad (4.54) \]
\[ \text{HO}_2^- + \text{H}^+ + \text{BiOCl} (e_{CB}^-) \rightarrow \text{H}_2\text{O}_2 + \text{BiOCl} \quad (4.55) \]
\[ \text{H}_2\text{O}_2 + \text{BiOCl} (e_{CB}^-) \rightarrow \text{HO}^+ + \text{OH}^- + \text{BiOCl} \quad (4.56) \]
\[ \text{NR}^{++} + \text{O}_2^- \rightarrow \text{degradation products} \quad (4.57) \]

From estimated value of COD and CO\(_2\), it is evident that 100 % of COD removal has been achieved in 10 h of irradiation under chosen reaction condition. A decrease in COD (see Fig. 4.86(a)) and increase in CO\(_2\) confirm the degradation of dye (see in Fig. 4.86(b)). Significant amount of NO\(_3^-\) released during the mineralization of dye (see in Fig. 4.86(b)). Complete disappearance of peaks in UV-Vis region indicates the absence of any organic moiety (Fig. 4.87). COD and CO\(_2\) estimations are in agreement with UV-Vis spectral analysis during mineralization.

### 4.3.18: Kinetic Studies:

Due to the practical applications, the degradation kinetics of NR was investigated under the conditions of the appropriate optimum catalyst concentrations, natural pH and temperature of 30 °C. From the results, it becomes clear that the degradation process proceeds in two parallel branches of only visible light degradation and when visible light is assisted with catalyst particles:

\[
\frac{\text{d}}{\text{dt}} [\text{NR}] = \text{R}_1 + \text{R}_2 \quad (4.58)
\]

where \( \text{R} \), \( \text{R}_1 \) and \( \text{R}_2 \) are the net degradation, the photocatalysis and photolysis the rates, respectively. The difference between the net rate and photolysis rate obtained experimentally, can be considered as the photocatalysis branch rate. Using the power law kinetic models in the forms:

\[ \text{R}_1 = k_1 [\text{NR}]^n_1 \quad (4.59) \]
\[ \text{R}_2 = k_2 [\text{NR}]^n_2 \quad (4.60) \]
where, \( n_1, n_2, k_1 \) and \( k_2 \) are the appropriate order and rate constant of the reaction respectively. In this work, to obtain the appropriate parameters of eq. (4.59) and (4.60), the differential method of analysis, based on the data of concentration vs. time, was used. Fig. 4.88 (a), (b) presents the goodness of fit of the rate eq. (4.59) and eq. (4.60) to the data.

**Fig. 4.88 (a):** The variation of NR degradation rate versus its concentration for photocatalysis: BiOCl = 3.0 gmL\(^{-1}\), Irradiation intensity = 82 \( \times 10^2 \) lux, pH = 9.0, Temperature = 30 ± 0.3 \( ^0\)C.

**Fig. 4.88 (b):** The variation of NR degradation rate versus its concentration for photolysis: BiOCl = 3.0 gmL\(^{-1}\), Irradiation intensity = 82 \( \times 10^2 \) lux, pH = 9.0, Temperature = 30 ± 0.3 \( ^0\)C.
Our results are in agreement with other studies reported in literature [44-46]. Under chosen experimental conditions, the rate of degradation of NR for photodegradation and photolysis has been found to be 2.33 mgL\(^{-1}\)min\(^{-1}\) and 2.14 mgL\(^{-1}\)min\(^{-1}\) respectively.

**References:**