Chapter - 5

Photocatalytic degradation of Violet GL2B by synthesized metal oxide nanoparticles
5. Introduction

Photocatalytic degradation by semiconductors is a new and effective technique for the removal of dyes from water (Daneshvar et al., 2004; Mahyar et al., 2011; Shivaraju, 2011; Shang et al., 2009; Marugan et al., 2007; Hua-yue et al., 2010). Photocatalytic activity is a process where semiconductor material absorbs light energy more than or equal to its band gap, thereby generating positive holes and negative electrons which further produces free-radicals in the system to oxidize the substrate. The resultant free-radicals are very efficient oxidizers of the organic compounds (Matthews and Mc-Evoy, 1992). During the past few decades, Photocatalytic processes involving TiO$_2$ semiconductor were used as a photocatalyst under UV lights only, which account for only 5% of the total sunlight energy (Kuo and Ho, 2006; Akyol et al., 2004).

With this background, the present work on photocatalytic degradation of Violet GL2B, an industrial azo dye on synthesized ZnO, CaAl$_2$O$_4$-I, CaAl$_2$O$_4$-II, CaZnO$_2$-I and CaZnO$_2$-II nanoparticles under natural sunlight has been investigated. Violet GL2B azo dye produces intense Violet colour. It is used mainly in cotton textile industry. The discharge water containing a small amount of Violet GL2B azo dye appears violet in colour. The structure of Violet GL2B shows the presence of amino groups and chloro groups (Fig. 13).

In the present study, the synthesized ZnO, CaAl$_2$O$_4$-I, CaAl$_2$O$_4$-II, CaZnO$_2$-I and CaZnO$_2$-II nanoparticle photocatalysts showed high efficiency in the degradation of Violet GL2B azo dye under natural sunlight. This is proved by the comparative study of the synthesized nanoparticles and procured TiO$_2$ nanoparticle.
5.1 Results and Discussion

5.1.1 Photocatalytic experimental procedure: Comparative study of photocatalytic degradation of Violet GL2B azo dye using the synthesized nanoparticles over procured TiO₂

Initially, photocatalytic experiments were carried out in the presence of direct sunlight of intensity between 100000 to 130000 Lux (TES 1332A digital Lux meter). The experiments were carried out during 10 am to 1 pm. The UV-VIS spectrophotometer 119 (Systronics) was used for the determination of absorbance in the range of 200 to 800 nm. The λₘₐₓ of Violet GL2B was found to be 545 nm. In all photocatalytic experiments, 100 ml of 30 ppm Violet GL2B azo dye solution was taken in seven separate 100 ml Borosil beakers. A known concentration of procured TiO₂ and synthesized ZnO, CaAl₂O₄-I, CaAl₂O₄-II, CaZnO₂-I and CaZnO₂-II (0.5 g/100 ml) were added to six separate beakers containing Violet GL2B azo dye solution and kept in the sunlight for photocatalytic activity along with the blank solution. Further experiments were conducted based on the degradation results obtained from the photocatalytic activity of the catalysts.

5.1.2 Effect of photocatalysts on photocatalytic degradation of Violet GL2B

Initially, blank experiments were performed under the direct sunlight without the addition of catalysts and no degradation was observed. A known concentration of procured TiO₂ and synthesized ZnO, CaAl₂O₄-I, CaAl₂O₄-II, CaZnO₂-I and CaZnO₂-II (0.5 g/100 ml) were added to six separate beakers containing Violet GL2B azo dye solution and kept in the sunlight for photocatalytic activity. The results showed that all the nanoparticles (ZnO, CaAl₂O₄-I, CaAl₂O₄-II, CaZnO₂-I and CaZnO₂-II) have exhibited
higher photocatalytic activity than TiO₂. In a span of 120 minutes, a degradation of 7.95% was recorded for TiO₂ nanoparticle and 23.18% for ZnO, 93.31% for CaAl₂O₄-I, 94% for CaAl₂O₄-II, 96.19% for CaZnO₂-I and 94.80% for CaZnO₂-II were recorded (Fig. 42) (Photo 1). All the synthesized nanoparticles have exhibited higher photocatalytic activity than the commercially available TiO₂ nanoparticle. Photocatalytic degradation of the azo dye is mainly due to the hydroxyl radical attack on the dye molecule (Giwa et al., 2012). These results indicate that the synthesized nanoparticles produce more number of hydroxyl radicals which are prime oxidizers of the dye molecule under visible light than the procured TiO₂. Based on the results further studies have been done concentrating on the synthesized ZnO, CaAl₂O₄-I, CaAl₂O₄-II, CaZnO₂-I and CaZnO₂-II nanoparticles.

Fig. 42: Rate of degradation of Violet GL2B at 120 minutes [VGL2B=30mg/L, pH=7, TiO₂=0.5g, ZnO=0.5g, CaAl₂O₄-I=0.5g, CaAl₂O₄-II=0.5g, CaZnO₂-I=0.5g, CaZnO₂-II=0.5g]
Photo 1: Rate of degradation of Violet GL2B at 120 minutes
[(a)=VGL2B/TiO2/ZnO, (b)=VGL2B/TiO2/CaAl2O4-1, (c)=VGL2B/TiO2/CaAl2O4-II, (d)=VGL2B/TiO2/CaZnO2-1, (e)=VGL2B/TiO2/CaZnO2-II]
5.1.3 Photocatalytic experimental procedure: Study on photocatalytic degradation of Violet GL2B using synthesized nanoparticles

Later, nanoparticles with high photocatalytic activity were selected for further studies. Photocatalytic suspensions from 0.1g, 0.2g, 0.3g upto 1g were tested on the dye samples of 100ml quantity. The suspension pH values were adjusted by using NaOH/HCl solutions using pH digital meter. Before irradiation, photocatalyst suspension was stirred in the dark to ensure the adsorption equilibrium and it was kept in the sunlight for the photocatalytic degradation. After every 30 minutes the suspension was sampled and centrifuged (using EBA-Hetlich) at 3000 rpm for 5 minutes and the process was repeated at 60, 90 and 120 minutes. The residual concentration of the solution sample was monitored by using UV-VIS spectrophotometer 119 (Systronics) at 545nm. The experiments were conducted in different pH range from 2 to 11 in order to study the efficiency of the nanoparticle in acidic, alkaline and neutral conditions. The data obtained from the photocatalytic degradation experiments were used to calculate the degradation efficiency ‘D’ using (Eq. 9).

5.1.4 Effect of catalyst concentration on Violet GL2B azo dye

The effect of catalyst concentration on the photocatalytic degradation was studied over a range of the catalyst amount from 0.1 to 1g/100ml for Violet GL2B azo dye. All the synthesized nanoparticles have shown appreciable results. Where, ZnO with the band gap of 3.2 eV showed maximum of 24.56% at 0.6g/100ml, CaAl$_2$O$_4$-I with the band gap of 2.8 eV showed 94.74% at 0.5g/100ml, CaAl$_2$O$_4$-II with 2.7 eV showed highest degradation of 95.38% at 0.3g/100ml, CaZnO$_2$-I with 2.5 eV showed 98.15% at 0.1g/100ml and CaZnO$_2$-II with the band gap of 2.6 eV showed 96.65% at 0.1g/100ml in 120 minutes (Fig. 43) (Photo 2).
The ZnO with the band gap of 3.2 eV has shown less degradation when compared to the other synthesized nanoparticles of band gaps 2.8 eV (CaAl$_2$O$_4$-I), 2.7 eV (CaAl$_2$O$_4$-II), 2.5 eV (CaZnO$_2$-I) and 2.6 eV (CaZnO$_2$-II) respectively.

The increase in degradation rate can be explained in terms of availability of active sites on the catalyst surface and sunlight penetration into the suspension as a result of increased screening effect and scattering of light. A further increase in the catalyst amount beyond the optimum dosage for all the nanoparticles decreases the photodegradation by some margin. This may be due to overlapping of adsorption sites as a result of overcrowding owing to collision with ground state catalyst (Subramani et al., 2007). Since, the photodegradation was most effective at 0.6g/100ml for ZnO, 0.5g/100ml for CaAl$_2$O$_4$-I, 0.3g/100ml for CaAl$_2$O$_4$-II and 0.1g/100ml for both CaZnO$_2$-I and CaZnO$_2$-II nanoparticle dosages, the following experiments were continued with same dosages.
Fig. 43: Effect of catalyst concentration on Violet GL2B at 120 minutes
[VGL2B=30mg/L, pH=7, (a)=ZnO, (b)=CaAl2O4-I, (c)=CaAl2O4-II, (d)=CaZnO2-I, (e)=CaZnO2-II]
**Photo 2:** Effect of catalyst concentration on Violet GL2B at 120 minutes. 
[VGL2B=30mg/L, pH=7, (a)=ZnO, (b)=CaAl₂O₄-I, (c)=CaAl₂O₄-II, (d)=CaZnO₂-I, (e)=CaZnO₂-II]

**Mechanism of the photocatalytic degradation:**

\[
\text{Nanoparticles} + \text{hv} \rightarrow (e_{CB}^\ast + h_{VB}^\ast) \quad \text{(Eq. 13)}
\]

\[
e_{CB}^\ast + O_2 \rightarrow O_2^{\ast}\quad \text{(Eq. 14)}
\]

\[
H_2O + O_2^{\ast} \rightarrow OOH^\ast + OH^\ast \quad \text{(Eq. 15)}
\]
Chapter 5: Photocatalytic Degradation of Violet GL2B

\[ 2\text{OOH}^+ \rightarrow \text{O}_2 + \text{H}_2\text{O}_2 \]  
(Eq. 16)

\[ \text{O}_2^{-} + \text{VGL2B} \rightarrow \text{VGL2B-OO}^+ \]  
(Eq. 17)

\[ \text{OH}^- + \text{H}_2\text{O} + \varepsilon_{\text{CB}} \rightarrow \text{H}_2\text{O}_2 + \text{OH}^- \]  
(Eq. 18)

\[ \text{H}_2\text{O}_2 + \varepsilon_{\text{CB}} \rightarrow \text{OH}^- + \text{OH}^- \]  
(Eq. 19)

\[ \text{H}_2\text{O}_2 + \text{O}_2^{-} \rightarrow \text{OH}^- + \text{OH}^- + \text{O}_2 \]  
(Eq. 20)

\[ \text{OH}^- / \text{O}_2^- / \text{Nanoparticles}^+ + \text{VGL2B} \rightarrow \text{VGL2B degradation} \]  
(Eq. 21)

The mechanism of photocatalytic activity of nanoparticles can be predicted. Under sunlight irradiation, nanoparticle molecules get excited and transfer electrons to the conduction band (Eq. 13). An electron in the conduction band of the nanoparticles can reduce molecular oxygen and produce the super oxide radical (Eq. 14). Molecular oxygen, adsorbed on the surface of the photocatalysts prevents the hole-electron pair recombination process (Di-Paola et al., 2003; Da-Silva and Faria, 2003). Recombination of hole-electron pair decreases the rate of photocatalytic degradation. This radical may form hydrogen peroxide or organic peroxide in the presence of oxygen and organic molecule (Eq. 15, 16, 17). Hydrogen peroxide can be generated in another path (Eq. 18). Hydrogen peroxide can form hydroxyl radicals which are powerful oxidizing agents (Eq. 19, 20). The radicals produced are capable of attacking dye molecules and degrade them (Eq. 21).
5.1.5 Effect of pH on Violet GL2B azo dye

In order to study the effect of pH on the degradation efficiency of ZnO, CaAl$_2$O$_4$-I, CaAl$_2$O$_4$-II, CaZnO$_2$-I and CaZnO$_2$-II catalysts, the experiments were carried out at pH ranging from 2 to 11. The results showed that pH significantly affected the degradation efficiency (Fig. 44) (Photo 3).

The degradation rate of Violet GL2B for ZnO increased from 20.64% to 25.37% from pH 2 to pH 10 and decreased to 24.45% at pH 11 in 120 minutes for 0.6g/100ml. For CaAl$_2$O$_4$-I the degradation of the dye increased from 75.31% to 96.07% from pH 2 to 10 and decreased 95.73% at pH 11 in 120 minutes for 0.5g/100ml. Further, CaAl$_2$O$_4$-II the degradation of the dye increased from 95.38% to 97.34% from pH 2 to 10 and decreased to 96.42% at pH 11 in 120 minutes for 0.3g/100ml. For CaZnO$_2$-I, the degradation increased from 44.40% to 98.61% from pH 2 to 9 and decreases to 89.96% at pH 11 in 120 minutes for 0.1g/100ml. Similarly for CaZnO$_2$-II the degradation increased from 55.24% to 97.57% from pH 2 to pH 9 and at pH 11 it decreased to 91% for 0.1g/100ml. The maximum degradation rate for all different nanoparticles was achieved at pH 10 and 9. As the used azo dye Violet GL2B is an anionic dye and contains amino groups and chloro groups which are more efficient in forming hydroxyl radicals in alkaline medium. Excess of hydroxyl anions increases the formation of OH$^-$ radicals. These OH$^-$ radicals are the main oxidizing species responsible for photocatalytic degradation (Nooijahan et al., 2003). On greater than optimum pH, the decrease in degradation efficiency can be explained on the basis of the amphoteric nature of the catalysts. Here the catalyst surface becomes negatively charged for higher pH value, which causes the electrostatic repulsion between the catalyst and negatively charged dyes (Turchi and Ollis, 1990).
Fig. 44: Effect of pH on the photocatalytic degradation of Violet GL2B at 120 minutes [VGL2B=30mg/L, (a)=ZnO, (b)=CaAl2O4-I, (c)=CaAl2O4-II, (d)=CaZnO2-I, (e)=CaZnO2-II]
5.1.6 Effect of initial dye concentration

The experiments were conducted to study the effect of initial dye concentration by varying the dye concentration from 30, 60, 90 and 120mg/L. The results obtained for ZnO were 25.37% at 30mg/L, 19.52% at 60mg/L, 13.49% at 90mg/L and 10.55% at 120mg/L. Similarly for CaAl$_2$O$_4$-I achieved 96.07%, 95.41%, 94.99% and 94.48% in 30,
60, 90 and 120mg/L respectively. CaAl₂O₃-I got 97.34%, 96.31%, 95.35% and 94.78% for 30, 60, 90 and 120mg/L. CaZnO₂-I obtained 98.61%, 92.08%, 89.85% and 87.74% for 30, 60, 90 and 120mg/L. In the same way CaZnO₂-II resulted 97.57%, 90.95%, 86.86% and 83.23% for the 30, 60, 90 and 120mg/L dye concentrations respectively (Fig. 45) (Photo 4). These experiments illustrated that the degradation efficiency was inversely affected by the concentration. The decrease in the degradation with an increase in dye concentration was ascribed to the equilibrium adsorption of dye on the catalyst surface which results in a decrease in the active sites. This phenomenon results in the lower formation of OH⁻ radicals which were considered as primary oxidizing agents of the organic dye (Mirkhani et al., 2009). According to Beer-Lambert law, as the initial dye concentration increases, the path length of photons entering the solution decreases. This results in the lower photon absorption of the catalyst particles, and consequently decrease photocatalytic reaction rate (Byrappa et al., 2006).

**Fig. 45:** Effect of initial dye concentration on the photocatalytic degradation of Violet GL2B [ZnO/pH=0.6g/10, CaAl₂O₃-I/pH=0.5g/10, CaAl₂O₃-II/pH=0.3g/10, CaZnO₂-I/pH=0.1g/9, CaZnO₂-II/pH=0.1g/9]
Photo 4: Effect of initial dye concentration on the photocatalytic degradation of Violet GL2B [(a)\(=\)ZnO/pH= 0.6g/10, (b)\(=\)CaAl₂O₃-I/pH= 0.5g/10, (c)\(=\)CaAl₂O₃-III/pH= 0.3g/10, (d)\(=\)CaZnO₂-I/pH= 0.1g/9, (e)\(=\)CaZnO₂-III/pH= 0.1g/9]
5.1.7 Effect of Sunlight Irradiation on Violet GL2B

The photocatalytic degradation of Violet GL2B azo dye (30 mg/L) under three different experimental conditions were examined, i.e., through sunlight alone, dye/dark/catalyst and dye/sunlight/catalyst for all the different catalysts. Violet GL2B azo dye solution when exposed directly to the sunlight without the catalyst, the degradation was found to be zero during the entire experiments. The degradation rate was found to increase with increase in irradiation time, for dye/sunlight/ZnO showed 25.37% and for dye/dark/ZnO 9.34% was recorded. Similarly, dye/sunlight/CaAl$_2$O$_4$-I showed 96.07% and for dye/dark/CaAl$_2$O$_4$-I 65.62% was recorded. For dye/sunlight/CaAl$_2$O$_4$-II showed 97.34% and for dye/dark/CaAl$_2$O$_4$-II 62.97% was recorded. The dye/sunlight/CaZnO$_2$-I recorded 98.61% and dye/dark/CaZnO$_2$-I 51.44% observed. Finally, dye/sunlight/CaZnO$_2$-II achieved 97.57% and dye/dark/CaZnO$_2$-II was 45.09% recorded within 120 minutes respectively (Fig. 46) (Photo 5).

These results clearly indicate that photodegradation occurs most efficiently in the presence of sunlight. Under sunlight, excitation of electrons from the catalyst surface takes place more rapidly than in the absence of light. Similar reports have been reported for photocatalytic degradation of azo dyes such as Congo red, Remozal red RR, and Benzopururine 4B (Guillen et al., 2010; Movahedi et al., 2009).
Fig. 46: Effect of sunlight irradiation on photocatalytic degradation of Violet GL2B in 120 minutes. [(a) = ZnO at pH 10, (b) = CaAl₂O₃-I at pH 10, (c) = CaAl₂O₃-II at pH 10, (d) = CaZnO₂-I at pH 9, (e) = CaZnO₂-II at pH 9]
Photo 5: Effect of sunlight irradiation on photocatalytic degradation of Violet GL2B in 120 minutes. [(a) = dye/sunlight/ZnO at pH 10, (b) = dye/sunlight/CaAl₂O₄-I at pH 10, (c) = dye/sunlight/CaAl₂O₄-II at pH 10, (d) = dye/sunlight/CaZnO₂-II at pH 9, (e) = dye/sunlight/CaZnO₂-II at pH 9] [(a1) = dye/dark/ZnO at pH 10, (b1) = dye/dark/CaAl₂O₄-I at pH 10, (c1) = dye/dark/CaAl₂O₄-II at pH 10, (d1) = dye/dark/CaZnO₂-I at pH 9, (e1) = dye/dark/CaZnO₂-II at pH 9]
Chapter 5
Photocatalytic Degradation of Violet GL2B

5.2 Summary

In the present investigation, five different nanoparticles were synthesized by simple solution combustion method, using two different combustion agents urea and acetamide. Results obtained showed that, both sunlight and photocatalysts are needed for the effective destruction of Violet GL2B azo dye, because it has been established that the photocatalytic degradation of organic matter in solution is initiated by the photo excitation of the semiconductor, followed by the formation of electron-hole pairs on the surface of the catalyst.

The synthesized metal oxide nanoparticles were applied as photocatalysts for the degradation of azo dye Violet GL2B under solar radiation. Among the synthesized nanoparticles the CaAl$_2$O$_4$-I, CaAl$_2$O$_4$-II, CaZnO$_2$-I and CaZnO$_2$-II were proved to be very efficient photocatalysts in degrading the azo dye by achieving 93.31%, 94%, 96.19% and 94.80% in 120 minutes at pH 7. But, the synthesized ZnO nanoparticle achieved only 23.18% of dye degradation in 120 minutes at pH 7. The experimental data showed that, the synthesized nanoparticles are more efficient than the procured TiO$_2$ nanoparticle which is able to achieve only 7.95% of degradation in 120 minutes at pH 7. It was observed that, when the pH was altered 25.37% at pH 10 from 0.6g/100ml, 96.07% at pH 10 from 0.5g/100ml, 97.34% at pH 10 from 0.3g/100ml, 98.61% at pH 9 from 0.1g/100ml and 97.57% at pH 9 from 0.1g/100ml were recorded for the respective ZnO, CaAl$_2$O$_4$-I, CaAl$_2$O$_4$-II, CaZnO$_2$-I and CaZnO$_2$-II metal oxide nanoparticles.

The experimental results proved that photocatalytic degradation of Violet GL2B was mainly dependent on the pH of the dye solution and catalyst dosage. The colour of Violet GL2B azo dye was completely removed in alkaline medium. The results also revealed that, the sunlight is most efficient source for the photocatalytic degradation as it is economically cheap and simple when compared to other oxidative processes.