

## Photocatalytic Degradation of Violet GL2B using Synthesized $\text{CaZnAl}_2\text{O}_5$ Metal Oxide Nano-Particle

Madhusudhana Narayanappa<sup>1</sup>, Yogendra Kambalagere<sup>1\*</sup>, Kittappa M Mahadevan<sup>2</sup> and Kiran G. Rajgopalakrishna<sup>1</sup>

<sup>1</sup>Dept. of PG Studies and Research in Environmental Science, Kuvempu Uni., Jnana Sahyadri, Shankaraghatta, Shimoga, Karnataka, India

<sup>2</sup>Dept. of PG Studies and Research in Chemistry, P.G. Center Kadur, Kuvempu University, Kadur(T), Chickmagalur(D), Karnataka, India  
yogendraku@gmail.com

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### Abstract

Azo dyes present in textile wastewater require a proper technique for their removal, due to their negative environmental and health effects. Although there are several ways to treat such wastewater, this study is focused on photocatalytic degradation on Calcium Zinc Aluminate ( $\text{CaZnAl}_2\text{O}_5$ ) nano catalyst. Violet GL2B (VGL2B) dye was used for photocatalytic degradation studies at 30 mg/L concentration. Colour degradation was monitored using UV-Vis spectroscopy. Complete colour removal was observed for the azo dye. It is found that, degradation rate of VGL2B for  $\text{CaZnAl}_2\text{O}_5$  the degradation was found to be 99.07% at pH 4 in 120 minutes for 0.6g/100ml. Also the results revealed that, the degradation facility is directly bear upon by the concentration of dye solution.

**Keywords:** AOPs, Azo dye, Catalyst,  $\text{CaZnAl}_2\text{O}_5$ , Nano-particle, Photo degradation, VGL2B.

### Introduction

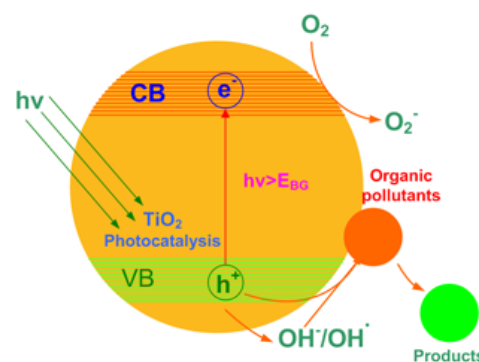
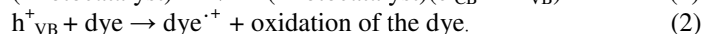
Among the list of industries, textile industry is the major and the copious water consuming and also chemical concentrated industries throughout the world<sup>1</sup>. Furthermore, the wastage of dye through effluents from textile industry can be up to 75%. These disposed effluents are said to be very tortuous since they contain salt, surfactants, ionic metals and their metal complexes, toxic organic chemicals, biocides and toxic anions<sup>2</sup>.

The azo dyes are typically azo grovel chromophores mixed with multiple reactive groups. Hence in many textile industries these azo dyes are used because of their favorable circumstances, such as bright color, water fastness, and simple application<sup>3</sup>. However, half of the dyes are lost through hydrolysis in dyeing process which results in a large quantity of dyes in wastewater<sup>4</sup>. So, these dyes are resistant to biodegradation and they cannot be easily removed from the disposals through wastewater treatments like activated sludge process<sup>5</sup>.

In recent times, more attention has been paid towards the usage of advanced oxidation processes (AOPs) for the degradation of dyes and azo dyes. AOPs are mainly dependent on the birth of reactive species such as hydroxyl radicals that oxidizes a wide range of organic contaminants quickly and non-selectively<sup>6</sup>. They are based on the photocatalytic system of semiconductors and light, and semiconductor and oxidants. Heterogeneous photocatalysis is one of the most prominent technologies which are successful in mineralizing the organic contaminants including the organic reactive dyes<sup>7-9</sup>.

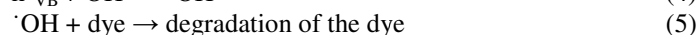
The photo catalyzed decolorization of dye solution is appeal by the photo excitation of the semiconductor, which intern forms

an electron-hole pair on the catalyst (Equation-1). Hence, the photocatalyst prefer a direct oxidation to the dye by high oxidative potential of the hole in the catalyst (Equation-2).



**Figure-1**  
**Mechanism of Photocatalytic activity**

Another reactive species responsible for the degradation is hydroxyl radical ( $\cdot\text{OH}$ ). It is either formed by the decomposition of water (Equation-3) or by reaction of the hole with  $\text{OH}^-$  (Equation-4). The hydroxyl radical is an extremely strong, nonselective oxidant, which leads to the partial or complete mineralization of several organic chemicals.



Many researchers have worked on the catalyst  $\text{TiO}_2$ , which is generally considered to be the best photocatalyst and has the ability to detoxify water from a number of organic pollutants<sup>10</sup>. Anyhow overall use of  $\text{TiO}_2$  is uneconomical for bulk water treatment; thereby interest has been generated towards the search for suitable alternatives to  $\text{TiO}_2$ . The synthesis and application of many metal oxide nano-particles like  $\text{CaO}$ ,  $\text{ZnO}$ ,  $\text{CaAl}_2\text{O}_4$ ,  $\text{CaZnO}_2$ ,  $\text{CaMgO}_2$  etc., have been studied in our laboratory.

Yogendra *et al.* has worked on the decolorization of Coralene Red F3BS dye under the sunlight irradiation and found that  $\text{ZnO}$  is efficient enough to decolorize the dyes<sup>11</sup>. Bhavya *et al.* worked on the synthesis of  $\text{CaO}$  nano-particle and its application on three different azo dyes Coralene Navy Blue 3G, Coralene violet 3R and Disperse Blue 2BL<sup>12</sup>. Madhusudhana *et al.* reported on the comparison of the two different nano-particles  $\text{CaAl}_2\text{O}_4$ -I and  $\text{CaAl}_2\text{O}_4$ -II against the textile effluent and found out that  $\text{CaAl}_2\text{O}_4$ -II is more efficient in the decolorization of the effluent<sup>13</sup>. Similarly, Gopalappa *et al.* has worked on Brilliant red azo dye using  $\text{CaMgO}_2$  nano-particle and achieved good results<sup>14</sup>.

Hence in the present study, to degrade the selected dye solution, synthesized  $\text{CaZnAl}_2\text{O}_5$  used as a photocatalyst in aqueous medium. The size of the photocatalyst is very small, especially in nano-meters, better photocatalytic activity is offered due to high surface area and high surface area to volume ratio values<sup>15</sup>. Here the study is mainly focused on the oxidative degradation of commercially available azo dye VGL2B. Hence, subsequent experiments were conducted with  $\text{CaZnAl}_2\text{O}_5$  nano-particle by varying different conditions such as initial dye concentration, pH and dosage of catalyst.

## Materials and Methods

**Materials and Reagents:** Chemicals used for the synthesis of  $\text{CaZnAl}_2\text{O}_5$  are Calcium nitrate ( $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ), Zinc nitrate ( $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ), Aluminium Nitrate  $\text{Al}_2(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (95% AR) and Urea ( $\text{NH}_2\text{CONH}_2$ ), are obtained from Hi media chemicals Mumbai, and used without further purification. The VGL2B ( $\lambda_{\text{max}}$  545nm) dye used for the photocatalytic study was purchased from Colourtex Limited, Surat, Gujarat.

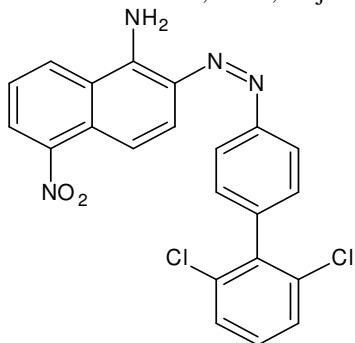


Figure-2  
Chemical Structure of VGL2B azo dye

**Synthesis of  $\text{CaZnAl}_2\text{O}_5$  nano-particle:** The  $\text{CaZnAl}_2\text{O}_5$  nano catalyst was synthesized based on solution combustion method by commercially available calcium nitrate, zinc nitrate, aluminium nitrate, and fuel Urea. Stoichiometric compositions of calcium nitrate (7.08g), zinc nitrate (8.92g), aluminium nitrate (22.50g) and fuel urea (15.12g) was taken in a  $100 \text{ cm}^3$  silica crucible by using double distilled water. After a while the Crucible was placed in the muffle furnace for calcination, which was preheated to  $600^\circ\text{C}$ . According to propellant chemistry the reaction is as follows;

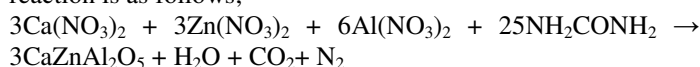


Figure-3  
Synthesized photo of  $\text{CaZnAl}_2\text{O}_5$

**Characterization of synthesized  $\text{CaZnAl}_2\text{O}_5$  nano-particle:**

**XRD:** In order to investigate the changes in the structure of nano-particles, XRD measurements have been taken in the range  $2\theta=10-80^\circ$  for the  $\text{CaZnAl}_2\text{O}_5$  photocatalyst. Rigaku diffractometer was used for the XRD analysis using  $\text{Cu-K}\alpha$  radiation ( $1.5406 \text{ \AA}$ ) in a  $\theta-2\theta$  configuration. The pattern obtained from the XRD analysis of the prepared  $\text{CaZnAl}_2\text{O}_5$  nano-particles are presented in Figure-4.

According to the Debye-Scherrer's formula  $D = \left( \frac{K\lambda}{\beta \cos\theta} \right)$ ,

Where:  $K$  = Scherrer's constant,  $\lambda$  = X-ray wavelength,  $\beta$  = full width at half maximum and  $\theta$  = Bragg diffraction angle.

The average crystallite size of  $\text{CaZnAl}_2\text{O}_5$  is 32 nm.

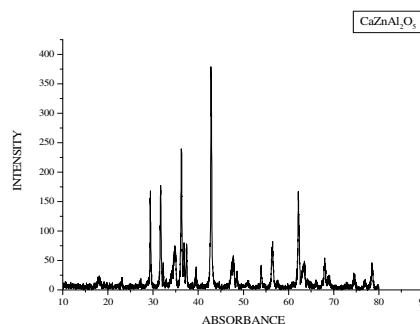
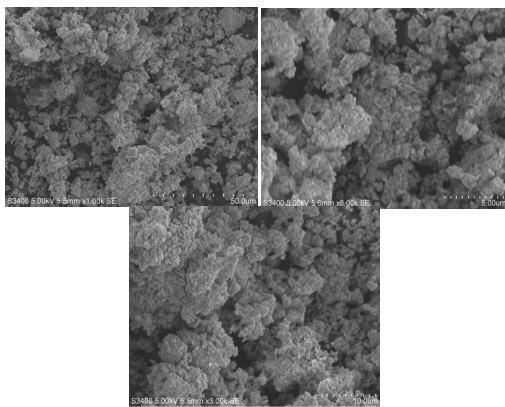


Figure-4  
XRD of  $\text{CaZnAl}_2\text{O}_5$

**SEM:** Scanning Electron Microscope pictures have been taken for the  $\text{CaZnAl}_2\text{O}_5$  photocatalyst. It is observed that the particle structures are irregular with the average size 32 nm. These pictures also reveal the clustered groups of nano-particles, which are attached and appear to be compactly packed with uneven size and structure. Also irregular groups of nano-particle clusters can be seen in the SEM images (Figure-5).



**Figure-5**  
SEM images of  $\text{CaZnAl}_2\text{O}_5$

**UV-Vis absorption spectroscopy:** UV-Vis absorption spectra of as prepared  $\text{CaZnAl}_2\text{O}_5$  were examined by using UV-Vis spectrophotometer of family Ocean Optics DH- 2000 by wavelength range from 200-800 nm at Research Laboratory, Department of Nanotechnology, Kuvempu University. According to the reflectance spectrum of  $\text{CaZnAl}_2\text{O}_5$  photocatalyst the band edge was found to be at 424.44 nm and the band gap was calculated by Planck's equation as follows.

Band Gap energy  $E_g = h \times \frac{c}{\lambda}$ , Where,  $h$  = Planks constant,  
 $C$  = Velocity of light (Speed of light),  
 $\lambda$  = Wave length of light,  $h = 4.135 \times 10^{-15} \text{ eV}$ ,  $C = 3 \times 10^8 \text{ m/s}$ ,  $\lambda = \text{-----} \times 10^{-9} \text{ nm}$ , Band Gap energy (eV) =  $4.135 \times 10^{-15} \text{ eV} \times 3 \times 10^8 \times 10^9$

$$(eV) = \left( \frac{1240}{\text{Wave length (nm)}} \right)$$

$$(eV) = \left( \frac{1240}{424.44} \right) = 2.9 \text{ eV}$$

The band gap of  $\text{CaZnAl}_2\text{O}_5$  is 2.9 eV. Hence band gap of the semiconductor is particle size dependent<sup>16</sup>.

## Results and Discussion

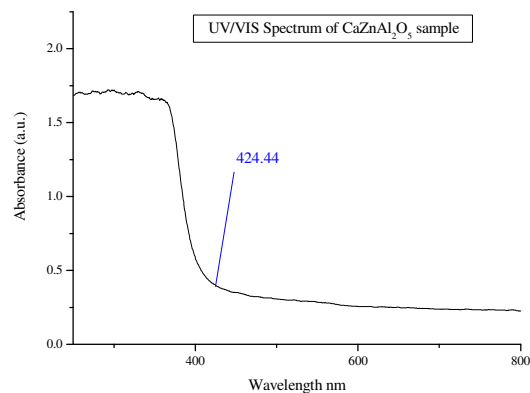
**Experimental Procedure:** The instrument UV-Vis spectrophotometer was used to determine the absorbance.  $\lambda_{\text{max}}$  of VGL2B was found to be 545nm. The photocatalytic experiments were carried out under direct sunlight. The known concentration of dye solution was prepared by dissolving 0.03g of VGL2B in 1000ml double distilled water and investigated for its decolourization in the presence of  $\text{CaZnAl}_2\text{O}_5$  nano-particle at different catalyst dosages and pH levels. After the

photocatalytic decolourization, the extent of decolourization was estimated by recording absorbance of the dye solution using UV-VIS spectrophotometer 169 in order to get the optimum catalyst dose. The experiments were repeated at different pH levels (from 2 to 11) for the 100ml of same standard dye solutions with the optimum catalyst dose.

$$\text{Decolourization} = \left( \frac{C_0 - C_t}{C_0} \right) \times 100$$

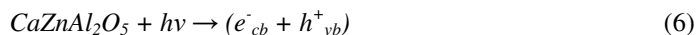
Where:  $C_0$  = initial absorbance of the dye.

$C_t$  = Final absorbance at time interval 't' after 120 minutes



**Figure-6**  
UV-Vis absorption spectra of  $\text{CaZnAl}_2\text{O}_5$

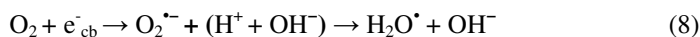
**Mechanism of the photocatalytic degradation:**  $\text{CaZnAl}_2\text{O}_5$  photocatalyst was found to be photoexcited under solar irradiation. When sunlight strikes on the nano-particle surface, an electron from its valance band (vb) jumps to the conduction band (cb) leaving behind positively charged hole ( $h^+_{vb}$ ). The negative charge is increased in the conduction band ( $e^-_{cb}$ ) and photocatalytic active centers are formed on the surface of  $\text{CaZnAl}_2\text{O}_5$  nano-particles according to the equation 6:



The valence band holes react with the chemisorbed  $\text{H}_2\text{O}$  molecules to form reactive species such as  $\cdot\text{OH}$  radicals, which subsequently react with dye molecules to cause their complete degradation (Equation-7).



The  $e^-_{cb}$  and  $h^+_{vb}$  can be trapped in surface states where they may react with species adsorbed or close to the surface of the particle. The  $e^-_{cb}$  can react with an acceptor, such as dissolved  $\text{O}_2$ , which consequently is transformed into a super oxide radical anion ( $\text{O}_2^{\cdot-}$ ) which leads to the formation of additional  $\text{H}_2\text{O}^{\cdot}$  in Equation 8.



On the other hand,  $h^+_{vb}$  could interact with donors, such as  $OH^-$  and  $H_2O$ , to form  $\cdot OH$  radicals. These radicals also attack the VGL2B (Equation-9).



Hence these radicals will attack the dye molecules and degrade them (Equation-10).



**Nano-particle dosage effect on VGL2B dye:** Initially, catalyst concentration was varied over a range from 0.1 to 1g/100ml for VGL2B and significant results have been observed during the experiment. The  $CaZnAl_2O_5$  with the nano-particle size 32 nm has shown 98.50% degradation. Since, the photo degradation was found to be effective at 0.6g/100ml in 120 minutes to  $CaZnAl_2O_5$  nano-particle dosages (Figure-7) further experiments were continued with same dosages.

The photocatalytic activity results in creating more number of  $H^+$  ions and  $e^-_{cb}$  by generating  $\cdot OH$  radicals which act as the main oxidizing species. In this result, maximum degradation is mainly due to the availability of number active sites on the nano-particle surface and sunlight irradiation into the suspension, which is because of the increased scattering of light

and screening effect. The more increase in the catalyst amount i.e., above 0.6g/100ml photocatalytic degradation is decreased by small extent. This is mainly because coincide of adsorption sites and also because of overcrowding owing to collision with ground state catalysts<sup>17</sup>.

**Consequence of pH on VGL2B:** According to many literatures, pH value will be the major criteria for the rate of photocatalytic process<sup>18</sup>. Hence, experiments were conducted to find the optimal pH for decolourization of VGL2B. After a series of experiments the pH range was set from 2 to 11 (Figure-9). After a series of experiments it is recorded that the maximum degradation was observed after 120 minutes in acidic solution at pH 4. So, degradation rate of VGL2B for  $CaZnAl_2O_5$  increased from 97.92% to 99.07% i.e., pH 2 to 4 and decreased to 96.30% at pH 11 in 2 hours for 0.6g/100ml. The highest degradation was found to be 99.6% at pH 4<sup>19</sup>.

Similarly, pH changes will influences this amphoteric behavior the metal oxide nano-particle surface, which is predominantly positively charged below pH and negatively charged above. Hence when the pH is less than 6 negatively charged VGL2B will be adsorbed on  $CaZnAl_2O_5$  nano-particle surface, because of the attraction of positively charged  $CaZnAl_2O_5$  and the dye with the negative charge. So, maximum degradation was noted at pH 4<sup>18</sup>.

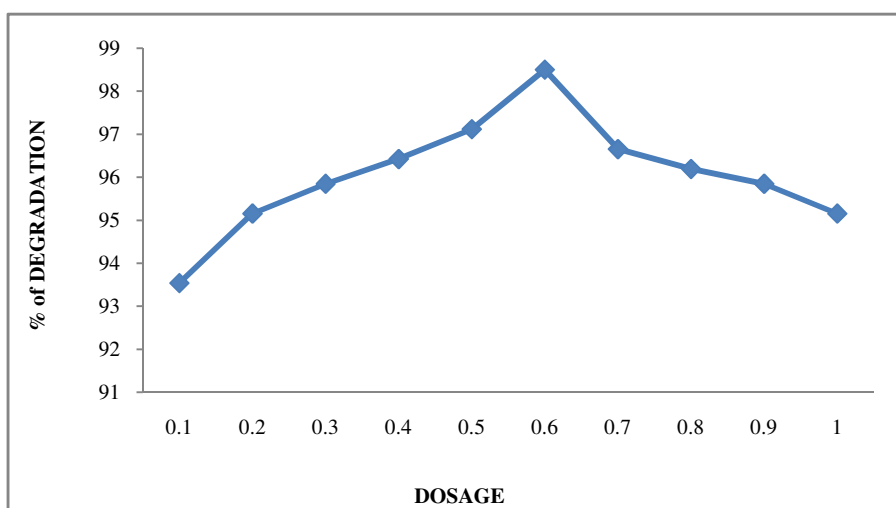


Figure-7  
 Effect of catalyst concentration on VGL2B at 120 minutes [VGL2B =30 mg/L, pH=7]

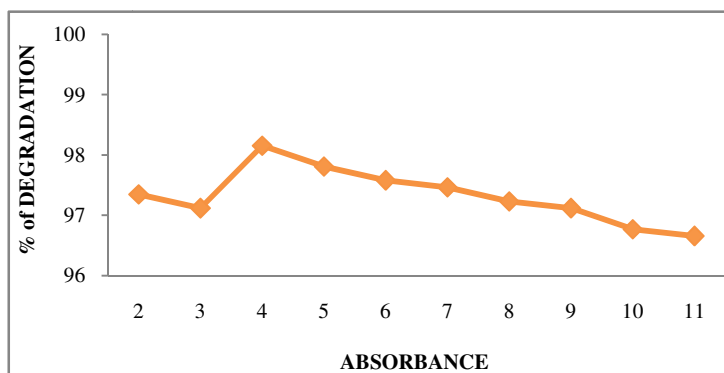


Figure-8  
 Effect of catalyst concentration on VGL2B at 120 minutes [VGL2B =30 mg/L, pH=7]



**Consequence of initial dye concentration:** The experiments were conducted by varying the VGL2B dye concentrations from 30, 50 and 70 mg/L respectively. The results obtained for  $\text{CaZnAl}_2\text{O}_5$  is 99.07% for 30ppm, 98.14% for 50ppm and 97.46% for 70ppm respectively (Figure-11). These results showed that, the degradation ability is directly affected by the concentration. The increase in concentration of the solution would decrease the rate of degradation, which is related to the equilibrium adsorption of dye on the surface of catalyst and will finally reduce the number of active sites<sup>20</sup>. So, from the Beer Lambert law, if dye concentration increases, the path length of photons entering the solution decreases. Hence, this shows the decrease of photocatalytic reaction rate<sup>21</sup>.

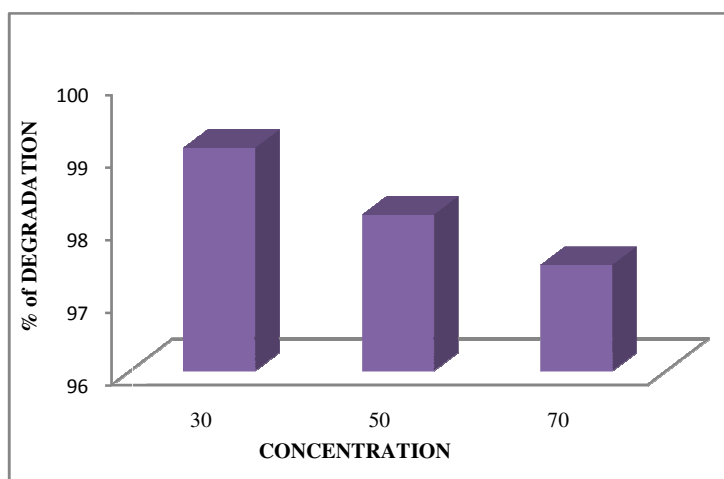
**Consequence of sun light irradiation on VGL2B:** The decolourization of VGL2B azo dye (30mg/L) were examined in different conditions, i.e., through sunlight alone without the catalyst, with the catalyst in dark condition, and with the catalyst in presence of sunlight. When the sample was directly exposed to the sunlight without the catalyst, the degradation was noticed to be zero during the whole experiments. The degradation was found to be increased with increase in irradiation time, for dye/sunlight/ $\text{CaZnAl}_2\text{O}_5$  which resulted in 99.07%, and for dye/dark/ $\text{CaZnAl}_2\text{O}_5$  is 9.34% was recorded (Figure-13). These results clearly indicate that photo degradation takes place most predominantly in presence of sunlight<sup>22, 23</sup>.



**Figure-9**  
 Effect of pH on VGL2B at 120 minutes [VGL2B =30 mg/L,  $\text{CaZnAl}_2\text{O}_5$ = 0.6g/100ml]



**Figure-10**  
 Effect of pH on VGL2B at 120 minutes [VGL2B =30 mg/L,  $\text{CaZnAl}_2\text{O}_5$  = 0.6g/100ml]



**Figure-11**  
 Effect of initial dye concentration on the photocatalytic degradation of VGL2B [ $\text{CaZnAl}_2\text{O}_5$  g/pH=0.6/4 and VGL2B = (30, 50 and 70) mg/L]



Figure-12

Effect of initial dye concentration on the photocatalytic degradation of VGL2B [ $\text{CaZnAl}_2\text{O}_5$  g/pH=0.6/4 and VGL2B = (30, 50 and 70) mg/L]

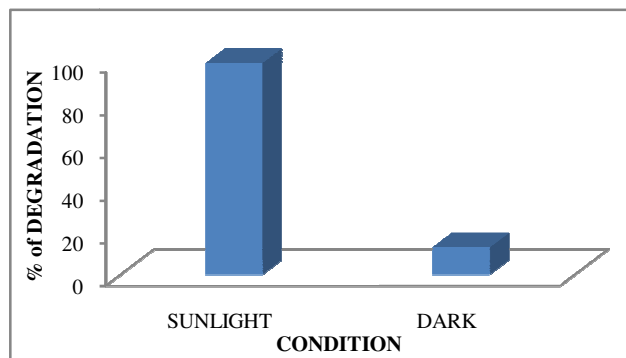


Figure-13

Effect of sunlight irradiation with respect to Dark condition on photocatalytic degradation of VGL2B in 120 minutes



Figure-14

Effect of sunlight irradiation with respect to Dark condition on photocatalytic degradation of VGL2B in 120 minutes

## Conclusion

A maximum decolorization has been achieved from the synthesized  $\text{CaZnAl}_2\text{O}_5$  nanoparticle for the selected dye solution under solar irradiation and also proved to be very efficient photocatalyst in decolorizing the azo dye by achieving 98.50% in 120 minutes at pH 7. Similarly, as the pH was changed in the solution, at pH 4 for 0.6 g/100ml the recorded degradation was 99.07%. So, from the present experiments it is very clear that photocatalytic decolorization of the dye sample is mainly dependent on pH of the dye solution and catalyst dosage. So, it is very clear that, the sunlight was found to be the most efficient source for  $\text{CaZnAl}_2\text{O}_5$  nano particle for photocatalytic activity. Thus further modification of the methodology for bulk degradation studies could be very useful to decolorize the textile effluents.

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