

## Solar Photocatalytic Degradation of Azo Dye Brilliant Red in Aqueous Medium by Synthesized CaMgO<sub>2</sub> Nanoparticle as an Alternative Catalyst

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**Abstract:** We have investigated the photocatalytic degradation of brilliant red, an azo textile dye in the presence of CaMgO<sub>2</sub> nanoparticles under natural sunlight. Complex metal oxide nanoparticle CaMgO<sub>2</sub> was synthesized by solution combustion method. Its band gap energy, particle size and morphology were studied by absorption spectra, XRD and SEM. We have examined the photocatalytic activity of these nanoparticles on Brilliant red dye by varying pH, amount of catalyst, dye concentration *etc.*

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**Keywords:** Photocatalyst, CaMgO<sub>2</sub>, Brilliant red, Nanoparticle

### Introduction

Water is the wellspring of life. It is the most important liquid in the world to maintain the plant and animal life. The two thirds of the earth's surface covered by water and human body consists of 75% of it, hence it is one of the prime element responsible for life on earth. Water is fouled due to the disposal of wastes generated from the various developmental activities and cause pollution problems. There are two choices to overcome these problems, *i.e.*, normally prevention and control by adopting various strategies to minimize the waste generation and by different treatment methods. Liquid waste is of great concern because of their harmful effects. Industrial wastewater contains wide variety of materials of both organic and inorganic nature including toxic substances like dyes and pigments, which are usually discharged with or without treatment.

Since the beginning of industrialization, the variety and quantity of pollutants emitted into the environment have steadily increased. But the rates of development of waste production are not likely to diminish; efforts to control and dispose of wastes are also rising.

Among the pollutants currently released into the water ways are thousands of tons of organic dyes discharged from textile mills. Out of nearly 80,000 tons of annual production of dyes, 10-15% of the world product dye is lost during the dyeing process and is released in textile effluents<sup>1</sup>. These colored dye effluents create several environmental pollution problems by releasing toxic and potential carcinogenic substances into the aqua sphere. This massive influx of untreated organic chemicals into the waterways not only introduces aesthetic concerns, but far more importantly, it promotes eutrophication and adversely affects the environmental health<sup>2</sup>. Several studies have been carried out for biological, physical and chemical treatment of dye containing effluents<sup>3</sup>. Among these, biodegradation, adsorption, chlorination and ozonation are the most commonly used conventional methods. Dyes are usually resistant to aerobic degradation. Hence bio treatment alone has been found to be ineffective for the treatment of dye effluents<sup>4</sup>. On the other hand, physical methods such as flocculation, reverse osmosis and adsorption are not destructive and mainly create pollutant concentrated phases, and many of this process are not found economically feasible<sup>5</sup>.

The use of heterogeneous photocatalytic treatment is more attractive for the degradation of organic dyes contrary to physical process; it can facilitate the complete mineralization of organic compounds to carbon dioxide, water and mineral acids<sup>6-8</sup>. Moreover, photocatalysis does not require expensive oxidant and can be carried out at natural sunlight. In the present work, the photocatalytic degradation of brilliant Red (BR), a textile azo dye on synthesized CaMgO<sub>2</sub> nanoparticles under natural sunlight has been investigated by varying other parameters such as initial dye concentration, solution pH and catalyst amount.

## Experimental

Chemicals such as calcium nitrate (Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O), magnesium nitrate (Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O) and acetamide (CH<sub>3</sub>CONH<sub>2</sub>), all are of A.R grade obtained from Hi media chemicals Mumbai and used without further purification. Brilliant Red (The molecular mass = 958, λ<sub>max</sub> = 517 nm) and distilled water was used for preparation of various solutions.

### *Apparatus and instruments*

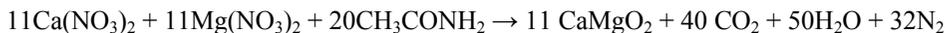
A 119 UV-Vis single beam spectrophotometer from Systronics has been used for recording absorbance at λ<sub>max</sub>. Later the absorbance was recorded in UV-Vis spectrophotometer 169 (Systronics).

### *Synthesis of nanoparticles*

The photocatalyst CaMgO<sub>2</sub> was synthesized by solution combustion method. Stoichiometric compositions of calcium nitrate, magnesium nitrate, and acetamide were calculated using the total oxidizing and reducing valencies of the components which serve as numerical coefficients for stoichiometric balance<sup>9,10</sup>.

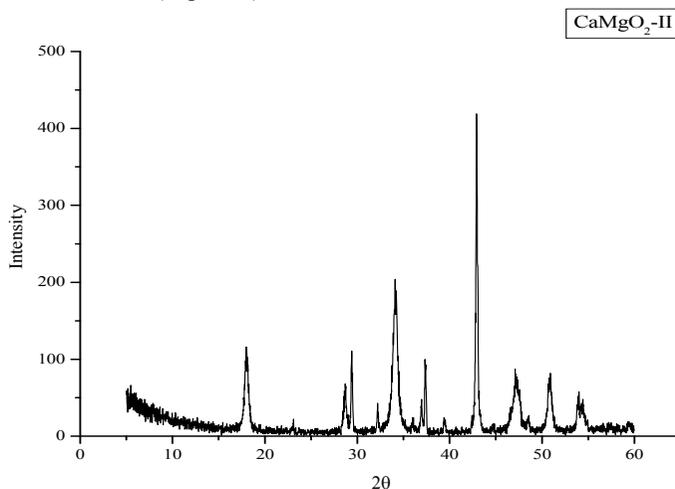
### *Synthesis of CaMgO<sub>2</sub>*

In a typical experiment 25.96 g of Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O and 28.19 g of Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O were dissolved in minimum quantity of water along with 11.8 g acetamide in a silica crucible (with volume of 200 cm<sup>3</sup>). The reaction mixture was introduced into the muffle furnace which was preheated at 450 °C. In the experiments the reaction mixture undergoes dehydration followed by decomposition with the release of CO<sub>2</sub>, N<sub>2</sub> and H<sub>2</sub>O. The mixture then froths and swells forming foam which ruptures with a flame and glows to incandescence. The product of combustion was a voluminous and foamy CaMgO<sub>2</sub> respectively. The obtained CaMgO<sub>2</sub> were crushed separately in mortar to make them amorphous. According to propellant chemistry the reactions are as shown.

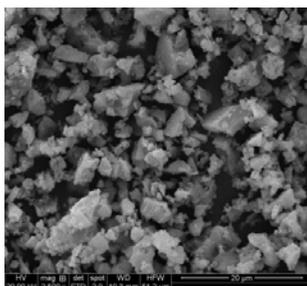


### *XRD and SEM of synthesized CaMgO<sub>2</sub> nanoparticles*

XRD analysis was performed on fresh sample to assess the purity of the expected phases and the degree of crystallization, *i.e.*, size, composition and crystal structure. XRD was performed by Rigaku diffractometer using Cu-K<sub>α</sub> radiation (1.5406 Å) in a θ-2θ configuration. The XRD pattern of the synthesized CaMgO<sub>2</sub> nanoparticle was as shown in Figure 1. According to the Debye–Scherrer’s formula ( $D = K\lambda / (\beta\cos\theta)$ , where K is the Scherrer’s constant, λ the x-ray wavelength, β is the peak width at half-maximum and θ is the Bragg’s diffraction angle) the average crystallite size of CaMgO<sub>2</sub> were found to be 36.85 nm. The SEM images of synthesized CaMgO<sub>2</sub> nanoparticle have shown the typical texture and morphology. SEM images obtained were depicted that the synthesized nanoparticles were crystal like structures (Figure 2).



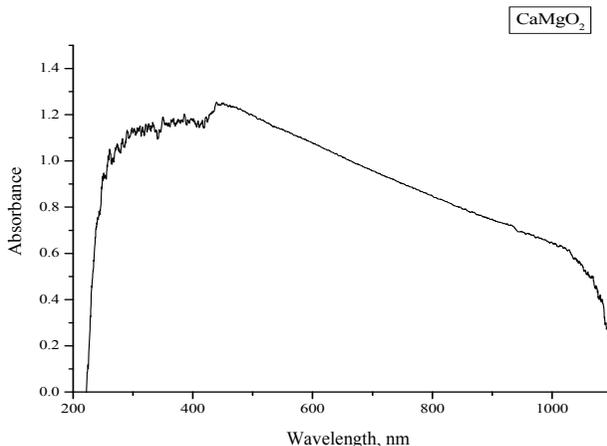
**Figure 1.** XRD of synthesized CaMgO<sub>2</sub> nanoparticle



**Figure 2.** SEM micrographs of CaMgO<sub>2</sub>

### *UV absorption spectroscopy*

Absorption spectra of CaMgO<sub>2</sub> nanoparticles were recorded using a UV-Vis spectrophotometer over the wavelength range of 200-1200 nm at Nano Research Laboratory, Department of Nanotechnology, Kuvempu University. From the spectrum, it has been inferred that CaMgO<sub>2</sub> nanoparticles have sufficient transmission in the entire visible and IR region. (Figure 3).



**Figure 3.** Absorption spectra of CaMgO<sub>2</sub>

The band gap energy of the CaMgO<sub>2</sub> was calculated using the following simple conversion equation<sup>11</sup>, the band gap equation was calculated using the Planck's equation as

$$e = hc/\lambda$$

$h$  = Planck's constant,  $C$  = Velocity of light,  $\lambda$  = wavelength,  $h = 4.135 \times 10^{-15}$  eV,

$C = 3 \times 10^8$  m/s,  $\lambda = \dots \times 10^{-9}$  nm, Band gap energy (eV) =  $4.135 \times 10^{-15} \times 3 \times 10^8 \times 10^9$

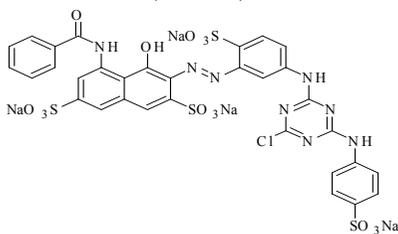
$$\text{Band gap energy (eV)} = \left( \frac{1240}{\text{wavelength (nm)}} \right)$$

The band gap energy of CaMgO<sub>2</sub> found to be 2.8 eV.

#### Procedure

Photodegradation experiments were carried out with BR dye (Figure 4) concentration 50 mg/L prepared using distilled water. A known concentration of CaMgO<sub>2</sub> nanoparticle was added to beakers containing BR dye solution. The suspension pH values were adjusted at desired level using dilute NaOH and H<sub>2</sub>SO<sub>4</sub> and then the pH values were measured with pH pen. After that, the beakers were kept in the sunlight. During irradiation, agitation was maintained to keep the suspension homogenous. The concentration of dye in each degraded sample was determined with UV-Vis spectrophotometer 169 (Systronics) at  $\lambda_{\text{max}} = 517$  nm. The percentage of photo degradation  $D$  was determined by using the following equation<sup>6</sup>, where  $C_0$  is initial concentration of BR and  $C_t$  is the concentration of BR at time 't'.

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



**Figure 4.** Structure of Brilliant Red

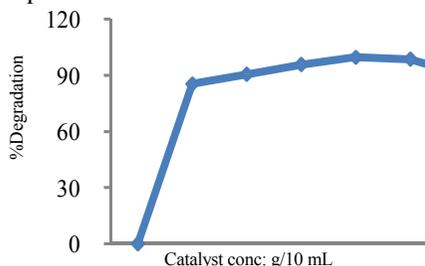
## Results and Discussion

### Catalyst type

Initially, blank experiments were performed under sunlight without addition of catalyst and no degradation was observed. To enhance the efficiency, different catalysts were added. The results are shown in Figure 5, at dye concentration = 50 mg/L, catalyst concentration = 0.4 g/100 mL, initial solution pH = 9, reaction time = 120 min. The results showed that CaMgO<sub>2</sub> nanoparticle exhibit higher photocatalytic activity. Similar results were also obtained in other studies with azo dyes<sup>12</sup>. This was explained on the basis of higher quantum efficiency of CaMgO<sub>2</sub>. The band gap energy of CaMgO<sub>2</sub> found to be 2.8 eV. Sun light energy was sufficient to cause excitation in CaMgO<sub>2</sub> nanoparticles<sup>13</sup>. Beside the band energy, the charge carrier density, as well as the catalyst structure and the crystallinity may also have important impacts on the photocatalytic activity<sup>14,15</sup>.

### Effect of catalyst concentration

To determine the effect of the catalyst concentration, a series of experiments were carried by varying the amount of catalyst from 0.1 to 0.7 g/100 mL (dye concentration = 50 mg/L, solution pH = 9). The photo degradation efficiency is as shown in Figure 5. As per the Figure, for a constant reaction time (120 min), the degradation efficiency increases sharply by increasing concentration up to 0.4g/100 mL and then decreased. At lower concentration, the catalyst surface and adsorption of light by the catalyst surface are the limiting factors and increase in catalyst greatly enhances the degradation efficiency. On the other hand at higher concentration levels, irradiation field inside the reaction medium will be reduced due to the light scattering by catalyst particles<sup>14</sup>.



**Figure 5.** Effect of catalyst concentration on photocatalytic degradation of BR (BR= 50 mg/L, pH=9, Time=120 min)

It has been established that the photocatalysed degradation of organic matter in solution is initiated by the photo excitation of the semiconductor, followed by the formation of electron-hole pair on the surface of the catalyst. The mechanism of photocatalytic degradation for an azo dye are characterized by nitrogen to nitrogen double bonds (N=N). The color of azo dye is determined by the azo bonds and their associated chromophores and auxochromes. Azo bonds are the most active bonds in azo dye molecules and can be oxidized by positive hole or hydroxyl radical or reduced by electron in the conduction band. The cleavage of N=N leads to the discoloration of dyes<sup>16</sup>. Mechanism of the photocatalytic degradation is as follows<sup>17</sup>.

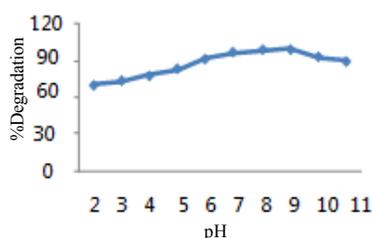




The mechanism of photocatalytic activity of  $\text{CaMgO}_2$  nanoparticle can be predicted based on the equations as shown above. Under sunlight irradiation  $\text{CaMgO}_2$  molecules get excited and transfer electron to the conduction band (Eq 1). Electron in the conduction band of  $\text{CaMgO}_2$  can reduce molecular oxygen and produce the super oxide radical  $\text{O}_2^{\cdot-}$  ions (Eq 2). This radical may form hydrogen peroxide or organic peroxide in the presence of oxygen and organic molecule (Eq 3, 4 & 5). Hydrogen peroxide can be generated in another path (Eq 6). Hydrogen peroxide can form hydroxyl radicals which are powerful oxidizing agents (Eq 7, 8). The radicals produced are capable of attacking dye molecules and degrade them (Eq 9)<sup>18</sup>.

### Effect of pH

In order to study the effect of pH on the degradation efficiency of  $\text{CaMgO}_2$  catalyst, the experiments were conducted at various pH (ranging from 2 to 11). The results showed that pH significantly affected the degradation efficiency. As shown in Figure 6, the degradation rate of BR increased from 70.5% to 98.6% when the pH was increased from 2 to 9 and then decreased to 89.6% at pH 11. The maximum degradation rate of BR was achieved at pH 9. BR is an anionic dye which contains sulphonated groups. Its photocatalytic activity is maximum at pH 9. More efficient formation of hydroxyl radicals occurs in alkaline medium. Excess of hydroxyl anions increases the formation of  $\text{OH}^{\cdot}$  radicals. These  $\text{OH}^{\cdot}$  radicals are the main oxidizing species responsible for photocatalytic degradation (Eq 7-8). Above pH 9, the decrease in the degradation efficiency could be explained on the basis of amphoteric nature of  $\text{CaMgO}_2$  catalyst.  $\text{CaMgO}_2$  surface becomes negatively charged for higher pH values. This causes the electrostatic repulsion between the catalyst and negatively charged BR dye<sup>19</sup>.

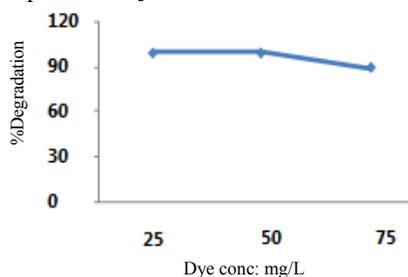


**Figure 6.** Effect of initial pH on photocatalytic degradation of BR (BR= 50 mg/L,  $\text{CaMgO}_2$  = 0.4 g/100 mL, Time=120 min)

### Effect of initial dye concentration

The effect of initial dye concentration on the degradation efficiency was investigated by varying the initial concentration. The initial concentration of dye was varied from 25, 50 and 75 mg/L.  $\text{CaMgO}_2$  resulted 100%, 98.6% and 87.3% for 25, 50 and 75 mg/L dye concentrations respectively. These series of experiments illustrated that the degradation efficiency was inversely affected by the concentration (Figure 7). 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<sup>·</sup> radicals which were considered as primary oxidizing agents of the organic dye<sup>20</sup>. On the other hand, 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 on the catalyst particles, and consequently decreases the photocatalytic reaction rate<sup>21</sup>.



**Figure 7.** Effect of initial dye concentration on photocatalytic degradation of BR (pH= 9, CaMgO<sub>2</sub>=0.4 g/100 mL, Time = 120 min)

## Conclusion

In this study solar photocatalytic degradation of textile dye brilliant red has been investigated using synthesized CaMgO<sub>2</sub> nanoparticle catalyst. CaMgO<sub>2</sub> has been found to be more active catalyst exhibiting high photocatalytic activity. From the studies, it has been found that CaMgO<sub>2</sub> nanoparticle can be synthesized economically conveniently and quickly. At lower catalyst concentration, the catalyst surface and adsorption of light on catalyst surface are the limiting factors. Thus an increase in catalyst concentration greatly enhances the process efficiency. On the other hand, at high concentration, overlapping of adsorption site and deactivation of activated catalyst reduces the process efficiency.

The degradation efficiency increases with increase in pH, attaining maximum value at pH 9. Above pH 9 the catalyst surface is negatively charged by means of adsorbed OH<sup>-</sup> ions, which causes electrostatic repulsion between catalyst and negatively charged BR this decreases the degradation efficiency.

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