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# Solar Light Induced Photodegradation of Brilliant Green Dye by Barium Calciate ($BaCaO_2$) Nanoparticles

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## ABSTRACT

The study on photodegradation of Brilliant Green dye was done by barium calciate nanoparticles ($BaCaO_2$). The $BaCaO_2$ was prepared by solution combustion synthesis. The analytical instruments like SEM, XRD, EDAX, and UV-absorption spectroscopy were employed for characterization. All the experiments were accomplished under various irradiation conditions such as sunlight, UV light and dark conditions. The obtained results examined the percentage of degradation capacity of $BaCaO_2$ on Brilliant Green by differing the Brilliant Green concentration, pH and catalyst loading. The percentage of degradation was 98.93% in 20ppm of dye concentration at pH 6 with a constant catalyst concentration of 0.7g/100mL. This proves that the synthesized barium calciate nanoparticles are more efficient in removing Brilliant Green from the wastewater.

## INTRODUCTION

Recent industrial developmental activities are posing one or the other negative impacts on the environment, like the discharge of contaminants or discharge of coloured effluents directly into the environment. These coloured discharges impart severe pollution on the environment and cause health problems due to their toxicity and ability to sustain in nature (Arslan et al. 2000, Sauer et al. 2002). The dye effluents discharged into the water body decrease the aesthetic value of the water by colouring it. The sunlight penetration into the water body is blocked due to its colouring and inhibits the growth of useful biota (Yogendra et al. 2011). Due to low biodegradation characteristics and highly aromatic condition dyes have become prominent water pollutants (Madhusudhana et al. 2013, Daneshvar et al. 2004).

Recent studies have reported that wide ranges of metal oxide nanoparticles are being synthesized and their applications have made a unique contribution in the field of nanotechnology because of its unique and wide-ranging physicochemical properties (Di-Paola et al. 2003, Turchi et al.1990). Nowadays degradation of dye effluents using nanoparticles has attracted more attention of the scientific community (Mirkhani et al. 2009). The traditional methods like biological, physical and chemical are not so effective when compared to photocatalytic degradation. Advanced oxidation processes are promising alternatives for photodegradation of industrial effluents especially from the environmental point of view. Heterogeneous photocatalysis concentrates on the dissociation of dyes into simpler molecules of $CO_2$, $H_2O$ and mineral acids by using metal oxide nanoparticles as catalysts (Vinodgopal et al. 1996, Movahedi et al. 2009). Hence, this work is a novel, simple and fast method to degrade the Brilliant Green dye by $BaCaO_2$ nanoparticles under solar irradiation.

## MATERIALS AND METHODS

Brilliant Green is an easily available dye in the market (Sigma Aldrich, Mumbai, India (Fig. 1). The chemicals (99% A.R.), $Ba(NO_3)_2$, $Ca(NO_3)_2$ and $NH_2CONH_2$ were procured from Hi-Media Chemicals, Mumbai. Through visible spectrophotometer (Elico, SL 177) the absorbance was recorded at λmax.

**Nanoparticles synthesis:** $BaCaO_2$ nanoparticles were prepared using solution combustion methodology by redox mixtures of stoichiometric amounts of metal nitrates and fuel.

$$3Ba(NO_3)_2 + 3Ca(NO_3)_2 + 10NH_2CONH_2^- = BaCaO_2 + 10CO_2 + 20H_2O + 16N_2 \quad \ldots(1)$$

**XRD:** The XRD of $BaCaO_2$ is displayed in Fig. 2 as stated by Debye Scherrer's formula:

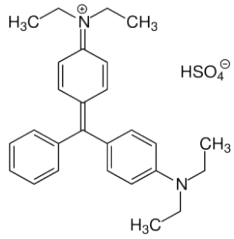


Fig. 1: Chemical structure of Brilliant Green.

$$D = K\lambda/\beta \cos\theta \quad \ldots 2$$

Where, K = Scherrer's constant, λ = X-ray wavelength, β = peak width at half-maximum, θ = Bragg's diffraction angle

In this work, the finely divided sample of $BaCaO_2$ by XRD studies was found to have a size varied from 25 nm to 60 nm with an average size of 40 nm.

**SEM:** Scanning Electron Microscope pictures of $BaCaO_2$ nanoparticles have shown scattered crystals with irregular shapes. The magnified images also have shown a sharp-edged uneven texture of the different nanoparticles with strong bonding of nanoparticles over one another (Fig. 3).

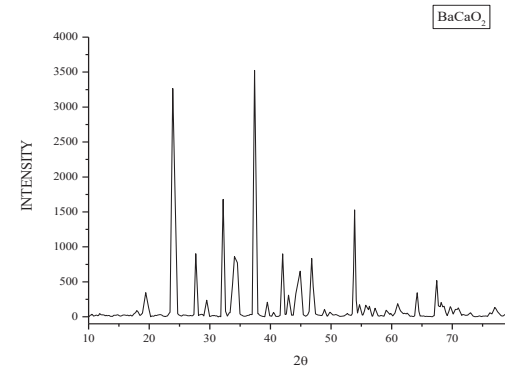


Fig. 2: XRD of synthesized $BaCaO_2$ nanoparticles.

**UV-Vis spectroscopy:** Optical absorption is a significant tool to get the optical energy band gap of the nanomaterials. The elemental absorption related to the electron jump from the valence band to the conductivity band. The spectrum reveals that the $BaCaO_2$ nanoparticle absorption in the visible radiation with a wavelength of 400 nm (Fig. 4). The value of optical band gap (OBG) was calculated from the TAUC's relation:

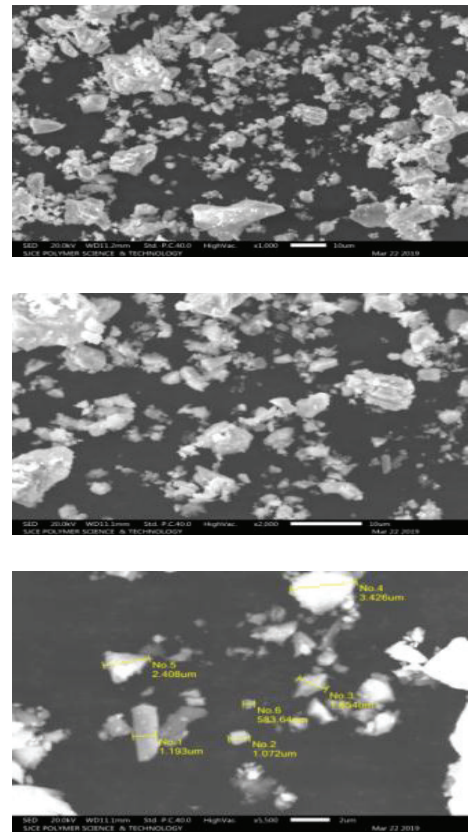


Fig. 3: Scanning Electron Micrographs of synthesized $BaCaO_2$ nanoparticles.

Table 1: Weight and atomic percentage of the elements in the barium calciate.

| Element | Weight % | Atomic % |
|---|---|---|
| C | 17.87 | 36.89 |
| O | 31.23 | 48.41 |
| Ca | 12.59 | 7.79 |
| Ba | 38.31 | 6.92 |

$$\alpha h\upsilon = B\,[h\upsilon - Eg]n$$

'hυ' = photon energy,

'B' = constant

'n' = power factor.

OBG of the $BaCaO_2$ nanoparticle was found to be 3.57eV.

**EDAX:** The EDAX analysis confirms the presence of $BaCaO_2$, carbon and oxygen in the nanoparticle sample. The vertical axis displays the number of x counts although, the horizontal axis displays energy in KeV (Fig. 5). The weight and atomic percentage (Table 1) of carbon, oxygen, calcium, and barium were found to be 17.87, 31.23, 12.59, 38.31 and 36.89, 48.41, 7.79, 6.92 which correspond to the spectrum without impurities peaks.

## Experimental Procedure

Using UV-visible absorption studies, the degradation of dye solutions was carried out. The spectral data noted using a spectrophotometer (Systronic UV-Visible) with 350-800 nanometre range. 492 nm was the maximum wavelength (λmax) of Brilliant Green. Solar irradiation is the main source for photocatalytic degradation experiments. The standard (20mg/L) dye solution was made by mixing 20 mg of Brilliant Green dye in 1 litre double distilled water. The dye solution then used for degradation experiments against $BaCaO_2$ nanoparticle. Different parameters such as pH levels, dye concentration and $BaCaO_2$ dosage were used to examine the degradation, and results were noted. pH balance of dye solution was maintained accurately by adding HCl or NaOH. Finally, the colour degradation percentage was calculated using the formula as follows.

$$\text{Decolorization} = \frac{V_0 - V_t}{V_0} \times 100$$

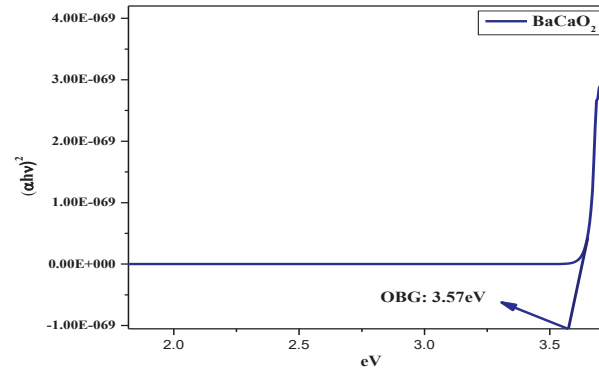


Fig. 4: UV-absorption spectra of synthesized barium calciate nanoparticles.

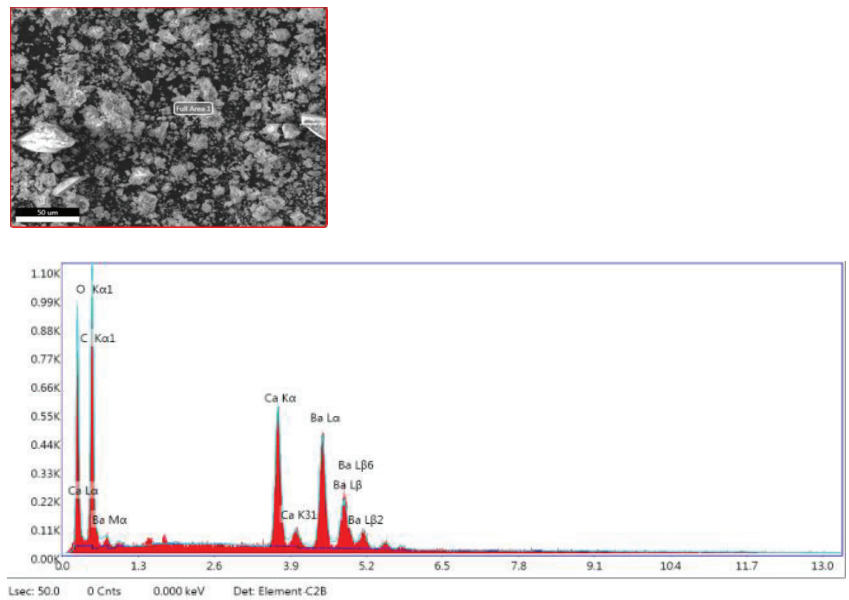


Fig. 5: Energy dispersive X-ray of synthesized $BaCaO_2$ nanoparticles.

Where, $V_0$ = initial absorbance of dye solution, $V_t$= absorbance at time 't'

## RESULTS AND DISCUSSION

### $BaCaO_2$ Dosage

$BaCaO_2$ dosage varied between 0.1 g and 1 g/100mL of selected dye solution and tested for its efficiency. The $BaCaO_2$ with the size 40 nm has shown 98.35% degradation. Since the photodegradation for the selected dye solution was highly successful at 0.7g/100mL within 2 hours (120 minutes), further experiments were continued with the effective dosage of 0.7 g for all the remaining parameters. The results are shown in Fig. 6.

The degradation of Brilliant Green was maximum at 0.7 g due to the availability of optimum active sites on $BaCaO_2$ surface area. In addition to this, the optimum sunlight into the solution and also a scattering of light by the catalyst also led to the photodegradation of the dye. Dosage level more than 0.7 g reduced the photodegradation due to overlying, overcrowding and collision with the ground state catalysts (Shanmugam 2006, Gandhi 2010, Thirugnanam 2017).

Hence, the dye molecules were degraded due to the high energy radicals formed in the reaction.

$$\text{Nanoparticles} + h\nu \rightarrow (\text{e-CB} + \text{h+VB}) \quad \ldots 1$$

$$e^{-CB} + O_2 \rightarrow O_2^{\bullet -} \quad \ldots 2$$

$$H_2O + O_2^{\bullet -} \rightarrow OOH^{\bullet} + OH^{-} \quad \ldots 3$$

$$2OOH^{\bullet} \rightarrow O_2 + H_2O_2 \quad \ldots 4$$

$$O_2^{\bullet -} + \text{Brilliant green} \rightarrow \text{Brilliant green-}OO^{\bullet} \quad \ldots 5$$

$$O\ OH^{\bullet} + H_2O + e^{-}CB \rightarrow H_2O_2 + OH^{-} \quad \ldots 6$$

Hydrogen peroxide can be generated in another path.

$$H_2O_2 + e^{-}CB \rightarrow OH^{\bullet} + OH^{-} \quad \ldots 7$$

$$H_2O_2 + O_2^{\bullet -} \rightarrow OH^{\bullet} + OH^{-} + O_2 \quad \ldots 8$$

$$OH^{\bullet} / O_2^{\bullet -} / \text{Nano-particles}^{\bullet +} + \text{Brilliant green} \rightarrow \text{Brilliant green degradation} \quad \ldots 9$$

### pH Effect on Brilliant Green

For pH experiments, the range was set to 2, 4, 6, 8 and 10 for dye solutions. The degradation rate for the dye solutions has shown a remarkable increase from 97.36% to 98.93% with a pH change from 2-6 and a reduction up to 98.28% at pH 10 (Fig. 7). An optimum degradation was achieved at pH 6. The time required to achieve the degradation was 120 minutes at the optimum dosage of 0.7g per 100 mL dye solution.

As the dye is a cationic compound which is very efficient in forming OH· radicals in acidic solution, OH· radicals are the main source of oxidation in carrying out photocatalytic degradation of Brilliant Green. Either positive or negative charge generate on the catalyst surface due to amphoteric effect and this is greatly influenced by changing pH value (Khan et al. 2017). In this reaction, the optimum amount of OH· radicals were generated at pH 6 in the solution. Acidic condition of solution less than pH 6 has noted a reduction in degradation. The basic condition has an inhibition effect on Brilliant Green a cationic dye due to overproduction of OH· radicals (Xiang et al. 2012, Liu 1999).

### Effect of Dye Concentration

Experiments were conducted by differing the Brilliant Green dye levels from 20-50 ppm. The results for $BaCaO_2$ are 98.93% for 20ppm, 93.39% for 30ppm, 88.7% for 40ppm and 87.36% for 50ppm, respectively (Fig. 8). This has proved that photodegradation capacity directly depends upon the concentration of dye solution. An increased path length at lower dye concentration directly influences the increased photodegradation. At higher dye concentrations the path length reduces and hence less absorption of a photon by the catalyst. This results in a reduced photodegradation rate.

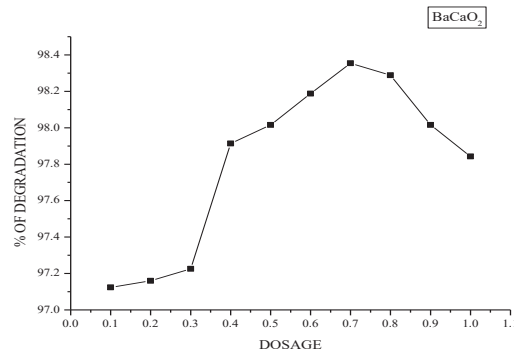


Fig. 6: Effect of catalyst concentration on Brilliant Green at 120 minutes (Brilliant Green=20 ppm, pH=6, $BaCaO_2$).

### Effect of Sunlight Irradiation

Under three different conditions, i.e. through sunlight alone, dye-dark-catalyst, dye-UV-catalyst and dye-sunlight-catalyst experiments were conducted to check the nanoparticle efficiency. In sunlight alone, without catalyst, the photodegradation of Brilliant Green was noted almost nil. 98.93% of degradation achieved at dye-sunlight-$BaCaO_2$ condition, 72% of degradation recorded at the dye-UV light-$BaCaO_2$ condition and 54.04% degradation observed at dye-dark-$BaCaO_2$ condition (Fig. 9). This clearly emphasizes the importance of different light conditions in the degradation of Brilliant Green dye.

The efficient photodegradation requires both sunlight as well as photocatalyst. The formation of electron-hole on the catalyst surface requires excitation of semiconductors. The sunlight gives the excitation energy to the semiconductors and thus efficient break down of organic dye molecule is achieved (Byrappa et al. 2006.)

## CONCLUSION

As per the results, synthesized $BaCaO_2$ has been proved to be photocatalytic and efficient in mineralizing the Brilliant Green. The proposed photocatalytic method proved to be very effective for the degradation of Brilliant Green, an industrial dye. For the degradation experiment, we have achieved 98.93% degradation at pH 6. With this result, we can say that the application of nano-sized materials is more suitable for degradation of dye effluents. This will certainly help in solving the problem of the textile effluent treatment process.

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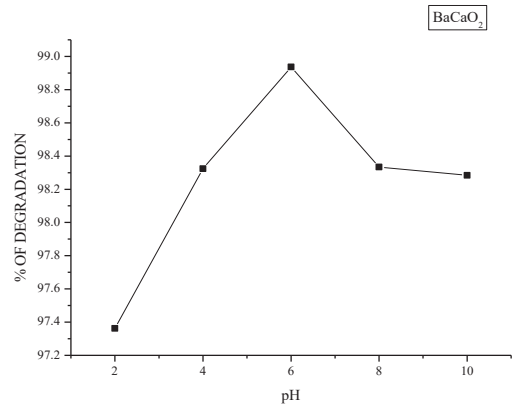


Fig. 7: Effect of pH on Brilliant Green at 120 minutes (Brilliant Green=20 ppm, $BaCaO_2$).

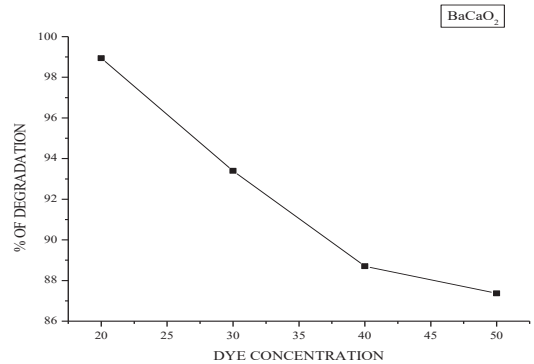


Fig. 8: Effect of dye concentration on the photodegradation of Brilliant Green [$BaCaO_2$ g/pH=0.7/4 and Brilliant Green= (20+30+40+50) ppm].

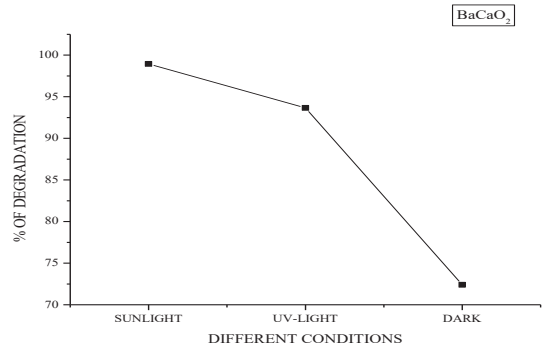


Fig. 9: Effect of sunlight irradiation with respect to the dark condition and UV condition on photocatalytic degradation of Brilliant Green in 120 minutes.

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