

A comparative study on Photocatalytic degradation of Violet GL2B azo dye using CaO and TiO₂ nanoparticles

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ABSTRACT

The photocatalytic degradation has become most efficient process for the degradation of dyes. In the present study, Violet GL2B azo dye was chosen for the degradation under visible light irradiation. The two different nanoparticles, synthesized CaO and commercially available TiO₂ were tested for the photocatalytic degradation. CaO nanoparticle was synthesized by solution combustion method (using urea as fuel). The nanoparticle was characterized by using X-ray diffraction (XRD) and Scanning Electron Micrograph (SEM). The average size of CaO nanoparticle was found to be 36 nm with the band gap of 4.94 eV. The nanoparticle was tested for the photocatalytic degradation by varying parameters such as catalyst concentration, pH and dye concentration and compared with the procured TiO₂ nanoparticle of size <25 nm. The experimental results demonstrated that, the synthesized CaO nanoparticle achieved maximum degradation (97%) when compared to procured TiO₂ nanoparticle (7.91%) at pH 7.

Keywords - CaO, Degradation, Nanoparticle, Photocatalyst, TiO₂, Violet GL2B

1. INTRODUCTION

The effluent produced by dyeing industries is harmful to the living beings. The undesirable substances present in liquid effluents pose severe threat to the immediate recipients. Wastewaters from dyeing industries have caused a serious problem to the environment. The discharged wastes containing dyes are toxic to microorganisms, aquatic life and human beings [1]. The release of coloured waste waters in the environment causes pollution and eutrophication and can originate dangerous byproducts through oxidation, hydrolysis, or through other chemical reactions [2]. It is reported that textile dyes and other industrial dyestuffs constitute one of the largest groups of organic compounds that represent an increasing environmental danger [3, 4]. The majority of these dyes are azo dyes, which are characterized by the presence of -N=N- group [5]. At the time of production and application about 10% of these dyes are lost as waste effluents [6]. The degradation of azo dyes in industrial wastewaters has therefore received increasing attention.

Traditional physical techniques (adsorption on activated carbon, ultra filtration, reverse osmosis, coagulation by chemical agents, ion exchange on synthetic adsorbent resins, etc.) have been used for the removal of dye pollutants [7, 8]. These methods only succeed in transferring organic compounds from water to another phase, thus creating secondary pollution. This will require a further treatment of solid-wastes and regeneration of the adsorbent which will add more cost to the process [9].

More recently the field of photocatalysis is developing fast because; solar energy is a renewable source of energy which is abundant and freely available for almost eight to nine months in a year over most part of the world. In the recent times, *Azarmidokht Hosseinnia et al.* has reported TiO₂ of size less than 20 nm can be used for the degradation of organic dyes with different chromophores [10]. Similarly, *Sylwia Mozia et al.* has worked on the photocatalytic degradation of azo dye Acid Red 18 by using the TiO₂ as a photocatalyst and reported it has a good catalyst [11]. Similar kind of work was reported by *Yogendra et al.* by using newly synthesized nanoparticles like CaAl₂O₄, CaZnO₂, ZnO, CaMgO₂ [12-17].

For the present study Violet GL2B (Fig 1) an azo dye was selected with the intension of degrading it by using the synthesized nanoparticle CaO and to compare it with the commercially available TiO₂ nanoparticle.

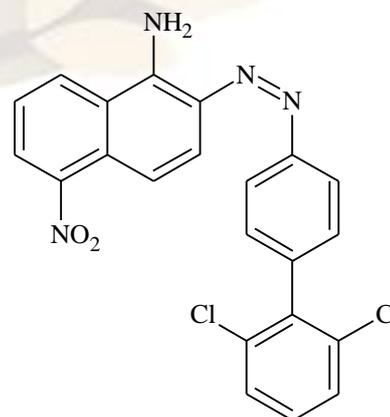


Fig 1: Structure of Violet GL2B

2. MATERIALS AND METHODS

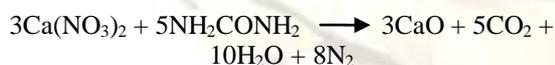
2.1 Materials and Reagents

From Sigma Aldrich, Mumbai the TiO₂ nanoparticle of size <25 nm was procured. CaO nanoparticle was synthesized in the laboratory condition by solution combustion method using Ca(NO₃)₂ and fuel urea. The commercially available azo dye Violet GL2B was used for the degradation study (Fig 1). The chemicals like calcium nitrate (Ca(NO₃)₂ · 4H₂O) (99%, AR) and urea (NH₂ CO NH₂) (99%, AR) were obtained from Hi-media chemicals, Mumbai. The UV-VIS single beam spectrophotometer 119 (Systronics) has been used for recording the absorbance at λ_{max}.

2.2 Synthesis of CaO

The solution combustion synthesis is a simple and rapid process, which allows effective synthesis of a variety of nanosize materials [18]. This process involves a self sustained reaction in homogeneous solution of different oxidizers (e.g., metal nitrates) and fuels (e.g., urea).

The CaO nanoparticle was prepared by solution combustion method, using calcium nitrate with fuel urea. Stoichiometric amounts of Calcium nitrate and fuel Urea were calculated using the total oxidizing and reducing valencies of the compounds which serve as numerical coefficients for stoichiometric balance. Ca(NO₃)₂ · 4H₂O (14.16 g) and fuel (NH₂ CO NH₂) (6 g) were dissolved in minimum quantity of water in a silica Crucible (with a volume of 100 cm³). The mixture was introduced into the muffle furnace which was preheated at 600 °C. The solution boils and undergoes dehydration followed by decomposition along with the release of certain amount of gases forming the Calcium oxide nanoparticle. The obtained nanoparticle was crushed in a mortar to make it amorphous. According to propellant chemistry the reaction is as shown (Scheme 1) [19].



Scheme 1: Synthesis of CaO

2.3 Characterization of the nanoparticle

CaO nanoparticle was characterized by XRD, SEM and UV absorption spectroscopy. As TiO₂ nanoparticle was procured the characterization was not necessary for it.

2.3.1 X-Ray Diffraction (XRD)

The powdered sample of CaO nanoparticle was examined by XRD and analysis was carried out 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_α radiation (1.5406 Å) in a θ-2θ configuration [20].

According to the Debye Scherrer's formula:

$$D = \left(\frac{K\lambda}{\beta \cos \theta} \right)$$

Where K = 0.90 is the Scherrer's constant,

λ the X-ray wavelength,

β is the peak width at half-maximum

θ is the Bragg diffraction angle

The average crystallite size of CaO was found to be 36nm and indexing was done using the TREOR program (Fig 2).

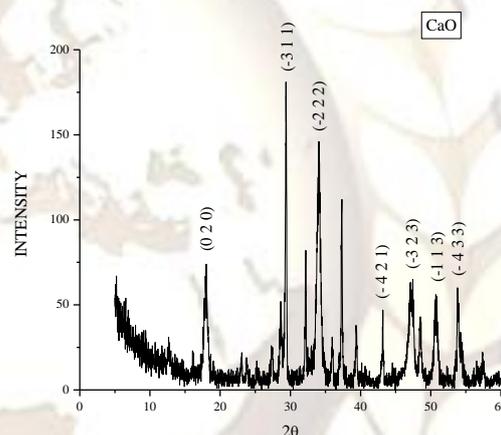


Fig 2: X-Ray Diffraction of CaO

2.3.2 Scanning Electron Micrograph (SEM)

In the present study, powdered sample of CaO nanoparticle was examined by using SEM technique. This study gave us the information about the surface of the nanoparticle and its internal structure. Figure 3 illustrates SEM photographs of single crystals of CaO. The images will show the cubic crystal morphology, which are scattered. The individual crystal particles are having sharp edges.

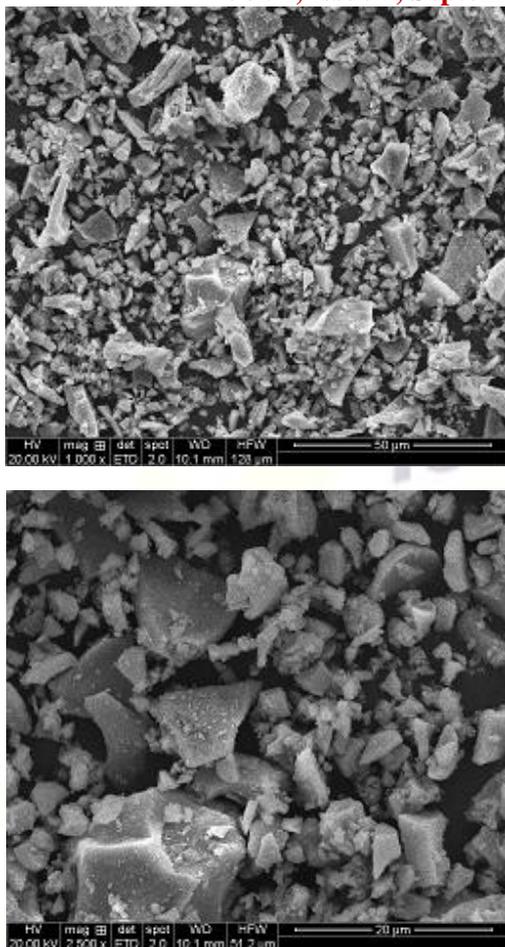


Fig 3: SEM micrographs of CaO

2.4 UV Absorption spectroscopy

Absorption spectra of CaO nanoparticle was recorded using (Ocean Optics DH-2000) UV-Vis spectrophotometer over the wavelength range 200-1200 nm at Department of Nanotechnology, Kuvempu University. From this spectrum, it has been inferred that CaO nanoparticle has sufficient transmission in the entire visible and IR region (Fig 4).

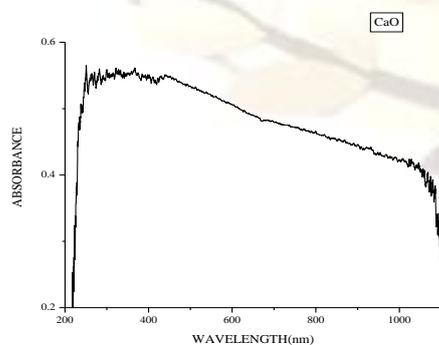


Fig 4: UV Absorption of CaO

The band gap energy of the CaO was calculated using the following simple conversion equation. The band gap equation is calculated using the Planck's equation as follows.

$$e = \frac{hc}{\lambda}$$

h = Planck's constant,

C = Velocity of light,

λ = wavelength,

$$h = 4.135 \times 10^{-15} \text{ eV},$$

$$C = 3 \times 10^8 \text{ m/s},$$

$$\lambda = \dots \times 10^{-9} \text{ nm}$$

$$\text{Band gap energy (eV)} = 4.135 \times 10^{-15} \times 3 \times 10^8 \times 10^9$$

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

Nanoparticle	λ_{max} (nm)	Band gap Energy (eV)
Calcium oxide (CaO)	251	4.94

Table 1: Band gap of CaO nanoparticles

The band gap energy of CaO is found to be 4.94 eV (Table 1). With this we can say that the band gap of semiconductor was found to be particle size dependent [21].

3. EXPERIMENT I

The photocatalytic experiments were carried out in presence of direct sunlight of intensity between 100000 to 130000 lux in the range 200000 (TES 1332A digital Lux meter). The experiments were carried out between 10.30 am to 1.30 pm. In all photocatalytic experiments, 100 ml of 30 ppm Violet GL2B solution was taken in 100 ml Borosil beakers. The UV-VIS spectrophotometer 119 (Systronics) was used for the determination of absorbance in the range of 200 to 800 nm. The λ_{max} of Violet GL2B was found to be 545 nm. A known concentration of TiO_2 and CaO (0.5 g/100ml) were added to two beakers containing Violet GL2B azo dye solution and kept in the direct sunlight for photocatalytic activity. Further experiments were conducted based on the degradation obtained from the photocatalytic activity of the catalysts.

3.1 EXPERIMENT II

The nanoparticle with high photocatalytic activity was selected for further studies. Photocatalytic suspensions from 0.1 g, 0.2 g, 0.3 g

upto 1 g were tested on the dye samples of 100 ml quantity. The suspension pH values were adjusted by using NaOH/HCl solutions using pH meter. Before irradiation, photocatalyst suspension was stirred in the dark to ensure the adsorption equilibrium and it was kept in sunlight for the photocatalytic degradation. Upto 120 minutes, the suspension was sampled at regular time intervals of 30 minutes and centrifuged using (EBA-Hetlich) at 3000 rpm for 15 minutes to remove photocatalyst particles. The residual concentration of the solution sample was monitored by using UV-VIS spectrophotometer 169 (Systronics) at 545 nm. The experiments were conducted for pH range 2 to 11 in order to study the efficiency of the nanoparticle on Acidic, Alkaline and Neutral conditions. The data obtained from the photocatalytic degradation experiments were used to calculate the degradation efficiency 'D'.

$$D = \left(\frac{A_0 - A_t}{A_0} \right) \times 100$$

Where, A_0 = initial absorbance of dye solution and

A_t = absorbance at time 't'.

4. RESULTS AND DISCUSSION

4.1 Effect on photocatalytic degradation

Initially, blank experiments were performed under direct sunlight without the addition of catalyst and no degradation was observed. A known concentration of TiO_2 and CaO (0.5 g/100ml) were added to two beakers containing Violet GL2B azo dye solution (30 ppm) and kept in the sunlight for photocatalytic activity. The results showed that CaO nanoparticle have exhibited higher photocatalytic activity than TiO_2 . 7.95% degradation was recorded for TiO_2 nanoparticle and 97% for CaO (Fig 5) (Photo 1). So, with this result further study was done concentrating on the synthesized CaO nanoparticle.

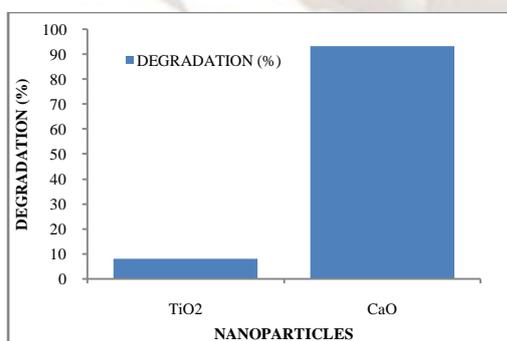


Fig 5: Rate of degradation of Violet GL2B at 120 minutes. [Violet GL2B=30mg/L, pH=7, TiO_2 =0.5 g, CaO=0.5 g].



Photo 1: Effect of photocatalytic degradation of Violet GL2B at 120 minutes. [Violet GL2B=30mg/L, pH=7, TiO_2 =0.5 g, CaO=0.5 g].

4.2 Effect of catalyst concentration

The photocatalytic degradation experiment was conducted over a range of catalyst amount from 0.1 to 1g/100ml for Violet GL2B azo dye. The CaO showed highest degradation of 97% for the 0.2 g/100ml in 120 minutes. The remaining dosages 0.1g/100ml and 0.3g/100ml to 1g/100ml the degradation rate was less and at 1g/100ml it was recorded 91.81% in 120 minutes (Fig. 6) (Photo 2).

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. Further increase in the catalyst amount in both the catalysts beyond 0.2g/100ml decreases the photodegradation by a little margin. This may be due to overcrowding owing to collision with ground state catalyst [22]. Since the photo degradation was most effective at 0.2g/100ml catalyst concentration, the following experiments were continued with 0.2g/100ml dosage.

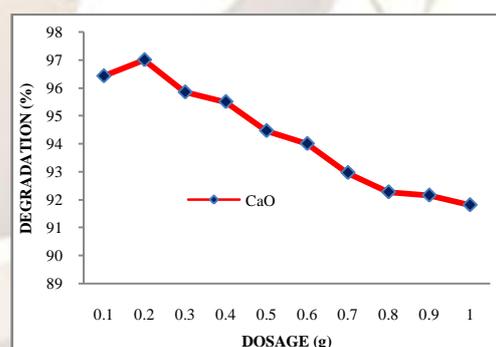


Fig 6: Effect of concentration of CaO on photocatalytic degradation of Violet GL2B at 120 minutes [Violet GL2B=30mg/L, pH=7].



Photo 2: Effect of concentration of CaO on photocatalytic degradation of Violet GL2B at 120 minutes [Violet GL2B=30mg/L, pH=7].

4.3 Effect of pH

In order to study the effect of pH on the degradation efficiency of CaO catalyst, the experiments were conducted at pH ranging from 2 to 11. The results showed that pH significantly affected the degradation efficiency (Fig 7) (Photo 3). The degradation rate of Violet GL2B for CaO increased from 94.34% to 97.57% from pH 2 to pH 10 and decreased to 96.88 % at pH 11 in 120 minutes. The maximum degradation rate for CaO nanoparticle was achieved at pH 10. More efficient formation of hydroxyl radicals was found to occur in alkaline medium because, excess of hydroxyl anions increases the formation of OH[•] radicals. Similarly, the NO₂ and Cl groups of the dye molecule may also facilitate the formation of OH[•] radicals and the These OH[•] radicals are the main oxidizing species responsible for photocatalytic degradation (Eq 7-8).

At pH greater than 10, the decrease in degradation efficiency can be explained on the basis of amphoteric nature of CaO. The catalyst surface becomes negatively charged for higher pH values causes the electrostatic repulsion between the catalyst and negatively charged dyes [23].

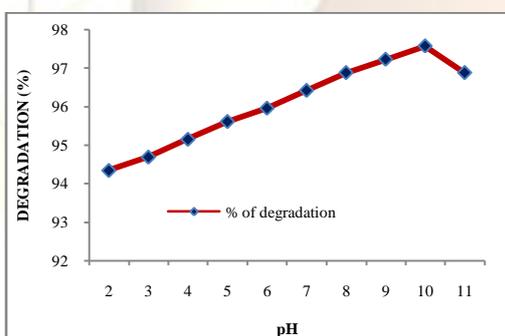


Fig 7: Effect of pH on photocatalytic degradation of Violet GL2B at irradiation time 120 minutes [CaO = 0.2g/100ml, Violet GL2B= 30 mg/L].



Photo 3: Effect of pH on photocatalytic degradation of Violet GL2B at irradiation time 120 minutes [CaO = 0.2g/100ml, Violet GL2B= 30 mg/L].

4.4 Effect of initial dye concentration

The initial concentration of dye was varied from 30, 60, 90 and 120 mg/L at catalyst loading 0.2g/100ml at pH 10. The Figure 8 (Photo 4) illustrate that the degradation efficiency was

inversely affected by the concentration. The decrease in the degradation with increase in dye concentration was ascribed to the equilibrium adsorption of dye on the catalyst surface which results in 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 [24].

According to Beer Lambert law, as the initial dye concentration increases, the path length of photons entering the solution decreases. This results in lower photon adsorption on the catalyst particles, and consequently decreases photocatalytic reaction rate [25].

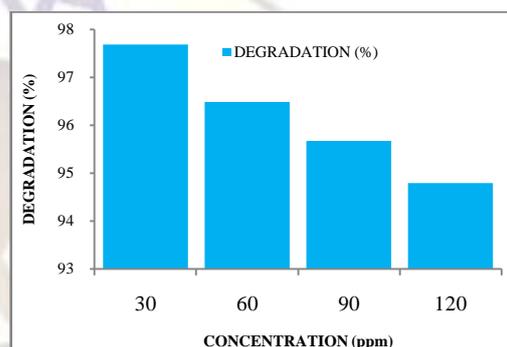


Fig 8: Effect of initial dye concentration on photocatalytic degradation of Violet GL2B [CaO = 0.2 g/100ml, pH = 10].



Photo 4: Effect of initial dye concentration on photocatalytic degradation of Violet GL2B [CaO = 0.2 g/100ml, pH = 10].

4.5 Effect of sunlight irradiation and catalyst

Figure 9 illustrates the photocatalytic degradation of 30 mg/L of Violet GL2B azo dye in aqueous solution under three different experimental conditions through sunlight alone, Dye/dark/CaO and Dye/sunlight/CaO (Fig 9) (Photo 5 and Photo 6). The degradation rate was found to increase with increase in irradiation time and in presence of sunlight 97.69% degradation was achieved (Dye/CaO/sunlight). When the same concentration of dye solution along with the CaO nanoparticle was magnetically stirred for the same optimum dosage and irradiation time in darkness, only 66.78% degradation was achieved (Dye/Dark/CaO). Degradation was zero for the dye in direct sunlight without adding catalyst (Dye/sunlight).

This result clearly shows that photodegradation occurs more efficiently in presence of sunlight. Under sunlight excitation of catalyst takes place at

rapid rate than in the absence of sunlight. Similar reports have been reported for ZnO assisted photocatalytic degradation of azo dyes such as Congo red, Remazol red RR, and Benzopururine 4B [26,27].

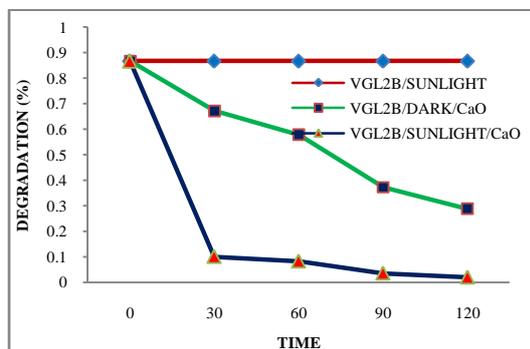


Fig 9: Effect of sunlight irradiation on photocatalytic degradation of Violet GL2B using CaO [CaO = 0.2 g/100ml, Violet GL2B=30mg/L, pH = 10].



Photo 5: Sunlight irradiation on photocatalytic degradation of Violet GL2B using CaO [(Dye/CaO/sunlight) CaO = 0.2 g/100ml, Violet GL2B=30mg/L, pH = 10].

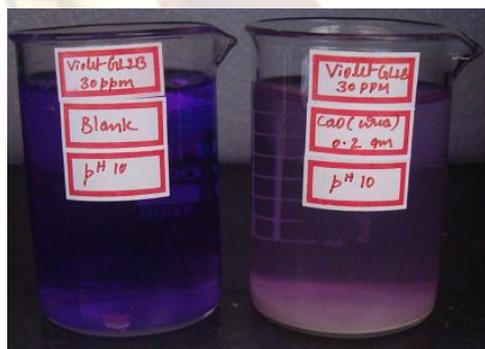
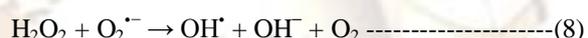
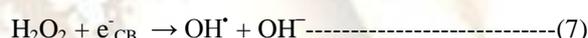
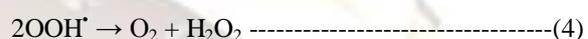
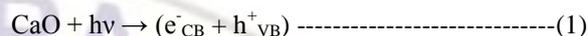


Photo 6: Sunlight irradiation on photocatalytic degradation of Violet GL2B using CaO [(Dye/dark/CaO) CaO = 0.2 g/100ml, Violet GL2B=30mg/L, pH = 10].

The experiment demonstrated that both sunlight and photocatalyst is needed for the effective destruction of Violet GL2B dye, because 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 colour 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 [28].

Mechanism of the photocatalytic degradation:



The mechanism of photocatalytic activity of CaO nanoparticle can be predicted. Under sunlight irradiation CaO molecules get excited and transfer electron to the conduction band (Eq 1). Electron in the conduction band of CaO can reduce molecular oxygen and produce the super oxide radical (Eq 2). Molecular oxygen, adsorbed on the surface of the CaO photocatalyst prevents the hole-electron pair recombination process [39, 30]. 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 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).

5. CONCLUSION

In the present study, the degradation efficiency of CaO nanoparticle was found to be higher than procured TiO₂ nanoparticle for the selected azo dye (Violet GL2B). The synthesis of CaO nanoparticle by solution combustion method is very easy and can be synthesized quickly. The application of CaO nanoparticle has proved to be most effective catalyst than the commercially available TiO₂ nanoparticle. This can be attributed to the more hydroxyl radicals (OH[·]) produced in CaO.

Further, the CaO nanoparticle can be used for the treatment of variety of effluents.

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