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SOLUTION COMBUSTION SYNTHESIS OF $BACAO_2$ NANOSCALE METAL OXIDE AND PHOTOCATALYSISOF METHYL VIOLET 10B DYE

NagendraNaik K., Yogendra K. and Mahadevan K. M.

[1]Department of P.G studies and Research in Environmental Science, Kuvempu University, JnanaSahyadri, Shankaraghatta, Shivamogga, Karnataka, India.
[2]Department of P.G studies and Research in Chemistry, Kadur P.G Center, Kuvempu University, Kadur, Karnataka, India.
*Author for Correspondence: Yogendra K. yogendraku@gmail.com

Abstract
Nanomaterials have played a vital role in the photocatalytic activity because of their efficiency in removing color and breaking the tough covalent bonds. $BaCaO_2$ nanoparticles were combined by solution combustion method utilizing fuel urea. The portrayal of incorporated nanoparticles was finished by X-ray diffraction (XRD), Scanning electron magnifying instrument (SEM), Energy Dispersive X-beam (EDX), and UV-Visible spectroscopy. The band gap of the nanoparticles was found to be 3.57eV. Photocatalytic degradation was determined against methyl violet 10B, by applying different conditions such as the concentration of catalyst, pH, the concentration of dye, and different irradiation conditions. The optimum value of catalyst concentration was found to be 0.5g/100ml and pH 10 by the experimental results. The highest degradation was achieved to be 96.5%. Hence, the efficiency of photo degradation of methyl violet 10B dye by using $BaCaO_2$ nanoparticles was ascertained.
Keywords -$BaCaO_2$, Degradation, Methyl violet 10B, Nanoparticles, Solution combustion.

1.INTRODUCTION

Methyl violet (Crystal violet) is a cationic dye belongs to the triphenylmethane class of dyes. This dye is used for biological staining to determine gram staining bacteria [1] [2]. This is also used as a textile dye, as a dermatological agent, and as paper print. Textile industries are the major source for water pollution, by releasing partially treated effluent containing chemicals to the water [3].

These untreated effluents damage to the aquatic living beings present in the water bodies[4] [5]. "These can harm to the living organisms because the water containing dye particles, these dyes have strong and different chemical structures, based on interchanged aromatic and heterocyclic groups"[6][7]. Dyes are non-degradable they can be easily dissolved in water, causing carcinogenic, mutagenic and cytotoxic effect to the living organisms. The removal of color from wastewater is a difficult process by traditional biological methods, but it transfers pollutants from one level to another level by producing secondary pollutants[8]. The utilization of advanced oxidation processes (AOPs) has been successful in the degradation of dyes; this includes the photocatalysis system which is dependent on the generation of powerful hydroxyl radicals, which are the critical species for the oxidation process [9]. The combining semiconductors with light and oxidants for the removal by using solar light of dyes and pollutants from water have emerged as a new and effective technique[10][11]. Due to their potential applications in environmental remediation, Advanced Oxidation Processes are increasingly popular[12] [13]. Among those, oxidation via ozone or hydrogen peroxide has been reported as an effective technique[14][15]. Since, ozonization requires artificial UV and H_2O_2 is expensive, employing such methods are not feasible.This investigation is executed to test the efficiency of synthesized Barium calciate nanoparticles in photocatalytic degradation of Methyl violet 10B. The impact of pH, dye concentration, irradiation conditions, and the catalyst concentration of Barium calciate nanoparticles were examined [16].

2. MATERIALS AND REAGENTS

Water-soluble dye Methyl violet 10B (λ_{max} 597nm) which is easily available in the market was obtained from Sigma Aldrich, Mumbai, India Fig. 1. "Chemicals like, Barium Nitrate ($Ba(NO_3)_2$ (99% A. R.), Calcium Nitrate ($Ca(NO_3)_2$) (99%, A. R.), Urea (NH_2CONH_2) (99.5%), were purchased from Hi-Media Chemicals, Mumbai. The UV-visible spectrophotometer (Elico, SL 177) was used for the absorbance recording at λ_{max}[17].

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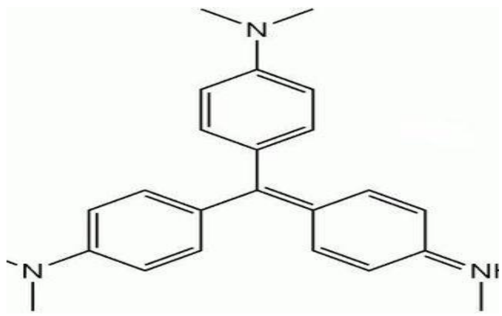


Fig 1:Chemical structure of Methyl violet 10B

2.1 SYNTHESIS OF NANOPARTICLES

$BaCaO_2$nanoparticles were prepared using solution combustion method, by redox mixtures of stoichiometric amounts of metal nitrates and fuel [18].

$3Ba(NO_3)_2 + 3Ca(NO_3)_2 + 10NH_2CONH_2 \rightarrow 3BaCaO_2 + 10CO_2 + 20H_2O + 16N_2$ Equation (1)

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

$$D = K\lambda / \beta \,\mathrm{COS}\theta$$

Where

$K = Scherrer's$ Constant

$\lambda =$ X - Ray Wavelength Equation (2)

$\beta =$ Peak width at half - maxima

$\theta =$ Bragg's Diffraction angle

2.2 CHARACTERIZATION OF NANOPARTICLES

2.2.1 XRD (X-RAY DIFFRACTION)

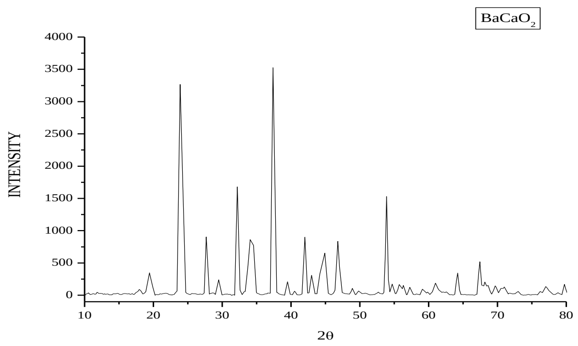
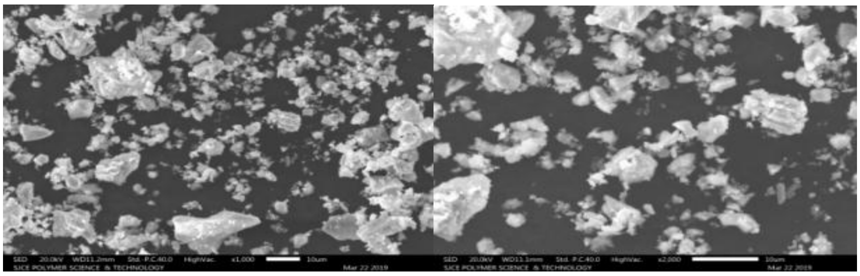


Fig 2: XRD of synthesized $BaCaO_2$

The XRD was done by using powder X-ray diffraction (Rigakudiffractometer) using Cu-Kα radiation (1.54 Å) in a θ-2θ configuration [19].In this work, the finely divided sample of $BaCaO_2$ by XRD studies found that the dimensions were varied from 25 nm to 60 nm and its average size was achieved at 40 nm.

2.2.2 SCANNING ELECTRON MICROGRAPH (SEM)

The SEM image of $BaCaO_2$ nanoparticle evinces the crystal morphology and exhibits uneven structure and size with sharp edges, the assembly of crystals can be observed in the image.



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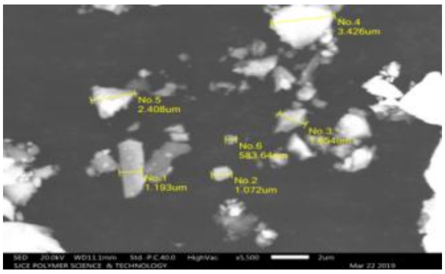

Fig 3:scanning electron micrographs of synthesized $BaCaO_2$nanoparticles

2.2.3 UV-VIS ABSORPTION SPECTROSCOPY

The $BaCaO_2$ absorption spectra were recorded employing UV-Vis spectrophotometer with a wavelength range of 200-800 nm [20]. It was admitted from the spectrum that, $BaCaO_2$ nanoparticles have sufficient transmission in the entire visible and IR region.OBG of the $BaCaO_2$ nanoparticle was found to be 3.57eV.

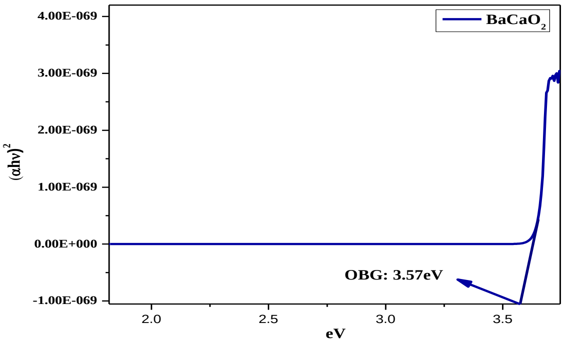

Fig 4: UV-absorption spectra of synthesized $BaCaO_2$nanoparticles

2.2.4 ENERGY DISPERSIVE X-RAY

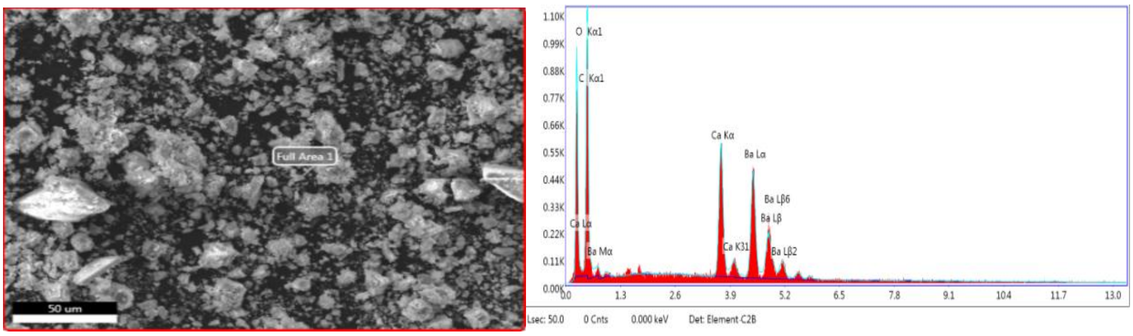

Fig 5:Energy dispersive X-ray of synthesized $BaCaO_2$nanoparticles

The EDX analysis of $BaCaO_2$ shows the uniform distribution of elements. The weight percentage of Carbon, Oxygen, Calcium, and Barium was observed to be 17.87, 31.23, 12.59, and 38.31. The atomic percentage recorded as 36.89, 48.41, 7.79, and 6.92. There was no impurity peaks found in the spectrum. Thus, the EDX analysis confirms the presence of $BaCaO_2$ composite without any impurity.

Table: EDX analysis of synthesized $BaCaO_2$ nanoparticle

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

3. RESULT AND DISCUSSION

Using the UV-Visible absorption studies the degradation of dye solutions was carried out, 597 nmwas the maximum wavelength (λ_{max})of Methyl violet 10B. Solar irradiation is the main source of photocatalytic

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degradation experiments. The standard of 20mg/L dye solution was made by mixing 20 mg. of Methyl violet 10B dye in 1 liter of double-distilled water and dye solution then used for degradation experiments against $BaCaO_2$ nanoparticle. Different parameters such as pH levels, Dye concentration, the $BaCaO_2$ dosage and different irradiation were used to examine the degradation, and results were noted. The pH balance of the dye solution is maintained accurately by adding HCl and NaOH. Finally, the color degradation percentage was calculated using the formula as follows.

$$Decolorization = \left(\frac{A0 - At}{A0}\right) \times 100$$

Equation (3)

3.1 EFFECT OF CATALYST CONCENTRATION

The photocatalyst concentration of the nanoparticle $BaCaO_2$was studied during the photocatalytic degradation over a range of 0.1 to 1g/100ml. for Methyl Violet 10B. The prepared nanoparticles in the lab have shown very good results. The $BaCaO_2$ nanoparticle with size 40 nm has shown 95.9% degradation. The photocatalytic activity was efficient at 0.5g/100ml in 120 minutes for $BaCaO_2$ concentration. With keeping the same dosage the experiments were repeated for accurate results. "The rapid degradation of Methyl Violet 10B dye is due to the generation of $OH^{\bullet}$ radicals, these radicals act as a main oxidizing species and also the availability of active sites on the surface of the nanoparticles" [21]. The percentage of degradation decreases from 0.6g to 1g is due to the overcrowding of the nanoparticles, hit with ground state catalysts, or the decrease in the photon entering into the solution.

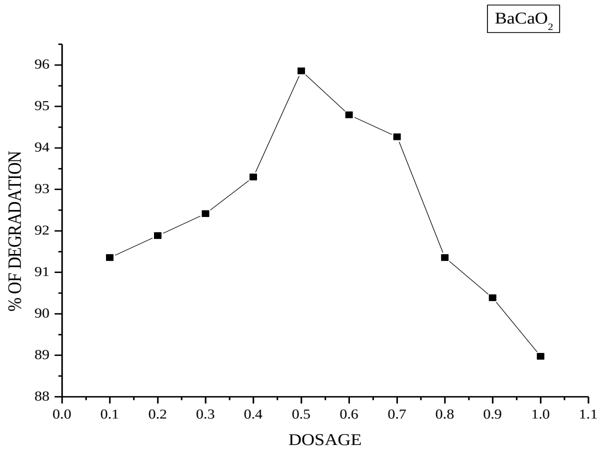

Fig 6: Effect of catalyst concentration on Methyl Violet 10Bat 120 minutes (Methyl Violet 10B=20 ppm, pH=7, $BaCaO_2$)

3.2 EFFECT OF PH

pH plays a main role in degrading dye solution and the experiments were conducted at pH starting from 2, 4, 6, 8 & 10. Based on the results it is proved that the capability of dye degradation essentially affected by the pH of the solution. On adding $BaCaO_2$ catalyst the degradation percentage was ranged from 89.4%, 90.2%, 91.00%, 93.3% to 96.5% for diverse pH levels of 2, 4, 6, 8and 10 at 120 minutes (0.5g/100ml) of nanoparticle for Methyl Violet 10B. The maximum degradation was achieved at pH 10.$BaCaO_2$ is protonated at low pH the active sites also be positively contents this results in the repulsion between active sites andMethyl Violet 10B dye[22]. As a result less degradation is observed at pH less than 10.The interaction between Methyl Violet 10B and $BaCaO_2$ nanoparticle leads to the generation of $OH^{\bullet}$ radicals and this generated $OH^{\bullet}$ radicals play a vital role as an oxidizing species required for photocatalytic degradation. The OH^{-} ions increase the formation of $OH^{\bullet}$ radicals by combing the semiconductor hole. The results illustrated that, the maximum degradation was shown in pH 10, and below pH 10 nanoparticle agglomerations reduce the adsorption sites of the dye molecules and also reduces the absorption of the photon.

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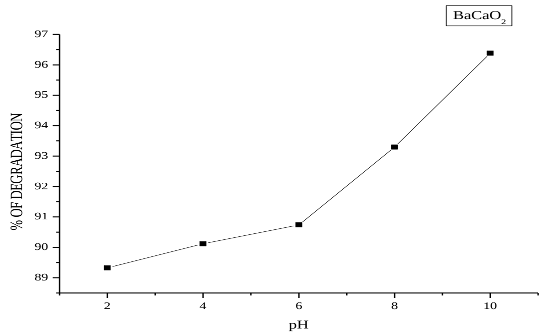

Fig 7:Effect of pH on Methyl Violet 10Bat 120 minutes (Methyl Violet 10B=20 ppm, $BaCaO_2$=0.5 g/100ml)

3.3 EFFECT OF INITIAL DYE CONCENTRATION

Methyl Violet 10B concentrations were varied from 20, 30, 40, and 50 ppm and experiments were executed.The obtained results for $BaCaO_2$ are 96.5% for 20ppm, 92.00% for 30ppm, 84.5% for 40ppm and 81% for 50ppm respectively Fig 8. As dye concentration increases the degradation decreases [23]. With the increase in the dye concentration the entering of photons is hindered and in the lesser concentration the reverse is noted [24][25]. These are the factors that are responsible for the degradation reaction.

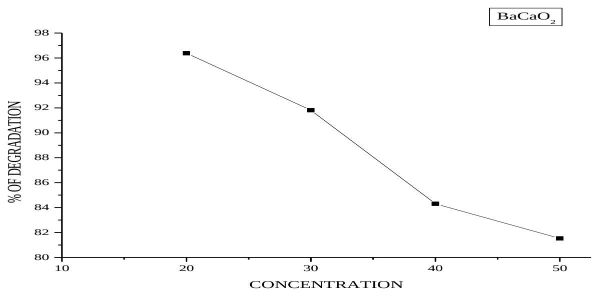

Fig 8: Effect of initial dye concentration of Methyl Violet 10B at 120 minutes.$BaCaO_2$ g/pH=0.5/10 and Methyl Violet 10B= (20, 30, 40 and 50 ppm)

3.4 EFFECT OF SUNLIGHT IRRADIATION

With three different experimental conditions of Dark, sunlight and UV were examined for irradiation studies. The rate of degradation was found to be increasing with irradiation time. For Dye/sunlight/$BaCaO_2$ experimental condition highest degradation of 96.5% was achieved, for dye/UV/$BaCaO_2$ 70.86% and for Dye/dark/$BaCaO_2$ 45% was recorded. "Degradation of Methyl violet 10B dye in dark condition is attributed to the concentration of more Ba^{2+} which enhances the movement of electrons from dye molecules and then to the OH^- which leads to increased hydroxyl production at the surface and decomposition of the adsorbed dye molecule"[26] [27] [28] Fig. 9. In the presence of sunlight, jumping of electrons from the catalyst surface takes place at a rapid speed than in the absence of light. These observations depict photo degradation occurs vigorously in the presence of natural sunlight[29].

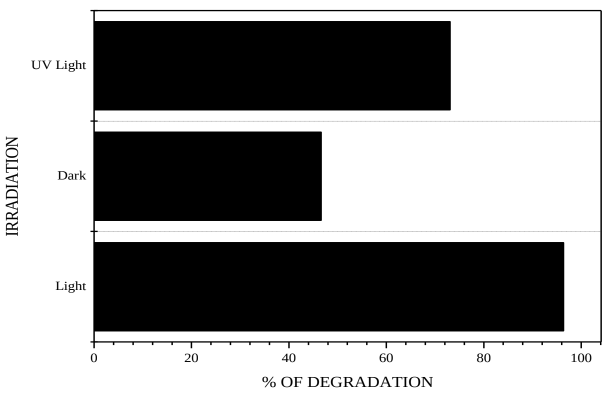

Fig 9: Effect of sunlight irradiation, Dark and UV conditions on photocatalytic degradation of Methyl Violet 10Bin 120 minutes

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4. CONCLUSION

The present study focused on the degradation of Methyl Violet 10Bdye under natural sunlight by synthesized $BaCaO_2$ nanoparticles. The degradation depends on the size and band gap of the nanoparticle [30]. $BaCaO_2$ nanoparticles achieved maximum degradation (96.5%) at 0.5g/100ml of catalyst for pH 10 in a short interval time (120 min) and compare to dark (45%) and UV (70.86%) condition. Hence, this can apply to the industry for the efficient treatment of the effluent which is hazardous to the environment and it is cost-effective.

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