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A Study on The Synthesis, Characterization and Photocatalytic Activity of Cao Nanoparticle Against Some Selected Azo Dyes

KEYWORDS: Coralene Navy Blue 3G, Coralene Violet 3R, Disperse Blue 2BL, CaO nanoparticle, Photocatalyst

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ABSTRACT *The Calcium oxide (CaO) nanoparticle was synthesized by solution combustion method using urea as a fuel. CaO nanoparticle was characterized by Scanning Electron Micrograph (SEM), X-Ray Diffraction (XRD) and UV-absorption spectroscopy. The average crystallite size was found to be 36nm and the band gap energy of CaO nanoparticle was 4.9eV. The photocatalytic degradation of Coralene Navy Blue 3G, Coralene Violet 3R and Disperse Blue 2BL in aqueous solution was investigated by using CaO nanoparticle by varying different parameters such as catalyst concentration, solution pH and dye concentration. All the experiments were conducted in presence of natural sun light. The highest degradation i.e., 99.79% (0.2g/100ml catalyst dose), 99.34% (0.4g/100ml catalyst dose) and 87.46% (0.3g/100ml catalyst dose) was achieved at pH 3 for Coralene Navy Blue 3G, Coralene Violet 3R and Disperse Blue 2BL in aqueous medium at 30ppm concentration of dyes.*

INTRODUCTION

Environmental pollutions associated with hazardous wastes and toxic water-pollutants have attracted much attention. Organic dyes are one of the major groups of pollutants in wastewaters released from textile and other industrial processes (Alemseged Eyasu *et. al.,* 2013). Within the overall category of dyestuffs, azo dyes constitute a significant portion and probably have the least desirable consequences in terms of the surrounding ecosystem (Bianco-Prevot *et. al.,* 2001& Ying Yu *et. al.,* 2005).

Colour is the first contaminant to be recognized from industries has to be removed before discharging into water bodies or on land. The wastewater contains coloured dye pollutants' can block both sunlight penetration and oxygen dissolution that are essential for aquatic life (Abdulraheem Giwa *et. al.,* 2012). In addition, the color of dyes also represents problems, like aesthetic merit, transparency and gas solubility in lakes and rivers causing an increase in biochemical oxygen demand (BOD) (Banat *et. al.,* 1996). Consequently, there is a considerable need to treat these coloured effluents before discharging them into various water bodies.

In recent years, a new class of techniques devoted to pollutant remediation, broadly referred to as advanced oxidation processes (AOPs). AOP methods are characterized by a common chemical action, which basically relies on the primary reactivity of $OH^{\bullet}$ radicals in driving oxidation processes, ultimately resulting in the mineralization of a variety of pollutants (Comparellia *et. al.,* 2005).

Within AOPs, photocatalyst-based degradation methods represent a very interesting branch of research as it does not require expensive oxidants and can be carried out at mild temperature and pressure and hence, it main advantages in comparison with other oxidation processes (Abdelkahhar Aguedach *et. al.,* 2008). With an appropriate light irradiation, the photocatalyst generates electron/hole pairs with free electrons produced in the empty conduction band leaving positive holes in the valence band. These electron/hole pairs are capable of initiating a series of chemical reactions that eventually mineralize the pollutants (Junpei Nishio *et. al.,* 2006).

There are many Semiconductor photocatalysts such as CdS, ZnS, CdSe, TiO_2, etc, have attracted extensive attention for the degradation of organic dye pollutants in water (Koca *et. al.,* 2002, Wu *et. al.,* 2001).

Among the semiconductors whose photocatalytic properties have been studied, TiO_2 is the most commonly used, because it is effective, stable, harmless, and inexpensive (Dindar *et. al.,* 2001, Rongliang Qiu *et. al.,* 2008 and Comparellia *et. al.,* 2005). Similar kind of work was reported by *Yogendra et. al.* by using newly synthesized nanoparticles like $CaAl_2O_4$, $CaZnO_2$, ZnO, $CaMgO_2$(Bhavya *et. al.,* 2015, Bhavya *et. al.,* 2014, Madhusudhana *et. al.,* 2012, Gopalappa *et. al.,* 2012, Yogendra *et. al.,* 2011, and Madhusudhana *et. al.,* 2011).

Keeping in view of advantages over the reported photocatalysts, and in continuation of our work on search of promising and efficient photocatalysts in this paper we report the synthesis, characterization and photocatalytic property of CaO nanoparticle. Its photocatalytic property was investigated against *Coralene Navy Blue 3G, Coralene Violet 3R and Disperse Blue 2BL* solutions as the model dyes.

MATERIALS

The commercially available water soluble azo dyes Coralene navy Blue 3G (λmax 530nm), Coralene Violet 3R (λmax 480nm) and Disperse Blue 2BL (λmax 642nm) were obtained from Colortex Limited, Surat, Gujrat (Figure 1, 2 and 3).

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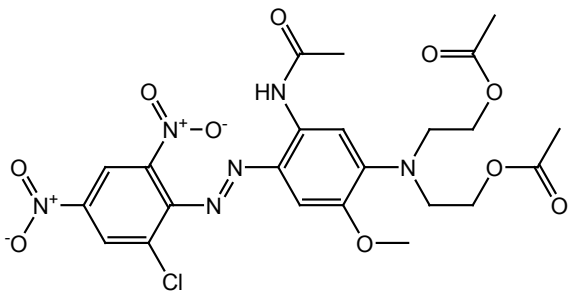

Figure 1: Chemical structure of Coralene Navy Blue 3G

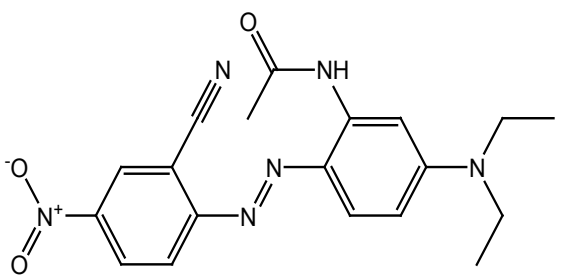

Figure 2: Chemical structure of Coralene Violet 3R

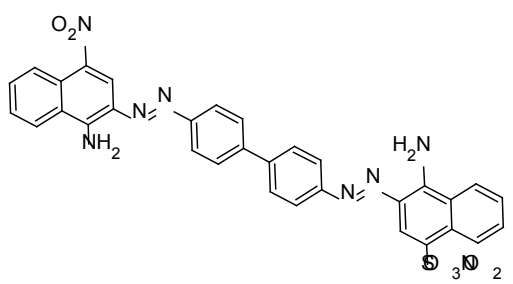

Figure 3: Chemical structure of Disperse Blue 2BL

The following materials were used to synthesize the CaO NPs: calcium nitrate (Ca (NO3)2.4H2O; 99%) and urea (NH2CONH2; 99.5%) purchased from Hi-Media chemicals, Mumbai, India and distilled water. All chemicals were analytical grade and were used as received. The UV-VIS single beam spectrophotometer-119 (Systronics) has been used for recording absorbance at λmax. Later the absorbance was recorded in UV-VIS spectrophotometer 169 (Systronics).

CaO NPs SYNTHESIS

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. Initially Ca(NO3)2.4H2O (14.16g) and NH2CONH2 (6.0g) were dissolved in 100cm3 silica crucible using distilled water. Then the crucible was placed in a preheated muffle furnace at 500°C for calcination. The resulting combustion product was grinded to make it amorphous. According to propellant chemistry the reaction is as follows (Madhusudhana et. al., 2012).

$6\ Ca(NO_3)_2 + 10\ NH_2\ CO\ NH_2 \rightarrow 6\ CaO + 10\ CO_2 + 20\ H_2O + 16\ N_2$

CHARACTERIZATIONS OF NPs

All synthesized NPs were characterized by powder X-ray diffractograms (XRD), which were measured over the angular range of 2θ = 0° - 60° using Rigaku diffractometer equipped with a copper tube (Cu Kα, λ = 1.54056 Å). Images revealing the morphologies and shapes of the NPs were obtained using a scanning electron microscope (SEM). Absorption spectra of the different metal oxide nanoparticles were recorded using a (Ocean Optics DH-2000) UV-Vis spectrophotometer over the wavelength range 200-1200 nm at Nano Research Laboratory, Department of Nanotechnology, Kuvempu University. From this spectrum, it has been inferred that the nanoparticles have sufficient transmission in the entire visible and IR region.

EXPERIMENTAL PROCEDURE FOR PHOTOCATALYTIC DEGRADATION OF SELECTED AZO DYES UNDER VISIBLE RADIATION:

The UV-VIS spectrophotometer 119 (Systronics) was used for the determination of absorbance. The λmax value of Coralene navy Blue 3G and Coralene Violet 3R was found to be 530nm and 480nm respectively. The photocatalytic experiments were carried out under direct sunlight. The known concentration of dye solutions were prepared by dissolving 30mg of Coralene Navy Blue 3G, Coralene Violet 3R and Disperse Blue 2BL separately in 1000ml double distilled water and investigated for its decolorization in the presence of Calcium oxide nanoparticle at different catalyst dosages and pH levels. Initially, 10ml of 30 mg/L dye samples were tested with different catalyst dosage (from 0.01g to 0.1g) in the presence of direct sunlight. After the photocatalytic decolorization, the extent of decolorization 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. The percentage of degradation was determined by using the following equation, the percentage of decolourization,

$$D = ((Ao - At) \div Ao) \times 100$$

Where, A_0 is the initial absorbance of the dye solution, At is absorbance at time interval't' i.e., after 120 minutes.

MECHANISM OF THE PHOTOCATALYTIC DEGRADATION:

The mechanism of photocatalytic activity of nanoparticles can be predicted as given below.

Step-1: Under sunlight irradiation, nanoparticle molecules get excited and transfer electrons to the conduction band.

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

Step 2: An electron in the conduction band of the nanoparticles can reduce molecular oxygen and produce the super oxide radical.

$e\text{-}\ CB+ O_2 \rightarrow O_2\bullet-$(2)

Step 3: Molecular oxygen, adsorbed on the surface of the photocatalysts prevents the hole-electron pair recombination process. 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.

$H_2O + O_2\bullet- \rightarrow OOH\bullet + OH-$ (3)

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$2OOH\bullet \rightarrow O2 + H_2O_2$ (4)

$O_2\bullet- + dye \rightarrow dye\text{-}OO\bullet$ (5)

Hydrogen peroxide can be generated in another path.

$OOH\bullet + H_2O + e\text{-}CB \rightarrow H_2O_2 + OH-$ (6)

Step 4: Hydrogen peroxide can form hydroxyl radicals which are powerful oxidizing agents.
$H_2O_2 + e\text{-}CB \rightarrow OH\bullet + OH-$ (7)

$H_2O_2 + O_2\bullet- \rightarrow OH\bullet + OH- + O_2$ (8)

Step 5: The radicals produced are capable of attacking dye molecules and degrade them.
$OH\bullet$ / $O2\bullet-$/ $CaO\bullet++dye \rightarrow$ Dye degradation (9)

RESULTS:
CHARACTERIZATIONS OF NPs:
The SEM images of synthesized CaO are shown in Figure 4. The SEM images in figure shows the NPs are crystal like structures.

The crystalline structures of NPs were examined by XRD (Figure 5). The crystallite size based on X-ray peak broadening was estimated using Debye-Scherrer's equation (Equation 1) (El-Trass et al., 2012):

Debye Scherrer's formula $D = \left(\frac{K\lambda}{\beta \cos \theta}\right)$ ----- Eq. 1

where k is an empirical constant equal to 0.9, λ is the wavelength of the X-ray source (1.5405 Å), β is the full width at half maximum of the diffraction peak, and θ is the angular position of the peak. The average value calculated for the crystallite size for CaO NPs is 36 nm.

The UV-absorbance spectrum of synthesized CaO is presented in Figure 6. The absorbance spectrum of synthesized CaO was recorded using UV-VIS spectrophotometer (Ocean Optics DH-2000) over the wavelength range 200-1200nm.The band gap energy of the CaO nanoparticle was calculated using the following simple conversion equation. The band gap equation is calculated using the Planck's equation as follows.

$E = hC/\lambda$

h = Planck's constant,

C = Velocity of light,

λ = wavelength,

h = 4.135×10−15 eV,

C = 3×108 m/s,

λ= −−−×10−9nm

Band gap energy (eV) = 4.135×10−15×3×108×109

Band gap energy (eV) = 1240/wavelength (nm)

The band gap energy of CaO particle was 4.94 eV.

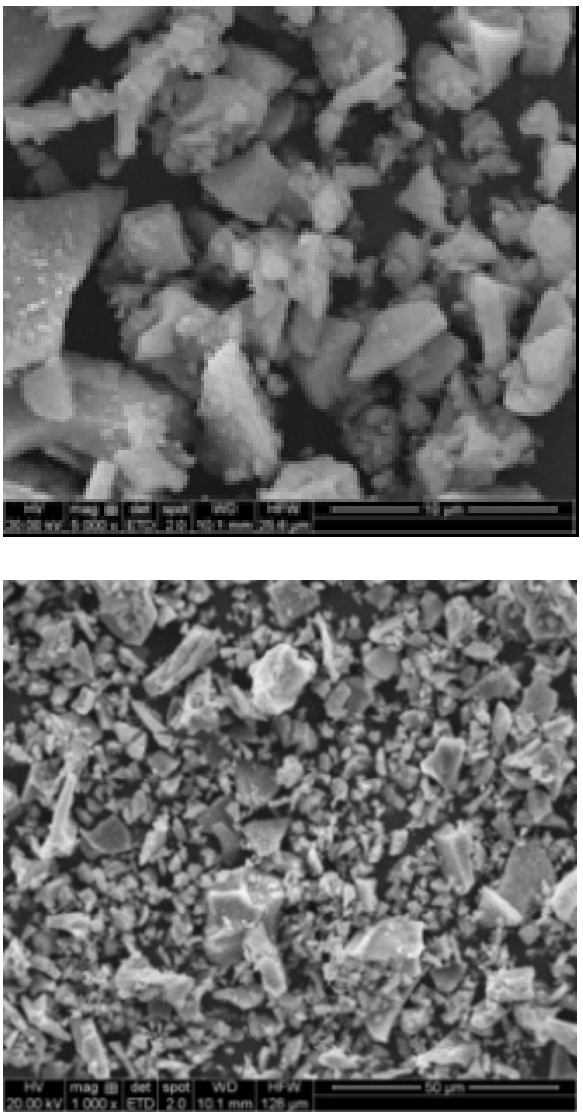

Figure 4: SEM image of CaO NPs

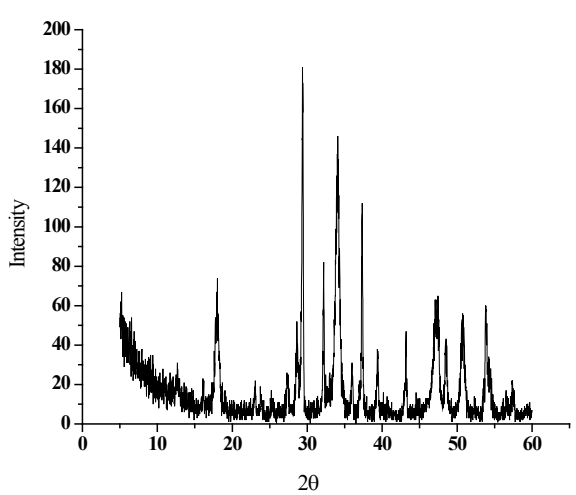

Figure 5: XRD of CaO NPs

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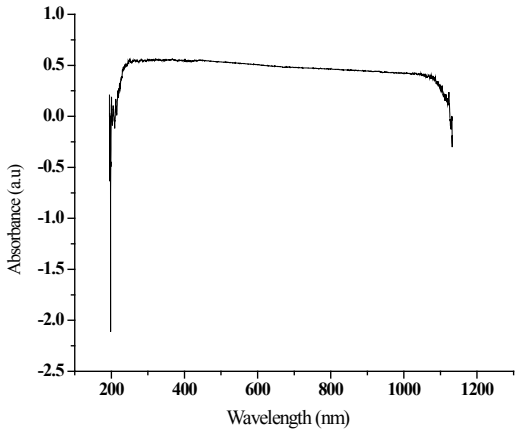

Figure 6: UV-absorption spectra of synthesized CaO

EFFECT OF CATALYST CONCENTRATION ON PHOTO-CATALYTIC DEGRADATION OF DYE:

Initially, percent photocatalytic degradation of dye increased with the increase in catalyst concentration upto 0.2g/100ml, 0.4g/100ml and 0.3g/100ml of Coralene Navy Blue 3G, Coralene Violet 3R and Disperse Blue 2BL respectively. At still higher catalyst concentration, however, the dye degradation decreased. This may be due to decreasing the electron-hole recombination. The highest degradation i.e., 93.26% for 0.2g/100ml of Coralene Navy Blue 3G, 99.52% for 0.4g/100ml of Coralene Violet 3R and 84.16% for 0.3g/100ml of Disperse Blue 2BL was observed.

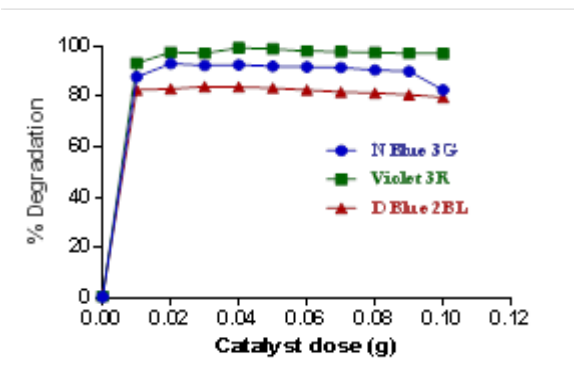

Figure 7: Plots of % photocatalytic degradation of dyes under visible radiation at varying catalyst concentration using i.e., from 0.01 to 0.1 g/10mlof catalyst (CaO) and pH (=7)

EFFECT OF pH ON PHOTOCATALYTIC DEGRADATION OF DYE:

Plots of percent degradation of dyes Vs. various pH using dye initial concentration = 30ppm and optimum catalyst load (0.2g/100ml, 0.4g/100ml and 0.3g/100ml of Coralene Navy Blue 3G, Coralene Violet 3R and Disperse Blue 2BL respectively) at 2h irradiation time are presented in Figure 8. It is observed that %degradation of dyes increases when pH is raised from 2 to 3 but at still higher pH the degradation of the dye is gradually decreased. Degradation of the dye remains almost invariant in the pH 3 to 7 for Coralene Navy Blue 3G and Coralene Violet 3R. But for Disperse Blue 2BL there was a sudden decreased degradation percentage can be seen after pH 3 which still more decreases gradually with increase in pH levels. This may be due to the existence of negative charge at CaO photocatalyst due to the adsorbed OH- ions at its surface and the adsorption of negatively charged dye at the photocatalyst surface is unlikely and hence a decrease in the observed photocatalytic degradation.

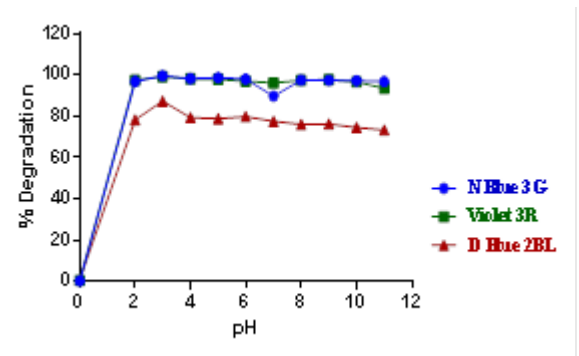

Figure 8: Plots of % degradation vs. pH for degradation of dye aqueous solution under visible radiation at time interval of 2h. Dyes initial concentration = 30ppm and optimum load of photocatalyst CaO

EFFECT OF DYE INITIAL CONCENTRATION ON PHOTO-CATALYTIC DEGRADATION:

Plots of % photocatalytic degradation of dyes at varying dye initial concentration using a fixed amount of catalyst CaO are presented in Fig.9. Photocatalytic degradation of the dye decreases with the increase in its initial concentration.

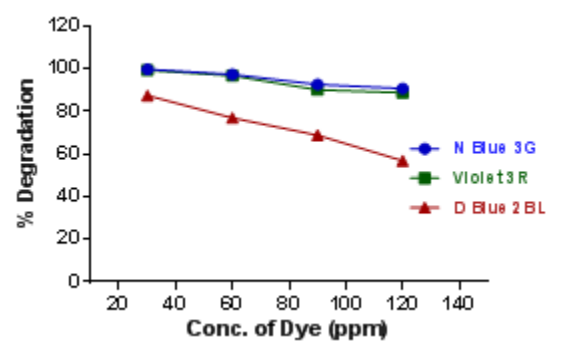

Figure 9: Plots of % photocatalytic degradation of dyes under visible radiation at varying dye initial concentration using fixed amount (0.2g/100ml, 0.4g/100ml and 0.3g/100ml of Coralene Navy Blue 3G, Coralene Violet 3R and Disperse Blue 2BL respectively) of catalyst (CaO) and pH (=3)

CONCLUSION:

Calcium oxide nano-size semiconductor photocatalyst was synthesized using chemical combustion method. The product obtained after combustion was characterized using SEM, XRD and UV-visible spectroscopic techniques. The effects of catalyst concentration, dye initial concentration and solution pH on photocatalytic degradation under

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visible radiation were studied. Among the three selected dyes i.e., Coralene Navy Blue 3G, Coralene Violet 3R and Disperse Blue 2BL, Coralene Navy Blue 3G, the Coralene Violet 3R showed 99% degradation whereas 87% of degradation was reported with respect to Disperse Blue 2BL. It was also found that, the degradation of the dye decreased with the increase of dye concentration over the studied concentration range, optimum catalyst concentration (0.2g/100ml, 0.4g/100ml and 0.3g/100ml of Coralene Navy Blue 3G, Coralene Violet 3R and Disperse Blue 2BL respectively) and optimum pH (= 3.0) was required for highest dye degradation.

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