

# Photocatalytic Degradation of Direct blue 14 in Sunlight/SrCaO<sub>2</sub> system

Kiran G.R<sup>1</sup>, Yogendra K<sup>1\*</sup>, Mahadevan K. M<sup>2</sup>, Madhusudhana N<sup>1</sup>, Santhosh A.M<sup>1</sup>.

<sup>1</sup>Department of P.G Studies and Research in Environmental Science, Kuvempu University, Jnana Sahyadri, Shankaraghatta, Shivamogga, Karnataka, (India)

<sup>2</sup>Department of Chemistry, Kador P.G Center, Kuvempu University, Kador, Karnataka, (India)

**Abstract:** The efficiency of synthesized SrCaO<sub>2</sub> nano powder as a promising material for the catalysis of direct blue 14 (DB 14) dye in presence of sunlight is established in the present study. The synthesized nanoparticles are characterized by using UV–VIS spectroscopy, XRD and SEM. An influence of selected parameters such as varying SrCaO<sub>2</sub> dosages, dye concentrations, solution pH and different conditions to model azo dye was verified. The results suggested that the photocatalytic efficiency of synthesized SrCaO<sub>2</sub> nanoparticles is found to be >90% for DB 14.

**Keywords:** Direct blue 14, SrCaO<sub>2</sub>, Photocatalyst and nanoparticle.

## I. INTRODUCTION

As we know that, we are struggling and affected because of environmental pollution it occurs when pollutants contaminate the surroundings, which brings about changes that affect our normal lifestyles adversely. Pollutants are the key elements or components of pollution which are generally waste materials of different forms. Pollution disturbs our ecosystem and the balance in the environment. With modernization and development in our lives pollution has reached its peak.

Among all sources of pollution industrial activities is one of the sources of environmental pollution [1]. The urbanization and the rapid growth of industrialization are causing through environmental pollution the greatest harm to the surrounding aquatic and terrestrial organisms [2]. In which the textile industry worldwide involves a large number of washing, bleaching, dyeing, and conditioning processes [3]. The industry is well-known for its extensive water consumption and discharges [4]. Each process wastewater stream has a unique pollutant characteristics and flow rate. The azo dyes and their breakdown products have been found toxic to aquatic life, mutagenic/carcinogenic and genotoxic [5], [6]. Now a day's traditional treatment are not able to remove the complete colour, it can transfer pollutants from one phase to another phase. However researcher has developed advance oxidation process (AOP) for the complete destruction of dyes and complete mineralization by generates powerful oxidising agent hydroxyl radicals [7]. In AOP photocatalysis plays important role in the removal of colour by using different metal oxide nanoparticles.

In continuation of our work, we synthesized strontium calcite metal oxide nanoparticle for the removal of direct blue 14 dye by varying parameters such as, catalyst concentration, pH and dye concentration.

## II. MATERIALS AND METHODS

The DB 14 is a di-azo dye, used as a model dye for the degradation experiment was provided by the Sisco Research Laboratories Pvt. Ltd., Taloja, Maharashtra. Its chemical structure is represented in figure 1. Strontium nitrate, Calcium Nitrate, urea were used as the starting materials. The chemical Strontium nitrate (Sr(NO<sub>3</sub>)<sub>2</sub> · 4H<sub>2</sub>O) (99%, AR) was purchased from Loba Chemie Pvt. Ltd, Mumbai and Calcium Nitrate (Ca (NO<sub>3</sub>)<sub>2</sub>) (99%, A. R.), Urea (NH<sub>2</sub>CONH<sub>2</sub>) (99.5%) were purchased from Hi-Media Chemicals, Mumbai and were used without further purification.

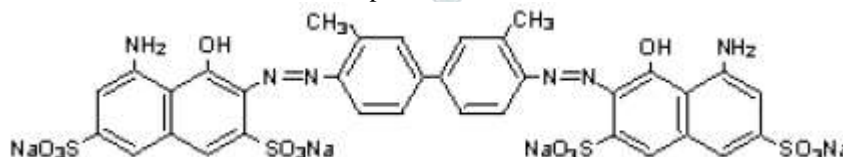
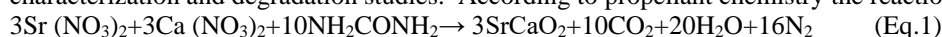


Fig. 1. Chemical Structure of DB 14 di- azo dye.

## 2.1 EXPERIMENTAL

### 2.1.1 SYNTHESIS OF NANOPARTICLE

The synthesis of SrCaO<sub>2</sub> nanoparticle was prepared by solution combustion method using urea as a fuel. The ratio was taken according to the stoichiometric equation for strontium calcite nanoparticle. Strontium nitrate (6.35g), calcium nitrate (7.09g) and urea (6.05g) were taken in a silica crucible and dissolved using 25ml of distilled water. Crucible was then introduced into the muffle furnace which was preheated to 600°C (Photo 1). The solution mixture boils and undergoes calcinations to form the product. Thus the obtained product was crushed in to a fine powder with the help of mortar and pestle which is then used for characterization and degradation studies. According to propellant chemistry the reaction is as follows.





**Photo 1:** Synthesis of Nanoparticles by solution combustion method SrCaO<sub>2</sub>.

### 2.1.2 CHARACTERIZATION OF NANOPARTICLE

The XRD was performed by powder X-ray diffraction (Rigaku diffractometer) using Cu-K $\alpha$  radiation (1.5406 Å) in a  $\theta$ -2 $\theta$  configuration. The band gaps measured using UV-VIS spectrophotometer (Ocean Optics DH- 2000) over the wavelength range 200-1000 nm at Nano Research Laboratory, Department of Nanotechnology, Kuvempu University. The surface morphology of SrCaO<sub>2</sub> was studied by SEM analysis using S-3400N at vijjana bhavan, Mysore University.

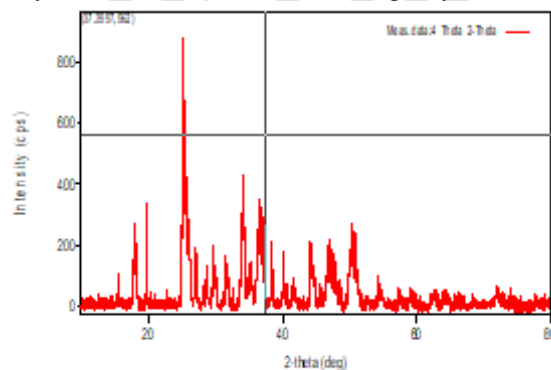
### 2.1.3 PHOTOCATALYTIC ACTIVITY

Photocatalytic efficiency of SrCaO<sub>2</sub> NPs was evaluated for DB 14 dye under visible irradiation. 0.2g/100ml of SrCaO<sub>2</sub> catalyst was added to the 100ml of 30PPM of aqueous DB14. The mixture was stirred and exposed to solar irradiation for 90min. The dye concentration was monitored spectrophotometrically at 711nm, where the absorbance is maximum for DB 14.

## III. RESULT AND DISCUSSION

### 3.1. X-RAY DIFFRACTION (XRD)

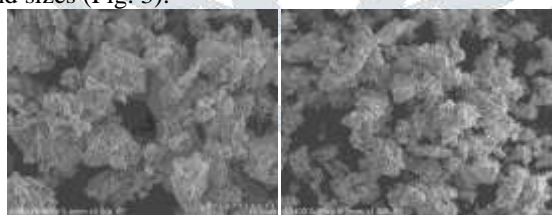
The XRD analysis of the prepared SrCaO<sub>2</sub> NP is presented in Figure 2. According to the Debye-Scherrer's formula  $D = K\lambda/(\beta \cos\theta)$ , where, K is the Scherrer's constant,  $\lambda$  the X-ray wavelength,  $\beta$  is the full width at half-maximum, and  $\theta$  is the Bragg diffraction angle calculated using the Debye-Scherrer's formula. The average crystallite size of the SrCaO<sub>2</sub> was found to be 37nm.



**Fig. 2:** X-ray Diffraction of SrCaO<sub>2</sub>.

### 3.2. SCANNING ELECTRON MICROGRAPH (SEM)

The SEM study shows thickly arranged layers of the nanoparticles which looks like sandwiched over one another. Also it can be seen with irregular shapes and sizes (Fig. 3).



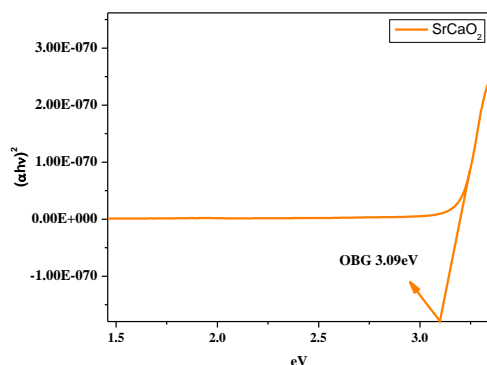
**Fig. 3:** SEM images of SrCaO<sub>2</sub>

### 3.3. UV-VIS ABSORPTION SPECTROSCOPY

Absorption spectra of the SrCaO<sub>2</sub> metal oxide NP was recorded using UV-VIS spectrophotometer over the wavelength range 200-1000 nm. From this spectrum, it has been inferred that, the NP have sufficient transmission in the entire visible and IR region. The band gap energy of the SrCaO<sub>2</sub> NP was calculated using The Optical band gap (OBG) equation.

$$(\alpha h\nu) = B(h\nu - E_g)^n$$

Where: ' $h\nu$ ' is the photon energy, ' $B$ ' is the constant and ' $n$ ' is the power factor and that takes 1/2, 2, 3/2 and 3 allowed direct, allowed indirect, forbidden direct and forbidden indirect transitions respectively. The OBG of the NaCaO found to be 3.09eV.



**Fig 4:** UV-absorption spectra of synthesized Nanoparticles SrCaO<sub>2</sub>.

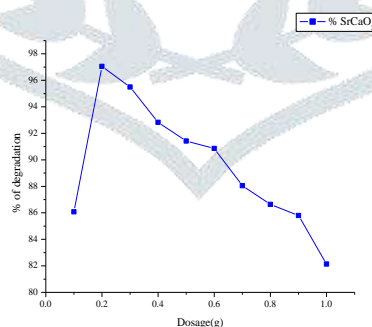
The band gap energy of SrCaO<sub>2</sub> was found to be 3.1 eV. With this, we can say that the band gap of the semiconductor has been found to be particle size dependent.

### 3.4. MECHANISM OF PHOTODEGRADATION

SrCaO<sub>2</sub> photocatalyst was found to be photo-excited under solar irradiation. When sunlight strikes the nanoparticle surface, an electron from its valance band (vb) jumps to the conduction band (cb) leaving behind positively charged hole (h<sup>+</sup><sub>vb</sub>). The negative charge is increased in the conduction band (e<sup>-</sup><sub>cb</sub>) and photocatalytic active centers are formed on the surface of SrCaO<sub>2</sub> NP. The valence band holes react with the chemisorbed H<sub>2</sub>O molecules to form reactive species such as ·OH radicals, which subsequently react with dye molecules to cause their complete degradation. The e<sup>-</sup><sub>cb</sub> and h<sup>+</sup><sub>vb</sub> can be trapped in surface where they may react with species adsorbed or close to the surface of the particle. The e<sup>-</sup><sub>cb</sub> can react with an acceptor, such as dissolved O<sub>2</sub>, which consequently is transformed into a super oxide radical anion (O<sub>2</sub><sup>-</sup>) which leads to the formation of additional H<sub>2</sub>O. On the other hand, h<sup>+</sup><sub>vb</sub> could interact with donors, such as OH<sup>-</sup> and H<sub>2</sub>O<sup>+</sup>, to form ·OH radicals. This is how these radicals also attack the DB 14 dye molecules and degrade them [8], [9].

### 3.5. Effect of Catalyst Loading

A series of experiment were carried out to assess the optimum catalyst loading by varying the amount of catalyst from 0.1g to 1g/100ml in neutral pH. The percentage of degradation of dye has shown appreciable results and highest percent degradation of 97.04 % was recorded at 0.2g/100ml (Fig. 5). The photodegradation rate of the DB14 was found to increases with increase in the catalyst loading, this increase in the degradation of active sites of DB14 dye with SrCaO<sub>2</sub> photocatalyst amount may be due to an increase in the active sites available on the catalyst surface for the reaction, which in turn increases the rate of radical formation and decrease with the increase in the catalyst concentration increased beyond the optimum catalyst a general characteristic of heterogeneous photocatalyst [10], further the increase in the catalyst loading the rate of degradation was decreases due to excess loading of catalyst leads to reduced the light penetration through the solution and decrease in the number of active sites on the surface area due to the aggregation of nanoparticle at high concentration, hence it requires a number active surface area. While below the level, it assumed that the catalyst surface and adsorption of the light by the catalyst are limiting factor [11], [12].



**Fig 5:** Effect of SrCaO<sub>2</sub> catalyst concentration on dye solution at 90 minutes=30ppm, pH=7.

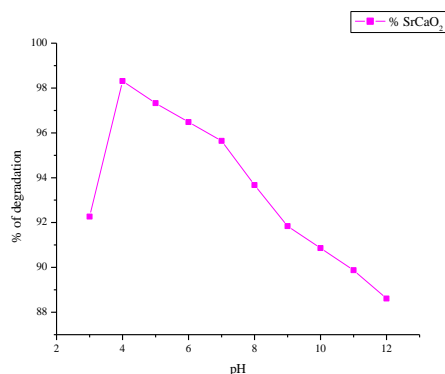


**Photo 2:** Effect of catalyst concentration on DB 14 at 90 minutes [DB 14=30 ppm, pH=7, SrCaO<sub>2</sub> (urea)]

### 3.6. Effect of pH

The pH plays a major role in the treatment of waste water and also generation of hydroxyl radicals. The degradation of DB14 dye was investigated by varying pH ranging from 3 to 12. The percentage of degradation of DB14 dye (Fig.6) increased from 92.26% to 98.31% when pH level was increased from pH 3 to pH 4 and decreased to 88.60% when pH was increased to 12 for the time interval of 90 minutes for the optimum catalyst dose of 0.2g/100ml. The maximum percent degradation was achieved at pH 4. The interaction of DB 14 dyes on the surface of the catalyst increases the generation of OH· radicals. These OH<sup>-</sup> ions will

generate more  $\bullet\text{OH}$  radicals by combining with the hole of the semiconductor and the  $\text{OH}\bullet$  radicals are the main oxidizing species responsible for photocatalytic degradation. The experimental data revealed that higher degradation of DB14 was observed in acidic medium. After the optimum pH the degradation efficiency was decreased, which can be attributed to the amphoteric nature of the catalyst [7], [13].



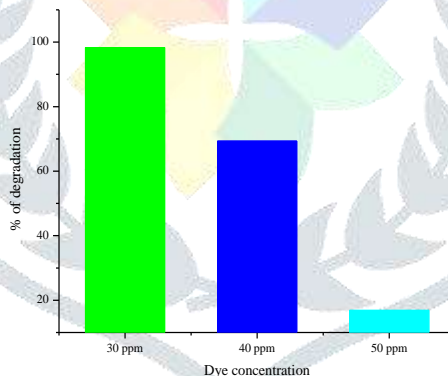
**Fig 6:** Effect of pH on DB 14 dye at 90 minutes [DB 14=30ppm,  $\text{SrCaO}_2$  (urea)]



**Photo 3:** Effect of pH on DB 14 at 90 minutes [DB 14=30 ppm,  $\text{SrCaO}_2$  (urea)]

### 3.7. Effect of Initial Concentration of Dye

The experiments were conducted to study the effect of initial dye concentration by varying the DB 14 concentration from 30ppm to 40 and 50ppm (Photo 3). The degradation efficiency and the solution concentrations are inversely related and the degradation percent for different concentrations are 98.31%, 69.33% and 16.87% for 30, 40 and 50ppm respectively (Fig 7). These experiments illustrated that the degradation efficiency was directly affected by the concentration of dye solutions. The decrease in the percent degradation with an increase in dye concentration ascribed to the equilibrium adsorption of dye on the catalyst surface which results in a decrease in the active sites and in low concentration the reverse effect is observed. Hence, the rate of degradation decreases with increase in the dye concentration [14], [15], [13], [16].



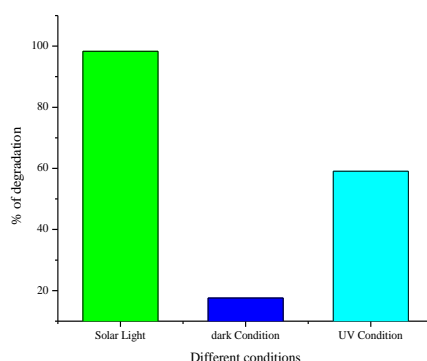
**Fig 7:** Effect of initial dye concentration on the photocatalytic degradation of DB14 ( $\text{SrCaO}_2$  g/pH=0.2/4)



**Photo 4:** Effect of initial dye concentration on the photocatalytic degradation of DB 14 [ $\text{SrCaO}_2$  (urea) g/pH=0.2/4 and DB 14 = (30, 40 and 50) ppm]

### 3.8. Effect of Different Conditions

The photocatalytic degradation of DB14 dye (30ppm) under three different experimental conditions were examined, *i.e.*, through, dye/dark/catalyst, dye/UV/catalyst and dye/sunlight/catalyst. DB14 dye solution when exposed directly to the sunlight without adding the catalyst, the degradation was found to be nil over a time interval of 90min. The degradation rate was found to be increased with increase in irradiation time for dye/sunlight/  $\text{SrCaO}_2$  condition. Maximum degradation recorded was 98.31%, 59.07% and 17.58% was recorded for dye/sunlight/  $\text{SrCaO}_2$ , dye/UV/  $\text{SrCaO}_2$  and dye/dark/ $\text{SrCaO}_2$  respectively. These results clearly indicate that, photodegradation occurs most efficiently in the presence of sunlight. Under sunlight, excitation of electrons from the catalyst surface takes place more rapidly than in the absence of light. Similar observations have been reported for photocatalytic degradation of dyes. [17], [18], [19].



**Fig 8:** Effect of sunlight irradiation with respect to Dark condition and UV condition on photocatalytic degradation of DB14 in 90 minutes.



**Photo 5:** Effect of sunlight irradiation with respect to Dark condition and UV condition on photocatalytic degradation of DB 14 in 90 minutes.

#### IV. CONCLUSION

In the present study, a simple and convenient method has been reported for the synthesis of SrCaO<sub>2</sub> nanoparticle. The synthesized SrCaO<sub>2</sub> nanoparticle was characterized by SEM, XRD and UV-absorption studies. The average crystallite size was found to be 37nm and the band gap energy of SrCaO<sub>2</sub> particle was 3.1eV. The photocatalytic degradation of DB 14 dye by SrCaO<sub>2</sub> nanoparticle in presence of sun light showed maximum degradation of 98.31% (0.2g/100ml catalyst dose and at pH 4) for DB 14 at 90 minutes when compared to the UV irradiation and dark conditions. The present protocol can also upgraded to large scale industrial decolourisation of DB14 azo dye.

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