Photocatalytic Degradation of Coralene Dark Red 2B Azo Dye Using Calcium Zincate Nanoparticle in Presence of Natural Sunlight: An Aid to Environmental Remediation


Abstract—Release of colored textile effluents is undesirable in the aquatic environment as it limits the utilization of the water resources. Photocatalytic decolorization is an alternative method to other conventional inefficient physico-chemical and biological methods to treat toxic effluents. In the present study, the synthesized Calcium zincate nanoparticle (CaZnO2) of average crystal size 43.59 nm was used as a photocatalyst in presence of sunlight against Coralene Dark Red 2B azo dye (30mg/L). Calcium zincate nanoparticle was synthesized by a simple solution combustion method and characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD). Adsorption studies were carried out at different pH, and photocatalyst dosages. The Calcium zincate nanoparticle was found to be an efficient low cost photocatalyst which degraded Coralene Dark Red 2B dye in presence of sun light in a relatively short period of time.

Index Terms—Calcium Zincate (CaZnO2), Coralene Dark Red 2B, Decolorization, Nanoparticle, Photocatalytic Activity.

I. INTRODUCTION

Dyes and pigments are widely used in the textiles, paper, plastics, leather, food and cosmetic industry to color their products. At present, more than 10,000 dyes have been effectively commercialized [1]. Azo dyes represent a major group of dyes and have wide application in textile industries because of their ease of synthesis, versatility and cost-effectiveness. Though many of these dyes are banned for commercial sale and use, they are still largely available and used in textile industries since they are cheap and applicable to a large variety of textiles. Due to inefficiencies of the industrial dyeing process, 10 - 15% of the dyes are lost in the effluents of textile units which render them highly colored [2], [3]. Azo dyes found in textile effluents pose a great environmental threat since its release is undesirable to the aquatic environment as they reduce light penetration, thereby affecting aquatic life and limits utilization of the water media. Most of commercial azo dyes are chemically stable and are difficult to remove from wastewater as they are stable to light, heat and oxidizing agents [4], causing environmental concern because of their color, biorecalcitrance, potential toxicity and carcinogenicity to animals and human beings [5], [6]. These dyes are xenobiotics and their decolorization in nature is commonly used do not achieve total decolorization of colored effluents or they have operational difficulties are too expensive, moreover traditional biological wastewater treatments have low removal efficiencies [7]. Further, adsorption and chemical coagulation processes transfer the dyes from the liquid to huge amount of solid phase (sludge) causing secondary pollution which also requires further treatment [8]. Thus, there is an urgent need to develop effective methods to treat these toxic textile industry effluents. Photocatalytic decolorization process is one of the emerging advanced technology which are considered as alternate method for the degradation of dyes in waste water [9]. Semiconductor-assisted photocatalysis has attracted considerable attention as an alternative treatment method among advanced oxidation process (AOP) as a promising technique for treating dye contaminated wastewater at low cost [10].

Photocatalysis is a process by which a semiconducting material absorbs light of energy more than or equal to its band gap, thereby generating holes and electrons, which can further generate free-radicals in the system to oxidize the substrate. The resulting free-radicals are very efficient oxidizers of organic matter. The degradation of organic compounds is the most widely used photocatalytic application of nanocrystalline particles [11]-[13]. The photocatalytic decolorization of many dyes has been extensively and prominently explored in many previous studies by using different nanoparticle [14], [15]. Photocatalysis has been considered and proved as a cost effective alternative for the purification of dye-containing wastewater [16]-[21].

Due to their high photosensitivity, chemical stability and non-toxicity, TiO2 and ZnO have been especially investigated in the degradation of several environmental pollutants [22]-[33]. Many studies revealed the effects of operating parameters on the photocatalytic degradation of textile dyes using TiO2-based photocatalysts and concluded that various parameters, such as the initial pH of the dye solution, oxidizing agents and catalyst loading exert their individual influence on the photocatalytic degradation of many dyes in aqueous solution [34]-[37]. Research has articles revealed that the TiO2 nanoparticles show photocatalytic activity only in presence of UV irradiation rather than natural solar radiation.

The present study was aimed at the synthesis of innovative solar light sensitive semiconductor nanoparticle (Calcium zincate) and to study the color removal of Coralene Dark Red 2B azo dye, which is being used extensively in textile industry, as a suitable alternative to TiO2 under natural
sunlight. The effect of light irradiation, pH and the amount of photocatalyst was examined. The effect of the addition of Calcium zincate nanoparticle was also studied for enhancing the elimination of Coralene Dark Red 2B dye.

II. MATERIALS AND METHODS

Materials and reagents - All the reagents were of analytical grade (Hi-Media Chemicals, Mumbai, India) and were used as received. The nanoparticle was prepared by simple method of solution combustion synthesis. The prepared soluble nanoparticle was used as a catalyst for the decolorization of an azo dye Coralene Dark Red 2B. Metal nitrates were chosen for the synthesis of the required nanoparticle because the NO$_3$ groups of metal nitrates act as the oxidizing agents. The high solubility metal nitrates in water allow a proper homogenization. Acetamide seems to be the most convenient fuel to be employed, as it is cheap and commercially available. The commercially available water soluble disperse azo dye Coralene Dark Red 2B was obtained from Colortex Limited, Surat, Gujarat. The chemicals Calcium nitrate (Ca(NO$_3$)$_2$·4H$_2$O) (99%, A. R.), Zinc nitrate (Zn(NO$_3$)$_2$·9H$_2$O) (99%, A. R.), Acetamide (CH$_3$CONH$_2$) (99%, A.R.), were obtained from Hi-Media Chemicals, Mumbai, India and used as received without any further purification. A disperse azo dye Coralene Dark Red 2B is widely used in textile industries and has been selected for the study.

![Chemical structure of Coralene Dark Red 2B azo dye.](image1)

**Apparatus and instruments** - A 119 (UV-VIS), single beam, spectrophotometer (Systronics) has been used for recording absorbance at $\lambda_{\text{max}}$ later the absorbance was recorded by using UV-VIS spectrophotometer 119 (Systronics).

Synthesis and Characterization of CaZnO$_2$ nanoparticle -

The Calcium zincate nanoparticle was prepared by solution combustion method. The procured Calcium nitrate, Zinc nitrate, and Acetamide (Fuel) were used for the synthesis of nanoparticle. A mixture of stoichiometric amounts of Calcium nitrate (8.65 g), Zinc nitrate (10.89 g), and Acetamide (3.93 g) was dissolved in a small quantity of distilled water in a silica crucible (100 cm$^3$ capacity) [38], [39]. The solution mixture in the crucible was introduced into the muffle furnace, which was preheated to 500°C. The solution undergoes dehydration and catches fire by spreading throughout the mass, finally yielding Calcium zincate. The obtained Calcium zincate is crushed in a mortar to make it amorphous. Thus Calcium zincate nanoparticle is formed by the complete combustion of the calcium nitrate and zinc nitrate with acetamide as fuel. According to the principle used in propellant chemistry the reaction is as shown below [40].

$$11 \text{Ca(NO}_3\text{)}_2 + 11 \text{Zn(NO}_3\text{)}_2 + 20 \text{CH}_3\text{CONH}_2 \rightarrow 11 \text{CaZnO}_2 + 40 \text{CO}_2 + 50 \text{H}_2\text{O} + 32 \text{N}_2$$

XRD and SEM of the prepared Calcium zincate nanoparticle -

XRD analysis was performed on fresh sample, to assess the presence and purity of the expected phases and to evaluate their degree of crystallization. XRD is normally used to obtain the structural parameters of the materials, such as size, composition and crystal structure. In order to know the crystal properties of the prepared Calcium zincate (CaZnO$_2$) nanoparticle, the XRD was performed by powder X-ray diffraction (Rigaku diffractometer) using Cu-K$_\alpha$ radiation (1.5406 Å) in a 0-20 configuration [41]. The output from XRD analysis of the prepared CaZnO$_2$ nanoparticle sample yields a plot of intensity versus angle of diffraction as shown in Fig. 2. Thus various reflections of CaZnO$_2$ are observed which indicate that the product was well crystallized. Further, no peaks of impurity were observed, confirming that the obtained Calcium zincate was in its purest form. In addition, the peak was widened implying that the particle size was very small 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, $\beta$ the full width of half-maximum, and $\theta$ is the Bragg diffraction angle calculated using the Debye–Scherrer’s formula. The average crystallite size $D$ is 43.59 nm.

![XRD of the synthesized Calcium zincate nanoparticle.](image2)

The SEM images taken for the prepared Calcium zincate nanoparticle have clearly shown the mixture of both rod and cluster like structured Calcium zincate nanoparticle (Fig. 3).

![SEM micrographs of synthesized Calcium zincate nanoparticle.](image3)

III. EXPERIMENTAL PROCEDURE

The UV-VIS spectrophotometer 119 (Systronics) was used for the determination of color intensity in the range of 200 to 800 nm. The $\lambda_{\text{max}}$ value of Coralene Dark Red 2B was found to be 473 nm. The photocatalytic reaction experiments were carried out under direct sunlight. The known concentration of dye solution was prepared by dissolving 30 mg of Coralene Dark Red 2B dye in 1000 ml distilled water and it was investigated for its decolorization in presence of Calcium
zincate nanoparticle at different catalyst dosages. Initially, 300 ml of 30 mg/L dye sample was tested with different catalyst dosage (300, 600, 900, 1200 and 1500 mg) in presence of direct sunlight. After the photocatalytic decolorization, the extent of decolorization was estimated by recording absorbance of the dye solution taken at each 30 minute time interval, using UV-VIS spectrophotometer 169 (Systronics). The experiments were repeated at different pH levels (2, 5, 9 and 12) for the same standard dye solution, with the same catalytic dosages. The percentage of decolorization was determined by using the following equation,

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

where, \(A_0\) is the initial absorbance of dye solution and \(A_t\) is absorbance at time \(t\).

IV. RESULTS AND DISCUSSION

Effect of catalyst loading- Catalyst loading is an important factor which can significantly influence the photocatalytic decolorization rate of Coralene Dark Red 2B dye solution. To study the effect of catalyst load, calcium aluminate dosage was varied from 300 mg, 600 mg, 900 mg, 1200 mg and 1500 mg for 30 mg/L of Coralene Dark Red 2B dye solution keeping all other parameters identical and the results are presented in Fig. 4. On exposure of reaction volume to sunlight after adding the catalyst, the dye color started to fade showing the visible signs of decolorization. In the first 30 minutes, percentage of decolorization recorded was 12.41 % for minimum dosage and 91.13 % for the maximum dosage and after 120 minutes, it was decolorized upto 53.90 % for minimum dosage and ~100 % for maximum dosage. Decolorization efficiency was more at the high catalyst dosage of 1500 mg/300ml.

The increase in the amount of catalyst load increased the number of active sites on the photocatalyst surface, which in turn, increased the number of hydroxyl radicals. Further, increasing the loading of photocatalyst increased the catalyst surface area and as a result increased the decolorization rate. It may be assumed that, it would have hindered the transmission of sun light in the reaction container if catalyst dosage was increased more than 1500mg/300ml and consequently decreased the decolorization rate. However, at all the dosages, the rate of decolorization is fast in the first 30 minutes and finally reaches to ~100 % within 120 minutes.

![Fig. 4. Effect on Coralene Dark Red 2B dye at different pH concentration on the decolorization efficiency of Calcium zincate nanoparticle.](image)

**Effect of pH –** The photocatalytic experiments were conducted at acidic (pH 2 & PH 5), neutral (pH 7) and alkaline (pH 9 & pH 12) condition on Coralene Dark Red 2B dye solution (30 mg/L). At pH 2, in the first 30 minutes, degradation was 6.38 % for minimum dosage and 81.91 % for the maximum dosage and after 120 minutes, it was decolorized upto 38.29 % and ~100 % respectively. The decolorization efficiency was higher at the high catalyst dosage of 1200 mg/300ml and 1500 mg/300ml. At pH 5, in the first 30 minutes, decolorization was 11.34 % for minimum dosage and 97.16 % for the maximum dosage and after 120 minutes it was decolorized upto 42.90 % and ~100 % respectively. At pH 7 (neutral), for the first 30 minutes decolorization was 12.41 % for minimum dosage and 91.13 % for the maximum dosage and after 120 minutes, it was decolorized upto 53.90 % and ~100 % respectively. The decolorization efficiency was maximum (~100%) at higher dosages of 900 mg/300ml, 1200 mg/300ml and 1500 mg/300ml at both pH 5 and pH 7 levels. At pH 9, for the first 30 minutes the decolorization was 20.92 % for minimum dosage and 97.51 % for the maximum dosage and after 120 minutes, it was decolorized upto 46.09 % and ~100 % respectively. At pH 12, for the first 30 minutes the decolorization was 12.76 % for minimum dosage and 97.16 % for the maximum dosage and after 120 minutes, it was degraded upto 65.24 % and ~100 % respectively. The decolorization efficiency of Calcium zincate nanoparticle was maximum at higher dosages of 600 mg/300ml, 900 mg/300ml, 1200 mg/300ml and 1500 mg/300ml at both pH 9 and pH 12 levels.

The decolorization is mainly attributed to the variation of surface charge properties of the photocatalyst at different pH values [44]. The ~100 % decolorization was observed irrespective of pH variation at different catalytic dosages from 600 mg/300ml to 1500 mg/300ml. The results of variation of pH on decolorization of Coralene Dark Red 2B dye are shown in Fig. 5.
Mechanism of the photocatalytic decolorization - The mechanism of the photocatalytic decolorization of Coralene Dark Red 2B dye is as follows [41], [45].

\[
\text{CaZnO}_2 + \text{h}^+ \rightarrow \text{CaZnO}_2(e^- + \text{h}^+_\text{VB}) \quad (i)
\]

\[
\text{h}^+_\text{VB} + \text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH}^- \quad \text{(ii)}
\]

\[
\text{h}^+_\text{VB} + \text{OH}^- \rightarrow \text{OH}^- \quad \text{(iii)}
\]

\[
\text{OH}^- + \text{Coralene Dark Red 2B dye} \rightarrow \text{decomposed Coralene Dark Red 2B dye} \quad \text{(iv)}
\]

\[
\text{CaZnO}_2 + 2\text{h}^+ \rightarrow \text{Ca}^{2+} + \text{Zn}^{2+} + 2\text{O}^*(\text{active oxygen}) \quad \text{(v)}
\]

Upon exposure to UV-irradiation, the Calcium zincate nanoparticle was photoexcited and an electron–hole pair is formed (i), where \(e^-\) is the electron in the conduction band, \(h^+\) is the hole in the valence band (\(e^- + h^+\)). Due to the amphoteric property of Calcium zincate semiconductor nanoparticle, water molecules were adsorbed on its excited surface and decomposed by oxidative potential of the hole (ii). The formed \(\text{OH}^-\) ions are further oxidized by the hole to produce \(\text{OH}^+\) radicals (iii) and lead to partial or complete dye decomposition (iv). On the other hand, Calcium zincate reacts with the photogenerated holes and undergoes self-oxidation (v). Thus, the Coralene Dark Red 2B dye will also be decomposed by the action of the more number of newly generated active oxygen’s.

V. CONCLUSIONS

In the present work, Calcium zincate nanoparticle was used as a catalyst for the Coralene Dark Red 2B dye solution which was synthesized and characterized them by SEM and XRD studies. The Calcium zincate nanoparticle was tested for photocatalytic decolorization of disperse azo dye called Coralene Dark Red 2B under natural sunlight. The Calcium zincate nanoparticle is of low cost and proved that the synthesized Calcium zincate nanoparticle was sensitive to sunlight degrading effectively the selected azo dye.

The photocatalytic decolorization of disperse Coralene Dark Red 2B azo dye is dependent on irradiation time and catalyst loading, i.e. higher the irradiation time and catalyst dosage, high will be the decolorization rate and vice versa.

The method of synthesis of Calcium zincate nanoparticle was tested as a catalyst for the Coralene Dark Red 2B dye solution and was synthesized and characterized by XRD studies. The Calcium zincate nanoparticle was tested as a catalyst for the Coralene Dark Red 2B dye solution and was synthesized and characterized by XRD studies. The Calcium zincate nanoparticle was tested as a catalyst for the Coralene Dark Red 2B dye solution and was synthesized and characterized by XRD studies.
Yogendra Kambalagere was born at Shimoga, Karnataka state, India on 1st June, 1971. He has obtained his Ph.D. degree in Environmental science in the year 2000 from the Department of Environmental science, Kuvempu University, Karnataka state, India. M.Sc. degree in Environmental science in the year 1994 from the Department of Environmental science, Kuvempu University, Karnataka state, India and B.Sc. in Chemistry, Botany and Zoology, 1992, Kuvempu University, Karnataka state, India.

He is working as ASSISTANT PROFESSOR in the Department of Post-graduate studies and research in Environmental science, Kuvempu University, Karnataka state, India. He was also worked as Research Associate in a research project supported by National River Conservation Directorate, Ministry of Environment and Forests, Government of India. He has published several research articles in the field of environmental science and recently published a research article in an International Journal of Environmental Sciences published by Integrated Publishing Association. His interest is in the areas of environmental chemistry particularly in the field of color degradation of dyes by using nano-sized semiconductor metal oxides.

Dr. Yogendra is a member for International Association for Ecology (INTECOL), Senior member for APCBEEs, Bangkok and member for Indian Science Congress Association (ISCA), Kolkata.