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Photocatalytic Decolorization of Coralene Dark Red 2B Azo Dye by Using Calcium Zincate Nanoparticles in Presence of Natural Sunlight

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Abstract. The present work is aimed at investigating the photocatalytic decolorization efficiency of prepared calcium zincate nanoparticles against Coralene Dark Red 2B azo dye solution under varying controlling parameters such as catalyst concentration and pH. The Calcium zincate nanoparticles ($CaZnO_2$) of average crystallite size 43.59 nm was prepared by solution combustion method and characterized by SEM and XRD studies. The results were evaluated by using ultraviolet and visible absorption spectroscopy. The obtained result witnessed the high photocatalytic decolorization efficiency of Calcium zincate nanoparticles which was synthesized by low cost, eco friendly, simple solution combustion method in laboratory scale.

Keywords: Calcium zincate ($CaZnO_2$), Coralene Dark Red 2B, Photocatalytic activity, Decolorization, Nanoparticle.

1. Introduction

Dyes and pigments are widely used in the textiles, paper, plastics, leather, food and cosmetic industries to color their products. Presently, more than 10,000 dyes have been effectively commercialized [1] and azo dyes are the major class of commercial dyes which are extensively used in textile industries because of their versatility and cost-effectiveness. Though many of these dyes are banned for commercial sale and use, they are still easily available and used in textile industries which pose a great environmental threat [2-3]. Most of the azo dyes are chemically stable and are common constituents of effluents in all above industries which demand an appropriate method to dispose them off. The removal of these azo dyes from effluents is difficult since, they are stable to light, heat and oxidizing agents [4]. The release of these colored effluents is undesirable to the environment because of their color, biorecalcitrance, potential toxicity, carcinogenicity to animals and human beings [5-6]. Most of the current physical and chemical methodologies do not achieve maximum decolorization of colored effluents. The traditional biological wastewater treatments are with low removal efficiencies [7].

In recent years, much attention is given to photocatalytic decolorization of azo dyes, which has been widely explored for the decolorization of various dyes using different nanoparticles [8-9] since it is cost effective alternate for the purification of dye-containing wastewater [10-13]. Photocatalytic activity is a process where semiconducting material absorbs light energy more than or equal to its band gap, thereby generating holes and electrons which further releases free-radicals in the system to oxidize the substrate. The resultant free-radicals are very efficient oxidizers of organic compounds.

The main objective of the present investigation is to study the efficiency of newly synthesized Calcium zincate nanoparticles in color removal of Coralene Dark Red 2B, an extensively used azo dye. The effect of

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pH and the different dosage of Calcium zincate nanoparticles as catalyst on the decolorization of Coralene Dark Red 2B dye were also studied.

2. Material and Methods

2.1. Materials and reagents

A widely used disperse azo dye in textile industries, Coralene Dark Red 2B has been selected for the present study (Fig. 1) and was obtained from Colourtex Limited, Surat, India. Calcium nitrate ($Ca(NO_3)_2.4H_2O$) (99%, AR), Zinc nitrate ($Zn(NO_3)_2$. $6H_2O$) (99%, AR), Acetamide (CH_3CONH_2) (99%, AR), were obtained from Hi-Media Chemicals, Mumbai and used as received without purification. Metal nitrates were used as starting material for the preparation of the required nanoparticles, as they are fundamental for this synthesis method (as oxidizing agent) and also for their high solubility in water which allows a proper homogenization. Acetamide is selected as a combustion fuel due to its low cost and convenience. UV-VIS Spectrophotometer-119 (Systronics) was used for recording the λ_{max} of Coralene Dark Red 2B dye and the absorbance of the decolorized solution at different time interval was recorded by using UV-VIS spectrophotometer-169 (Systronics).

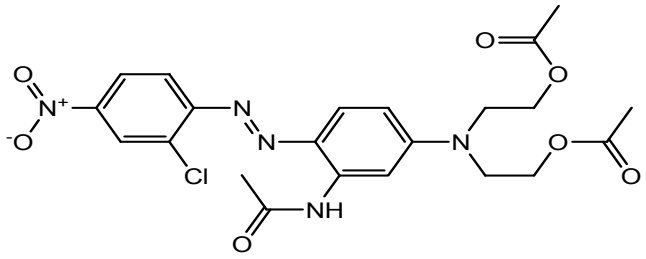


Fig. 1: Chemical structure of Coralene Dark Red 2B azo dye.

2.2. Synthesis and Characterization of Calcium zincate nanoparticles

A stoichiometric amount of Calcium nitrate (8.65 g), Zinc nitrate (10.89 g), and Acetamide (3.93 g) was dissolved in ~25 ml of distilled water in a silica crucible (100 cm^3 capacity). The Silica crucible was then kept for calcination in the muffle furnace (preheated to 500^0 C) till complete combustion of the Calcium nitrate and Zinc nitrate with the fuel acetamide [14-15]**.** The obtained 5.027 g of Calcium zincate nanoparticles were crushed in a mortar to make it amorphous. According to propellant chemistry the reaction is as follows [16].

$$11\ Ca(NO_3)_2 + 11\ Zn(NO_3)_2 + 20\ CH_3CONH_2 \longrightarrow 11\ CaZnO_2 + 40\ CO_2 + 50\ H_2O + 32\ N_2$$

2.3. XRD and SEM of the prepared Calcium zincate nanoparticles

XRD analysis was performed by using Rigaku diffractrometer at Cu-K_α radiation (1.5406 Å) in a θ-2θ configuration for fresh sample of Calcium zincate ($CaZnO_2$) nanoparticles to study the size, composition and structure. The obtained intensity readings of the prepared Calcium zincate nanoparticle samples are plotted against angle of diffractions (Fig. 2). Fine and narrow peaks of obtained XRD pattern indicated that, the product was well crystallized. Peaks representing impurities were not observed, confirming the obtained Calcium zincate nanoparticles after calcinations is pure. According to Debye–Scherrer's formula $D = K\lambda/(\beta\cos\theta)$, (K-the Scherrer's constant, λ-the X-ray wavelength, β-the full width at half-maximum, and θ-the Bragg diffraction angle calculated) the average crystallite size was found to be 43.59 nm.

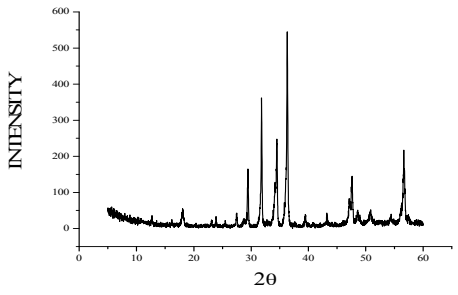


Fig. 2: XRD of the Calcium zincate Nanoparticles.

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

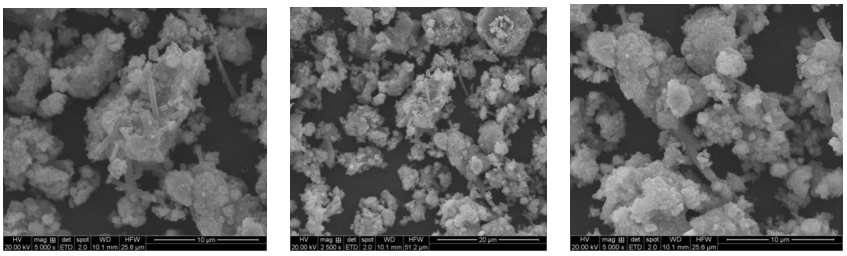


Fig. 3: SEM micrographs of the Calcium zincate Nanoparticles.

2.4. Experimental procedure

The degradation of the dye molecules was evaluated using ultraviolet and visible absorption spectroscopy. An absorbance spectrum of the dye solution was taken using UV-VIS Spectrophotometer 119 (Systronics) in the range of 200 to 800 nm. The λ_{max} of Coralene Dark Red 2B was found to be 473 nm. The photocatalytic reaction experiments were carried out in the presence of direct sunlight. The standard (30mg/L) dye solution was prepared by dissolving 30 mg of Coralene Dark Red 2B dye in 1000 ml distilled water and investigated for its decolorization by using Calcium zincate nanoparticles as catalyst at different dosages and pH levels. The pH of the dye solution was adjusted by using dilute hydrochloric acid and sodium hydroxide. At each pH levels (ranging from 2 to 12) the reaction volume of 300 ml dye solution (of 30 mg/L concentration) was taken and catalyst dosages (of 300mg, 600mg, 900mg, 1200mg and 1500 mg) were added for the color degradation efficiency study under direct sunlight. After the dispersion of the catalyst, the absorbance of dye solution was recorded at an interval of 30 minutes time using UV-VIS Spectrophotometer -169 (Systronics). The percentage of color degradation was calculated by using the following formula.

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

Where, $\mathbf{A_0}$ is the initial absorbance of dye solution and $\mathbf{A_t}$ is absorbance at time‘t’.

2.5. Result and Discussion

Effect of concentration of catalyst on degradation of dye

To study the effect of catalyst concentrations on the removal of color, catalyst at various concentrations were employed for the decolorization of Coralene Dark Red 2B dye at neutral pH condition. During the first 30 minutes, decolorization was only 12.41 % for minimum catalyst dosage (300mg) and 91.13 % for the maximum dosage (1500mg). Further, in the next 120 minutes of duration the decolorization was increased to 53.90 % for minimum dosage of catalyst and 100 % decolorization was recorded for maximum dosage (Fig. 5)**.**

Effect of pH on rate of decolorization

The effect of pH on the decolorization efficiency of the selected dye solution was studied at different pH conditions. The decrease of pH from neutral condition has slightly decreased the decolonization efficiency at lower dosages of Calcium Zincate nanoparticles (Fig.4). At higher dosages, 100% color degradation was observed in all the pH conditions. The alkaline condition is more suitable when compared to acidic condition as it gives effective and good results in smaller dosages of catalyst. The percentage of decolorization of Coralene Dark Red 2B dye at different pH levels are shown in (Fig 5).

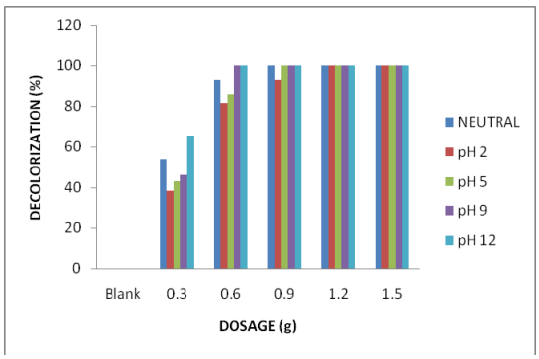
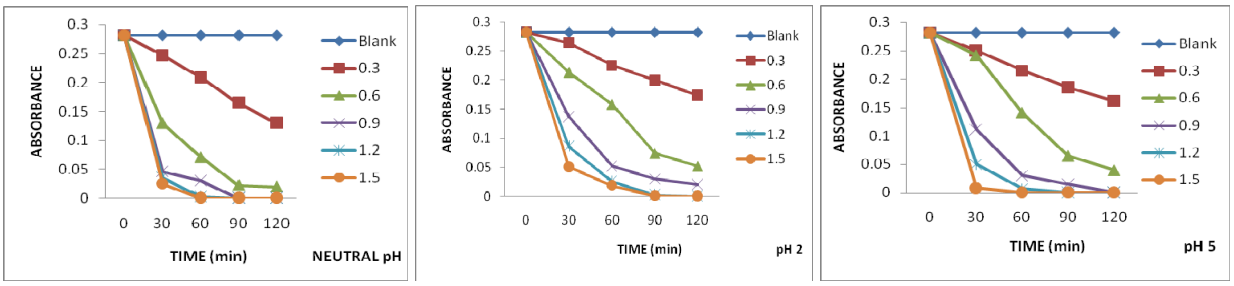
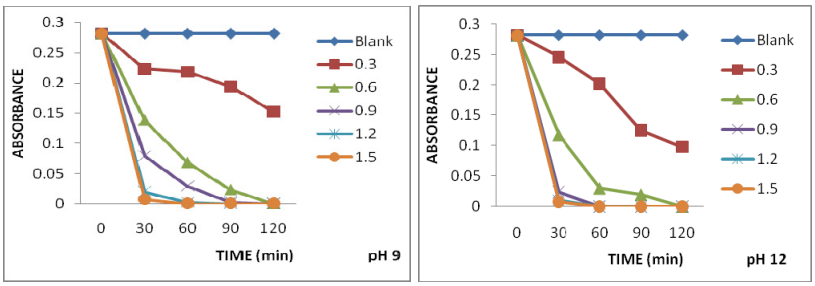


Fig. 4: Effect on Coralene Dark Red 2B dye at different pH concentration on the decolorization efficiency of Calcium zincate nanoparticles.



(a) (b) (c)



(d) (e)

Fig. 5: Effect of catalyst dosage on the decolorization of Coralene Dark Red 2B dyes at concentration 30mg/L, on Neutral (a), pH 2 (b), pH 5 (c), pH 9 (d), and pH 12 (e) with respect to time.

Mechanism of the photocatalytic decolorization

The mechanism of the Photocatalytic decolorization of Coralene Dark Red 2B dye is as follows [17].

$CaZnO_2 + h\upsilon \rightarrow CaZnO_2 (e^-_{CB} + h^+_{VB})$. . . . . .(i)

$h^+_{VB} + H_2O \rightarrow H^+ + OH^-$. . . . . (ii)

$h^+_{VB} + OH^- \rightarrow OH^{\cdot}$. . . . . .(iii)

$OH^{\cdot}$ + Coralene Dark Red 2B dye → decomposed Coralene Dark Red 2B dye. . . . . .(iv)

$CaZnO_2 + 2\ h^+_{VB} \rightarrow Ca^{2+} + Zn^{2+} + 2O^*$ (active oxygen). . . . . (v)

Upon exposure to UV-irradiation, the Calcium zincate nanoparticle ($CaZnO_2$) is photoexcited and an electron–hole pair is formed (i), where e^-_{CB} is the electron in the conduction band, h^+_{VB} is the hole in the valence band in Calcium zincate ($e^-_{CB} + h^+_{VB}$). 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 OH^- ions are further oxidized by the hole to produce $OH^{\cdot}$ radicals (iii) and lead to partial or complete dye decomposition (iv). On the other hand, Calcium zincate nanoparticle 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 more number of newly generated active oxygen.

The results of the present investigation proved that, the synthesized Calcium zincate is found to be an efficient photocatalyst for the complete decolorization of Coralene Dark Red 2B dye solution under solar radiation. This protocol is an effective technique in decolorizing the Coralene Dark Red 2B azo dye solution and can be employed effectively in the treatment of textile dye effluents which are hazardous to the environment.

3. Acknowledgement

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4. References

[1] R. Leena, and D. Selva Raj. Bio-decolourization of textile effluent containing Reactive Black-B by effluent-adapted and non-adapted bacteria. *J. African Biotech.* 2008, **7** (18)**:** 3309-3313.

[2] Hazrat Ali, and Shah Khalid Muhammad. Biodecolorization of acid violet 19 by Alternaria solani. *J. African Biotech*. 2008, **7** (6)**:** 831-833.

[3] O. D. Olukanni, A. A. Osuntoki, and G. O. Gbenle. Textile effluent biodegradation potentials of textile effluent-adapted and non-adapted bacteria. *J. African Biotech.* 2006, **5** (20)**:** 1980-1984.

[4] M. Mamdouh, H. Nassar, Yehia, and Magdy. Removal of different basic dyes from aqueous solutions by adsorption on palm fruit bunch particles. *J. Chem. Engi.* 1997, **66** (3)**:** 223-226.

[5] Muhammad Faisal Siddiqui, Saadia Andleeb, Naeem Ali, Pir Bux Ghumro and Safia. Up-flow immobilized fungal Column Reactor for the Treatment of Anthraquinone dye Drimarene blue K2RL. *J. African Biotech.* 2009, **8** (20)**:** 5570-5577.

[6] N. S. Raju, G. V. Venkataramana, S. T. Girish, V. B. Raghavendra, and P. Shivashankar. Isolation and Evaluation of Indigenous soil fungi for Decolourization of Textile Dyes. *J. Appl. Sci.* 2007, **7** (2)**:** pp. 298-301.

[7] Praveen Sharma, Lakhvinder Singh, and Neeraj Dilbaghi. Biodegradation of Orange II dye by phanerochaete chrysosporium in simulated wastewater. *J. Scientific & Ind. Res.* 2009, **68:** 157-161.

[8] K. Ioannis, Konstantinou, A. Triantafyllos, and Albanis. TiO_2-assisted photocatalytic degradation of azo dyes in aqueous solution: kinetic, and mechanistic investigations: A review. *J. Appl. Catal. B: Envi.* 2004, **49** (1)**:** 1-14.

[9] Yizhong Wang. Solar photocatalytic degradation of eight commercial dyes in TiO_2 suspension. *J. Water Res.* 2000, **34** (3)**:** 990-994.

[10] Radia Tafer, and Abdelaziz Boulkamh. Direct Photolysis of an Azo-Dye, Erichrome Black T. *Res. J. Appl. Sci.* 2008, **3** (5)**:** 339-344.

[11] R. Aplin, and T. D. Waite. Comparison of three advanced oxidation processes for degradation of textile dyes. *J. Water Sci.and Tech.* 2000, **42** (5)**:** 345–354.

[12] F. Ayrton, Martins, L. Marcelo, Wilde, and Carla da Silveira. Photocatalytic Degradation of Brilliant Red Dye and Textile Wastewater. *J. Environmental Science and Health Part A*. 2006, **41:** 675–685.

[13] Sushil Kumar Kansal, Navjeet Kaur, and Sukhmehar Singh. Photocatalytic Degradation of Two Commercial Reactive Dyes in Aqueous Phase Using Nanophotocatalysts. *J. Nanoscale Res. Lett.* 2009, **4:** 709–716.

[14] C. Kashinath Patil, S. T. Aruna, and Tanu Mimani. Combustion synthesis: an update. *J. current Opinion in solid state and Mater. Sci.* 2002, **6:** 507-512.

[15] J. J. Kingsley, K. Suresh, and K. C. Patil. Combustion synthesis of fine particle metal aluminates. *J. Mater. Sci.* 1990, **25:** 1305-1312.

[16] A. S. Prakash, A. M. A. Khadar, K. C. Patil, and M. S. Hegde. Hexamethylenetetramine: A New Fuel for Solution Combustion Synthesis of Complex Metal Oxides. *J. Mater. Syn. and Process.* 2002, **10:** 135-141.

[17] Junpei Nishio, Masahiro Tokumura, T. Hussein Znad, and Yoshinori Kawase. Photocatalytic decolorization of azo-dye with zinc oxide powder in an external UV light irradiation slurry photoreactor. *J. Hazard. Mater. B.* 2006, **138:** 106–115.