

PHOTOCATALYTIC DEGRADATION OF CONGO RED DYE ON COMBUSTION SYNTHESIZED
 CaZrO₃ CATALYST UNDER SOLAR LIGHT IRRADIATION

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ABSTRACT

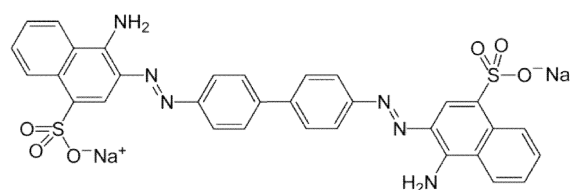
 The Calcium Zirconate (CaZrO₃) catalyst was prepared by solution combustion synthesis method and extensively characterized by XRD, SEM, TGA, DTA, Reflectance spectroscopy, BET surface area and powder density. Congo Red (CR) dye was used as model pollutant to study its photocatalytic degradation under solar light irradiation. The degradation of CR was investigated by COD analyzer and UV-Visible spectroscopy. The influences of catalyst amount, initial CR concentration, pH of the reaction solution and irradiation time were investigated. Results of characterization indicated the successful formation of CaZrO₃ catalyst. Recycling experiments confirmed the relative stability of the catalyst.

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INTRODUCTION

Dyes are an abundant class of synthetic colored organic compounds that indicate an increasing environmental hazard. About 1-15% of the total world production of synthetic textile dyes is lost during dye production and textile manufacturing process [1-3]. The textile effluent is highly colored, its discharge in the environment is a considerable source of non aesthetic pollution and impedes light penetration, thus upsetting aquatic life [4-5]. Waste water is commonly characterized by its strong color, high chemical oxygen demand (COD), variable pH, total dissolved solids (TDS) content and low biodegradability, implying the presence of recalcitrant organic matter [6]. Especially azo dyes, which are non-biodegradable, toxic and potentially carcinogenic in nature, are widely used [7]. Hence removal of these dyes from effluents is a major environmental problem because conventional physicochemical and biological treatment methods are ineffective for decolorization and degradation. Many chemical and physical techniques including adsorption, coagulation, precipitation, filtration, electrodialysis, membrane separation and oxidation have been used efficiently for removal of dye pollutants [8]. However, they are non-destructive, since they transfer organic compounds from water to another phase, thus causing secondary pollution [9]. Recently, Advanced oxidation processes (AOP's) in which heterogeneous photocatalysis appears as an emerging destructive method, leading to mineralization of organic water contaminants is widely used [10].

Congo Red (CR) is a benzidine-based anionic disazo dye toxic to many organisms and are susceped carcinogen and mutagen. CR is difficult to degrade due to its structural stability [11].



Congo Red (CR), Molecular weight: 696.66 g mol⁻¹, λ_{max}: 500 nm

Various attempts have been made earlier for the removal of CR dye from water and waste water. Apart from adsorption over natural coagulant like chitosan, surjana seed powder, maize seed powder [12], Leucaena leucocephala seed pods [13], Alginate extracted from a red algae [14], Rice husk carbon [15], Triton X-100 surfactant [16], Ozonation [17], biological [18] and photocatalysis [19] techniques have also been explored.

In this study, the CaZrO₃ catalyst was synthesized by combustion synthesis method in which fuel were taken in deficient proportion and characterized in detail. CR dye was selected as object pollutant. Indoor solar light was used for irradiation source. Different factors for degradation were investigated. The results obtained in this study could provide fundamental information for the treatment of waste water containing organic dyes. Literature survey reveals that the CaZrO₃ not used earlier for removal of Congo red dye from water and waste water.

Experimental

Commercially available Congo Red, Calcium nitrate and Zirconium nitrate were purchased from LOBA Chemie company (Mumbai, India). Ammonium nitrate, glycine and urea were purchased from Merck (India). All chemicals used as received without further purification. All solutions were

prepared in double distilled water. Dilute nitric acid and dilute sodium hydroxide in proper amount was used to adjust the suitable pH value.

Synthesis of CaZrO₃ catalyst

CaZrO₃ was synthesized by solution combustion synthesis method in which corresponding metal nitrates were used as oxidizer and glycine, urea and ammonium nitrate were used as fuels in deficient proportion (2:1). The redox mixture was dissolved in a cylindrical pyrex dish of approximately 250 ml capacity. The amount of oxidizer and fuel were taken in such a way that the desired product i.e. CaZrO₃ obtained was 5 g. Dish containing the solution was introduced into muffle furnace preheated at 400 °C. mixture boils, foams and ignites to burn, yielding voluminous and foamy CaZrO₃ which occupies the entire volume of the dish. The time required for completion of reaction was less than 15 min. Finally, it was calcined at 800 °C for 2 hr in air to obtain pure form of CaZrO₃.

Physicochemical characterization of CaZrO₃ catalyst

The crystallinity and phase identification of the powder was determined by powder XRD using Philips PW-1700 diffractometer with Ni filtered CuK α radiation. A reflectance spectrum was recorded on GBC Cintra 10e (Australia) spectrophotometer. Surface area measurements were done using nitrogen gas adsorption multipoint Brunquer-Emmett-Teller (BET) method on Micromeritics ASAP 2010 model, assuming a cross sectional area of 0.162 nm² for nitrogen molecule. Powder density was measured using pycnometer with xylene as the liquid medium. The diameter of the primary particle was calculated from superficial area using following equation – (I):

$$D_{BET} = 6/S_{BET} \cdot \rho \quad \text{----- (I)}$$

Where S_{BET} is the superficial area (m² g⁻¹) measured by BET analyses; ρ , the density of powders (g cm⁻³); and D_{BET}, the diameter of the produced particle. SEM micrograph was recorded on JEOL 6380A electron probe analyzer instrument after coating the sample with gold for evaluation of particle morphology.

Photodegradation study of Congo red dye

A specially designed cylindrical glass tube having capacity 250 ml was used for irradiation of model dye solution. Air was allowed to pass into dye solution using airator. A known amount of dye solution (100 cm³) and CaZrO₃ catalyst was taken in glass tube. Solution was irradiated under indoor solar light. At given irradiation time intervals, 10 ml of the suspension were collected, centrifuged and filtered to separate the photocatalyst particles. After each irradiation the CR concentration was measured by UV-Visible Spectrophotometer (UV-1800, Simadzu, Japan) at 500 nm and COD analysis were carried out on UNIPHOS India make COD analyzer, before that, sample were digested for 2 hr at 150 °C in UNIPHOS COD digester. The degradation and removal of COD were studied by varying different parameters such as catalyst amount, initial concentration of dye, pH of the dye solution and irradiation time.

Regeneration of catalyst

After irradiation, catalyst was separated from solution. Washed with small amount of distilled water and kept in

muffle furnace at 600 °C for 2 hr. Also stability of CaZrO₃ in acid and alkali was studied by keeping it in 1M HCl and 1M NaOH for 24 hr. Experiments were carried out for CR dye with regenerated catalyst at its optimized parameters.

RESULTS AND DISCUSSION

Characterization of CaZrO₃

Fig. 1 shows the XRD pattern of CaZrO₃. An excellent match is found with ICDD file 35-0790. It is observed that a single phase, crystalline nature with cubic structure has been formed.

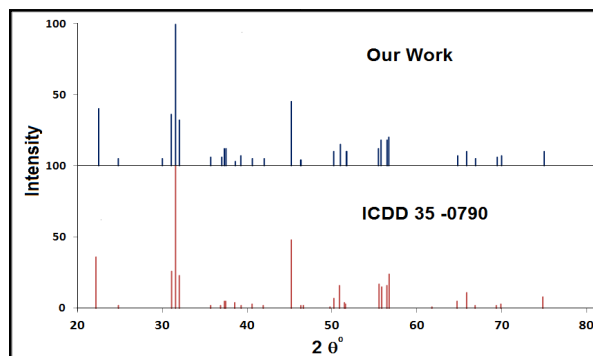


Fig. 1 X-ray diffraction pattern of CaZrO₃

DTA and TGA curves of CaZrO₃ (Fig. 2) shows the compound is almost stable with very small weight loss. DTA graph of CaZrO₃ shows three endothermic peaks. The endothermic break at 320 °C reaches a peak at 350 °C and end at 390 °C. The second endothermic curve begins at 640 °C reaches a peak at 730 °C end at 760 °C and The third endothermic curve begins at 770 °C reaches a peak at 830 °C end at 900 °C .

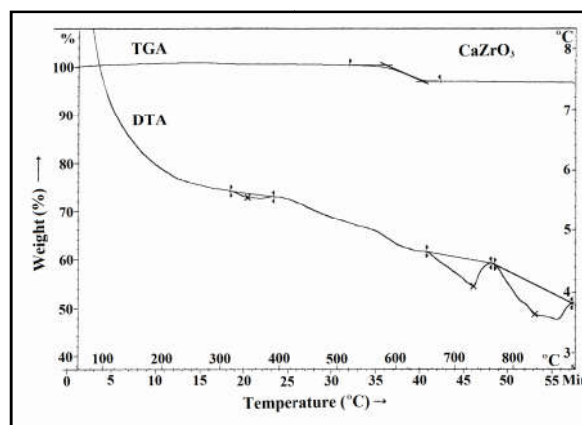


Fig. 2 Thermogram of TGA and DTA of CaZrO₃

The diffuse reflectance spectra is an efficient tool for the determination of energy band gap of CaZrO₃. The band gap energy of CaZrO₃ was found to be 3.94 eV. BET surface area was found to be 39.57 m² g⁻¹. Powder density was found to be 2.34 g cm⁻³. The average particle diameter was found to be 65 nm which was calculated from BET surface area measurement and density value.

The morphology of CaZrO₃ samples was investigated by scanning electron microscopy (SEM) with JEOL 6380A microscope. SEM image of CaZrO₃ powders calcined at 800 °C is shown in Fig. 3. The SEM image clearly indicates the high homogeneity of the CaZrO₃ powders.

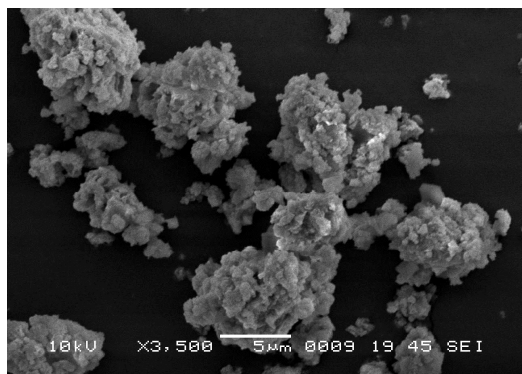


Fig. 3 Scanning electron microscopy image of CaZrO₃

Photocatalytic degradation studies

Effect of pH

Employing CaZrO₃ as a photocatalyst the decomposition and mineralization of CR dyes in aqueous suspension of CaZrO₃ was studied in the pH range between 4 and 10 (Fig. 4). In this work, results illustrate that the degradation rate for CR dye under investigation is strongly influenced by reaction pH. As the pH of solution increases from 4 to 10, the efficiency of degradation of dye decrease. At low pH value, electrostatic interaction between the positively charged surface of CaZrO₃ and dye anions in aqueous solution lead to strong adsorption of the dye on the catalyst surface. The dissociation of metal hydroxide complexes at lower pH causes surface to become positively charge which is very ideal for the removal of anionic dyes. In acid medium, positive charge develops on the surface of oxides and may be represented as,

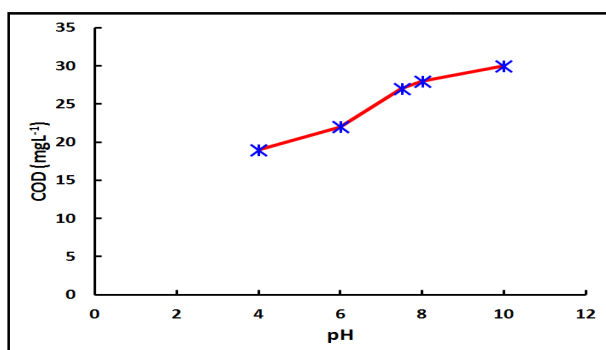
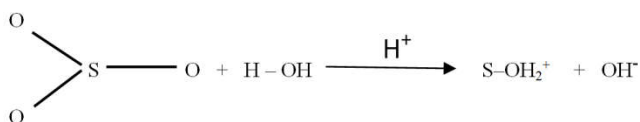
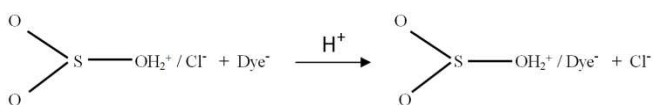


Fig. 4 Effect of pH on COD removal of CR dye



Where, S stand for semiconductor. Since the solution is acidified by HCl, the outer surface of the positively charged interface will be associated with Cl⁻ ions. The chloride ions are exchanged with dye anions,



Effect of catalyst concentration

The effect of catalyst concentration on the degradation of CR was investigated employing different concentration of CaZrO₃ ranging from 1 to 3.5 g l⁻¹ shown in Fig. 5. As expected the

COD of dye solution was found to decrease with increase in catalyst concentration up to 2.5 g l⁻¹, further increase in catalyst concentration found increase value of COD. The increase in the efficiency seems to be due to the effective surface area of catalyst and the absorption of light. At lower catalyst loading, the absorption of light controlled the photocatalytic process due to the limited catalyst surface area. However, as the catalyst loading increased, an increase in the active sites of CaZrO₃ is obtained. The large amount of photons adsorbed and the amount of dyes adsorbed on the CaZrO₃ surface improved the photocatalytic degradation. When the CaZrO₃ loading was high, nevertheless, owing to an increase in the particles aggregation, the surface that absorbed the photons is not increasing in a geometrical ratio. In addition, the number of active sites on the CaZrO₃ surface also decreased because of the decrease in light penetration due to light scattering effect. With an increase in the turbidity of the suspension and shrinking of the effective photoactivated volume of suspension, the degradation rate is decreased. The integration of these two reasons resulted in a reduced performance of photocatalytic activity rather than the linearly increase with the overloaded catalyst. Hence, catalyst loading was optimized to 2.5 g l⁻¹ for further study.

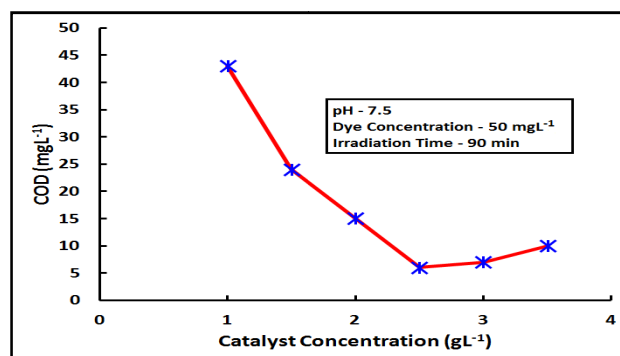


Fig. 5 Effect of catalyst concentration on COD removal of CR dye

Effect of dye concentration

It is important both from a mechanistic and from an application point of view to study the dependence of the photocatalytic reaction rate on the dye concentration. The initial dye concentration can influence the extent of photocatalytic reaction rate at the surface of catalyst. Hence the effect of dye concentration on degradation of CR was studied at varying concentration from 25 mg L⁻¹ to 200 mg L⁻¹ keeping other parameters constant (Fig. 6). It is interesting to note that the COD of dye solution increase with increase in dye concentration from 25 mg L⁻¹ to 200 mg L⁻¹. The initial dye concentration dependence of the degradation rate of dye can be realized by the fact that the photocatalytic reaction occurs on CaZrO₃ particles as well as in solution. On the surface of CaZrO₃ particles, the reaction occurs between the OH⁻ radicals generated at the active OH⁻ sites and dye molecule from the solution. In addition, a significant amount of light may also be absorbed by the dye molecules rather than the CaZrO₃ at a higher initial dye concentration. This condition can be ascribed to the increase in the initial concentration which led to less photons reaching on the CaZrO₃ surface and resulted in a slower production of ·OH radicals. Consequently, the degradation rate is decreased.

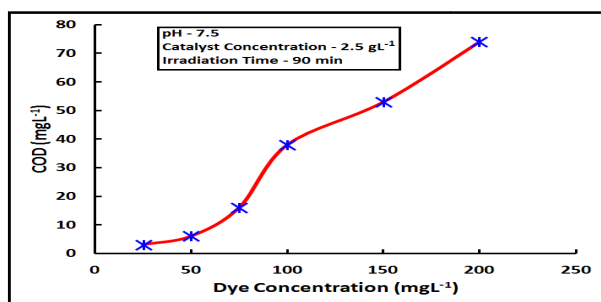


Fig. 6 Effect of dye concentration on COD removal of CR dye

Effect of irradiation time

The effect of irradiation time on degradation of CR dyes was investigated and same is shown in Fig. 7. The irradiation time was varied from 30 min to 120 min keeping other parameters constant. It was observed that the maximum quantity of CR dye was degraded up to 90 min.

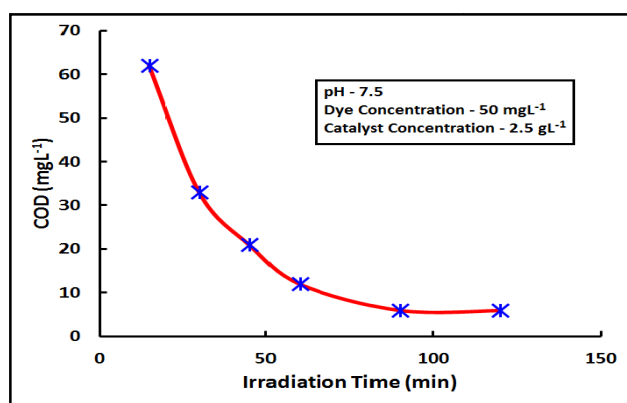


Fig. 7 Effect of irradiation time on COD removal of CR dye

Degradation and Decolorization

The UV-vis spectra of the original CR solution and degraded dye solution are presented in Fig. 8. The full spectrum scanning pattern showed extremely obvious difference. No peak was detected in analyzed wavelength range at the end of 90min of reaction time in presence of CaZrO_3 (2.5 g L^{-1}) under indoor solar light irradiation indicating complete destruction of CR dye. As a result, both an appropriate light source and catalyst are essential for photocatalytic decolorization and degradation of the CR dye on CaZrO_3 to occur.

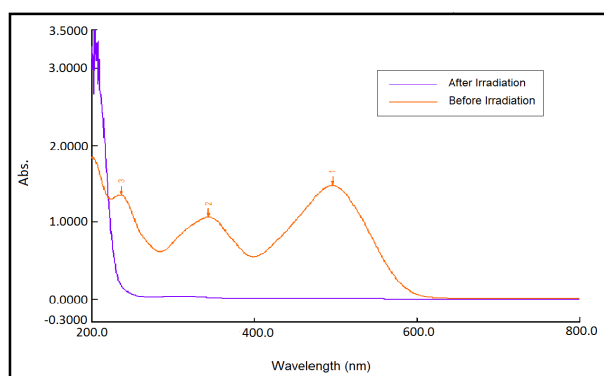


Fig. 8 UV-vis spectrum of before and after irradiation of CR dye

CONCLUSION

Calcium Zirconate was successfully synthesized by using combustion synthesis method at $400 \text{ }^\circ\text{C}$ within 15 min. time

interval. Calcium Zirconate was found to be efficient photocatalyst for photodegradation of Congo Red dye, nearly 97 percent COD removal and 98 percent color removal was observed in 90 min using indoor solar light as a source of irradiation. CaZrO_3 can be regenerated and reused effectively and degradation efficiency from observation was found to be nearly similar to that of original CaZrO_3 .

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