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RESEARCH ARTICLE

PHOTOCATALYTIC DEGRADATION OF INDIGO CARMINE DYE OVER CALCIUM ZIRCONATE CATALYST UNDER UV IRRADIATION

Hatwar, C.R*., Deshpande, P.S., Dafare, S., Hatwar, L.R., Talwatkar, C.B and Bhavsar, R.S

Department of Chemistry, Institute of Science, Nagpur-440 001 (M.S.) India

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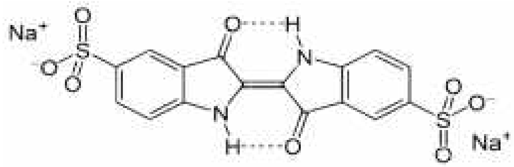
A B S T R A C T

The Calcium Zirconate ($CaZrO_3$) catalyst was prepared by solution combustion synthesis method and extensively characterized by XRD, SEM, TGA, DTA, Reflectance spectroscopy, BET surface area and powder density. Indigo carmine (IC) dye was used as model pollutant to study its photocatalytic degradation under UV light irradiation. The degradation of IC was investigated by COD analyzer and UV-Visible spectroscopy. The influences of catalyst amount, initial IC concentration, pH of the reaction solution and irradiation time were investigated. Results of characterization and photocatalytic study indicated the successful formation of $CaZrO_3$ catalyst and nearly 92 percent IC dye was degraded in 90 min. Recycling experiments confirmed the relative stability of the catalyst.

INTRODUCTION

Environmental protection, which requires strictly sustainable development to avoid jeopardizing current natural resources, is gradually becoming a matter of major social concern. Every day, increasingly tough legislation is being imposed with regard to effluent discharge [1]. The textile effluent is highly colored; its emancipation in the environment is a considerable source of non aesthetic pollution and encumbers light penetration, thus disturbing aquatic life [2-3]. 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 refractory organic matter [4]. Especially azo dyes, which are non-biodegradable, toxic and potentially carcinogenic in nature, are widely used [5]. These azo dyes were found to have immense hazardous effects on human health and environment [6]. 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 [7]. However, they are non destructive, since they transfer organic compounds from water to another phase, thus causing secondary pollution [8]. Recently, Advanced oxidation processes (AOP's) in which heterogeneous semiconductor photocatalysis emerge as an promising destructive method, leading to mineralization of organic pollutants from wastewater [9-13]. Photocatalysis is based on the principle that when a semiconductor is exposed to a light source with appropriate wavelength, the electrons from the valence band are promoted to the conduction band leaving positive holes in the valence band. The generated electron–hole pair moves to the semiconductor surface and reacts with organic pollutants degrading them into non hazardous by-products [14].

The consumption of Indigo carmine dye causes permanent injury to cornea and conjunctiva, it is carcinogenic and can lead to reproductive, developmental, neuron and acute toxicity [15]. It also causes gastrointestinal irritations with nausea, vomiting and diarrhea [16, 17]



Indigo Carmine (IC), Molecular weight: 466.36 g mol^{-1} , λ_{max} : 600 nm

Various attempts have been made for the removal of indigo carmine dye from water and wastewater [18, 19]. Apart from adsorption over chitin and chitosan [20] and charcoal from extracted residue of coffee beans [21], electrochemical [22], biological [23] and photochemical [24] techniques have also been explored.

In this study, the $CaZrO_3$ catalyst was synthesized by combustion synthesis method in which fuel were taken in deficient proportion and characterized in detail. IC dye was selected as object pollutant. UV light (365 nm) 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 $CaZrO_3$ not used earlier for removal of Indigo carmine dye from water and waste water.

Experimental

Commercially available Indigo carmine, 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 hydrochloric acid and dilute sodium hydroxide in proper amount was used to adjust the suitable pH value.

Synthesis of $CaZrO_3$ catalyst

$CaZrO_3$ 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. $CaZrO_3$ obtained was 5 g. Dish containing the solution was introduce into muffle furnace preheated at 400 °C. Mixture boils, foams and ignites to burn, yielding voluminous and foamy $CaZrO_3$ 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 $CaZrO_3$.

Physicochemical characterization of $CaZrO_3$ catalyst

The crystallinity and phase identification of the powder was determined by powder XRD using Philips PW-1700 diffractometer with Ni filtered CuKα radiation. A reflectance spectrum was recorded on GBC Cintra 10e (Australia) spectrophotometer. Surface area measurements was done using nitrogen gas adsorption multipoint Brunquer-Emmett-Teller (BET) method on Micromeritics ASAP 2010 model, assuming a cross sectional area of 0.162 nm^2 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):

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

Where S_{BET} is the superficial area ($m^2\ g^{-1}$) 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 Indigo carmine dye

A Heber Immersion type photo reactor (model: HPSLIV 16254) was used for irradiation of model dye solution. Air was allowed to pass into dye solution using aerator. A known amount of dye solution (100 cm^3) and $CaZrO_3$ catalyst was taken in reactor. Solution was irradiated under UV light (365 nm). At given irradiation time intervals, 10 ml of the suspension were collected, centrifuged and filtered to separate the photocatalyst particles. After each irradiation the IC concentration was measured by UV-Visible Spectrophotometer (UV-1800, Simadzu, Japan) at 600 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 $CaZrO_3$ in acid and alkali was studied by keeping it in 1M HCl and 1M NaOH for 24 hr. Experiments was carried out for IC dye with regenerated catalyst at its optimized parameters.

RESULTS AND DISCUSSION

Characterization of $CaZrO_3$

Fig. 1 shows the XRD pattern of $CaZrO_3$. 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.

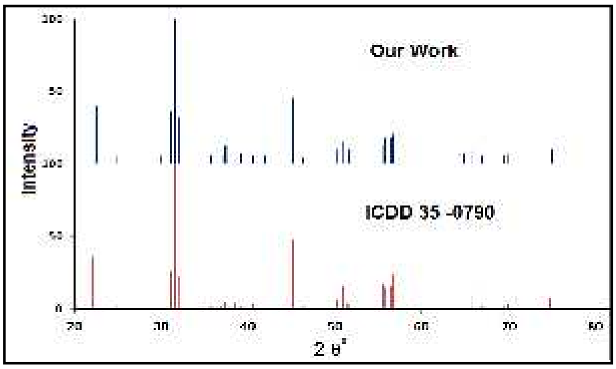


Fig. 1 X-ray diffraction pattern of $CaZrO_3$

DTA and TGA curves of $CaZrO_3$ (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 .

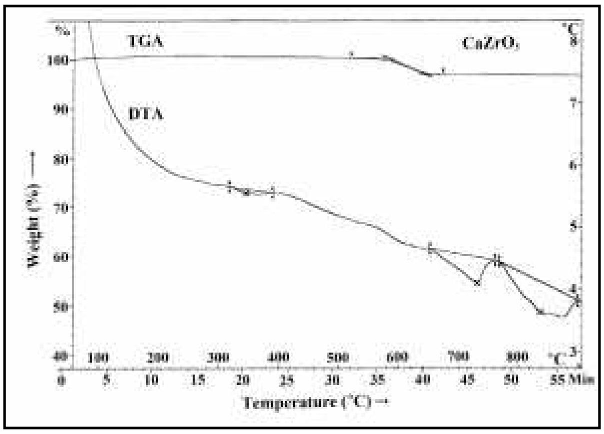


Fig. 2 Thermogram of TGA and DTA of $CaZrO_3$

The diffuse reflectance spectra is an efficient tool for the determination of energy band gap of $CaZrO_3$. The band gap energy of $CaZrO_3$ was found to be 3.94 eV. BET surface area was found to be 39.57 $m^2\ g^{-1}$. 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 $CaZrO_3$ 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 $CaZrO_3$ powders.

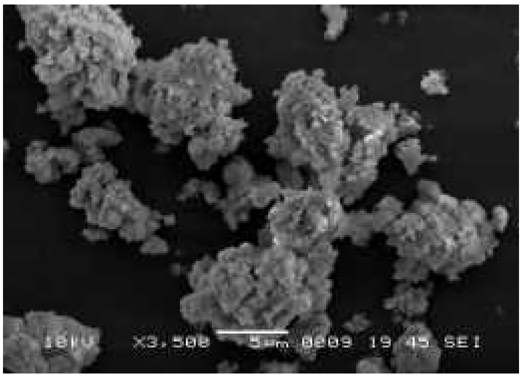


Fig. 3 Scanning electron microscopy image of $CaZrO_3$

Photocatalytic degradation studies

Effect of pH

Employing $CaZrO_3$ as a photocatalyst the decomposition and mineralization of IC dyes in aqueous suspension of $CaZrO_3$ was studied in the pH range between 4 and 10 (Fig. 4). In this work, results illustrate that the degradation rate for IC 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 increases. The efficiency of degradation of IC dye in alkaline solution was more and it was lower in acidic pH. In alkaline solution, there is a higher concentration of OH^- ions, which can lead to the photogeneration of more of the reactive $^{\cdot}OH$ radicals and thus increasing the efficiency of IC dye degradation,

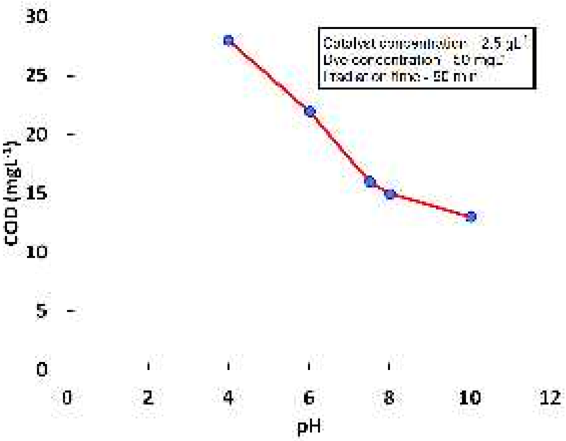


Fig.4 Effect of pH on COD removal of IC dye

Effect of catalyst concentration

The effect of catalyst concentration on the degradation of IC was investigated employing different concentration of $CaZrO_3$ 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 no change in 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 $CaZrO_3$ is obtained. The large amount of photons adsorbed and the amount of dyes adsorbed on the $CaZrO_3$ surface improved the photocatalytic degradation. When the $CaZrO_3$ 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 $CaZrO_3$ 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.

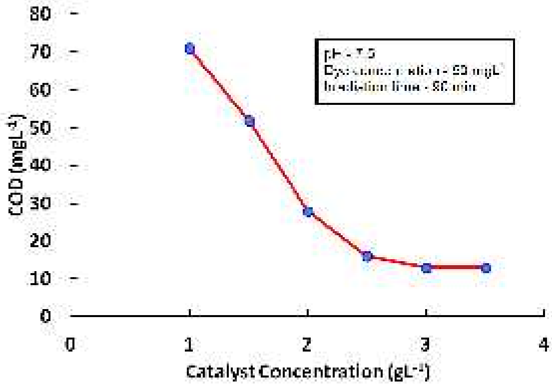


Fig. 5 Effect of catalyst concentration on COD removal of IC dye

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 IC was studied at varying concentration from 25 mg L^{-1} to 200 mg L^{-1} keeping other parameters constant (Fig. 6). 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 $CaZrO_3$ particles as well as in solution. On the surface of $CaZrO_3$ particles, the reaction occurs between the $OH^{\cdot}$ radicals generated at the active OH^- sites and dye molecule from the solution.

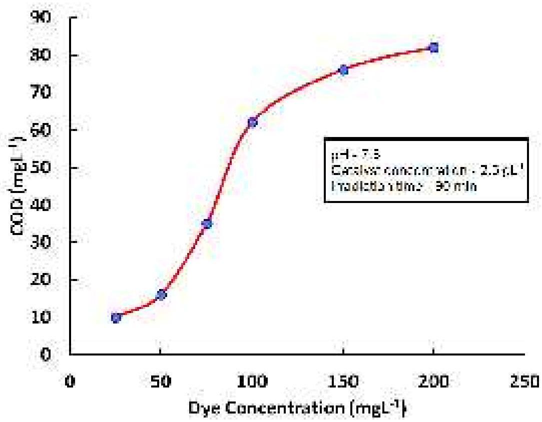


Fig.6 Effect of dye concentration on COD removal of IC dye

In addition, a significant amount of light may also be absorbed by the dye molecules rather than the $CaZrO_3$ 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 $CaZrO_3$ surface and resulted in a slower production of $^{\cdot}OH$ radicals. Consequently, the degradation rate is decreased.

Effect of irradiation time

The effect of irradiation time on degradation of IC dyes was investigated and same is revealed in Fig.7. The irradiation time was varied from 15 min to 120 min keeping other parameters constant. It was observed that the maximum quantity of IC dye was degraded up to 90 min.

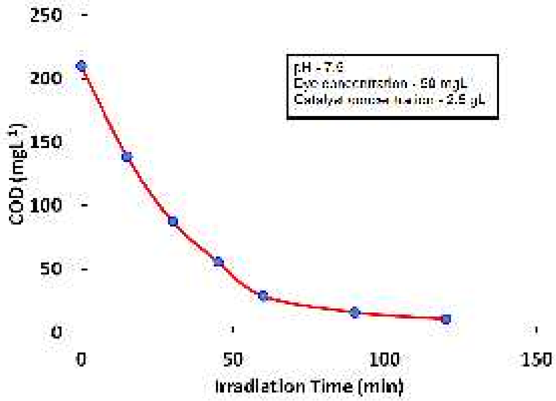


Fig. 7 Effect of irradiation time on COD removal of IC dye

Degradation and Decolorization

The UV-vis spectra of the original IC 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 UV light irradiation indicating complete destruction of IC dye. As a result, both an appropriate light source and catalyst are essential for photocatalytic decolorization and degradation of the IC dye on $CaZrO_3$ to occur.

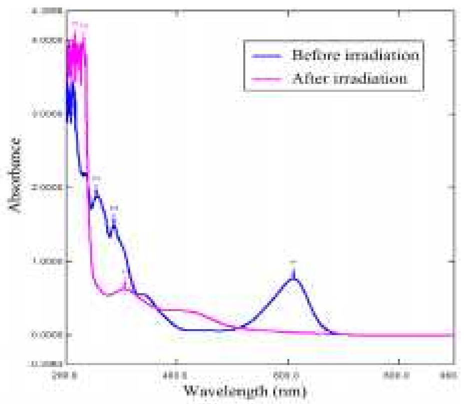


Fig. 8 UV-visible spectrum of before and after irradiation of IC dye

CONCLUSION

Calcium Zirconate was successfully synthesized by using combustion synthesis method at 400 °C within 15 min. time interval. Calcium Zirconate was found to be efficient photocatalyst for photodegradation of Indigo carmine dye, nearly 92 percent COD removal and 98 percent color removal was observed in 90 min using UV 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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