INTERNATIONAL JOURNAL OF RESEARCHES IN BIOSCIENCES, AGRICULTURE & TECHNOLOGY
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www.vmsindia.org

Photocatalytic degradation of Indigo Carmine dye on combustion synthesized SrZrO3 catalyst under UV irradiation

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Abstract
The Strontium zirconate ($SrZrO_3$) catalyst was prepared by solution combustion synthesis method and extensively characterized by XRD, SEM, TGA, DTA, Reflectance spectroscopy, BET surface area and powder density. An 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 concentrations, pH of the reaction solution and irradiation time were investigated. Results of characterization indicated the successful formation of $SrZrO_3$ catalyst. Recycling experiments confirmed the relative stability of the catalyst.

Key words: Photocatalysis; Degradation; SEM; Strontium zirconate; Combustion Synthesis;

1. Introduction

Dyes are an abundant class of synthetic, colored, organic compounds. About 1-15% of the synthetic textile dyes used is released in wastewater streams during synthesis and processing [1,2]. The discharge of highly colored wastewater is aesthetically displeasing and impedes light penetration [3]. The reagents used in textile industry are very diverse in chemical composition. The non-biodegradability of textile wastewater is due to the high content of dyestuffs, surfactants and other additives, which are generally organic compounds of complex structure [4]. Thus disturbing biological process within a stream. Hence, removal of dyes from such wastewater is a major environmental problem and complete dye removal is necessary because dyes will be visible even at low concentrations. Due to the large variability in composition of textile wastewater and the relative stability of dye molecular structures, most of the conventional physicochemical and biological treatment methods are inadequate for their effective removal [5-7]. Among the new oxidation methods or 'advanced oxidation processes' (AOP), heterogeneous photocatalysis appears as an emerging destructive technology leading to the total mineralization of many organic pollutants [8-14]. The indigo carmine can cause skin and eye irritations. It can also cause permanent injury to cornea and conjunctiva. The consumption of the dye can also prove fatal, as it is carcinogenic and can lead to reproductive, developmental, neuron and acute toxicity [15]. It has also been established that the dye leads to tumours at the site of application [16]. When administered intravenously to determine potency of the urinary collecting system, it is also known to cause mild to severe hypertension, cardiovascular and respiratory effects in patients [17-19]. It may also cause gastrointestinal irritations with nausea, vomiting and diarrhea [20,21]. Various attempts have been made for the removal of indigo carmine dye from water and wastewater [22,23]. Apart from adsorption over chitin and chitosan [24] and charcoal from extracted residue of coffee beans [25], electrochemical [26], biological [27] and photochemical [28] techniques have also been explored. Strontium zirconate have been synthesized by combustion synthesis method with Stoichiometry proportion of oxidizer and fuel [29]. Literature survey reveals that the $SrZrO_3$ not used earlier for removal of indigo carmine dye from wastewater.

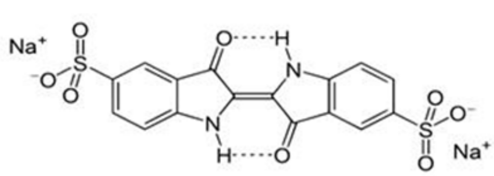

Fig.1. Indigo Carmine (IC), Molecular weight: 466.36 g mol^{-1}

In this present study, the $SrZrO_3$ catalyst was synthesized by combustion synthesis method in which fuel were taken in deficient proportion and characterized in detail. Indigo carmine was selected as object pollutant. UV light (254nm) was used for irradiation. Different factors for degradation were investigated. The results obtained from this study could provide fundamental information for the treatment of organic dye contaminated industrial effluents.

2. Experimental

2.1. Materials

Commercially available indigo carmine, Strontium nitrate and Zirconium nitrate was purchase from LOBA Chemie Company (Mumbai, India). Ammonium nitrate, glycin and urea purchase from Merck (India). All the chemicals used as received without further purification. All the solutions were prepared in double distilled water. Dilute nitric acid and dilute sulphuric acid in proper amounts was used to adjust the suitable pH value.

2.2. *Methods*

2.2.1. *Synthesis of $SrZrO_3$ catalysis*

In combustion synthesis method corresponding metal nitrates were used as oxidizer and glycin, urea and ammonium nitrate ware used as fuels in fuel deficient proportion. The redox mixture was dissolved in minimum quantity of deionised water taken 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. $SrZrO_3$ obtained was 5g. Dish containing the solution was introduced into muffle furnace preheated at 400 ^{0}C. Mixture boils foams and ignites to burn, yielding voluminous and foamy $SrZrO_3$ 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^{0}C for 2 h in air to obtain pure form of $SrZrO_3$.

2.2.2. *Physicochemical characterization of $SrZrO_3$ catalysis*

The crystallinity and phase identification of the powders were 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 and Micromeritics ASAP 2010 model, assuming a cross sectional area of 0.162nm^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:

$$D_{BET} = 6/S_{BET}.\rho$$

Where S_{BET} is the superficial area (m^2g^{-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 analyser instrument after coating the sample with gold for evaluation of particle morphology.

2.2.3. *Photodegradation and analysis of Indigo Carmine*

A specially designed cylindrical reactor in which UV light and air was facilitate to insert in dye solution. A known amount of 100 cm^3 dye and $SrZrO_3$ catalyst was taken in reactor, air was passed inside the solution throughout the experiment and irradiate under UV light. At given irradiation time intervals, 10 ml of the suspension were collected, then centrifuged and filter to separate the photocatalyst particles. After each irradiation the IC concentration was measured by UV1800 Model UV-Visible Spectrophotometer (Simadzu, Japan) at 600nm and COD analysis was carried out on UNIPHOS India make COD analyzer before that sample were digested (2 h) at 150^{0}C in UNIPHOS COD digester. The degradation and removal of COD were studied by varying different parameter such as catalyst amount, initial concentration of dye, pH of the solution and irradiation time.

After irradiation catalyst was regenerated. For regeneration, previously used catalyst was separated from dye solution, washed several times with distilled water and kept in muffle furnace at 600°C for 2h. Also stability of $SrZrO_3$ in acid and alkali was studied by keeping it in 1M acid and 1M alkali for 24h. Experiment was carried out for all three dyes with regenerated catalyst at their optimized parameter.

3. Results and Discussion

3.1. *Characterization of $SrZrO_3$*

Fig. 2. shows the XRD pattern of $SrZrO_3$. A good match is observed with ICDD file 44-0161. It is observed that a single phase, crystalline nature with cubic structure has been formed.

DTA and TGA curve of $SrZrO_3$ are presented in Fig.3. It is observed that the compound is almost stable with very small weight loss. DTA results of $SrZrO_3$ shows four endothermic peak. The endothermic break at 490°C reaches a peak at 500°C and end at 520°C. The second endothermic curve begins at 580°C reaches a peak at 600°C end at 620

°C. The third endothermic curve begins at 670°C reaches a peak at 750°C end at 770 °C and the fourth endothermic curve begins at 790°C reaches a peak at 865°C end at 910 °C.

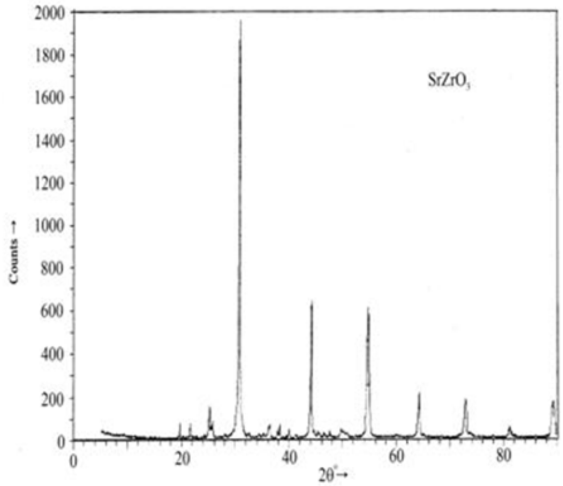

Fig.2. X-ray diffraction pattern of $SrZrO_3$

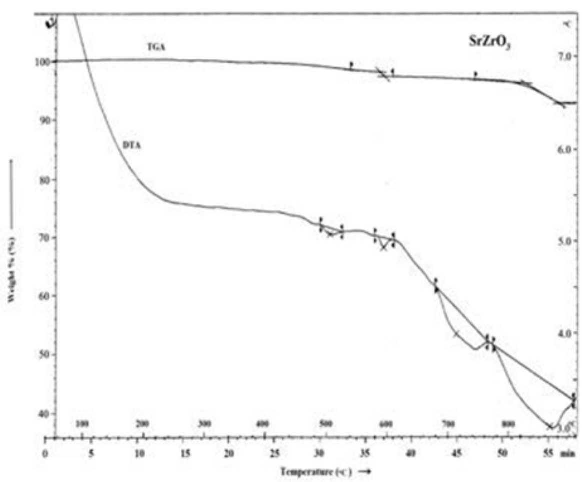

Fig.3. Thermogram of TGA and DTA of $SrZrO_3$

The diffuse reflectance spectra of $SrZrO_3$ is an efficient tool for the determination of band gap of materials. It shows absorption in UV region. The band gap of $SrZrO_3$ was found to be 3.79eV. BET surface area was found to be $34.25 m^2 g^{-1}$. Powder density was calculated by pycnometer using xylene as liquid medium. Powder density was found to be 2.898 gcm^{-3}. The average particle diameter was found to be 60nm which was obtained from BET surface area measurement and density value.

The morphology of $SrZrO_3$ samples was investigated by scanning electron microscopy (SEM) with JEOL 6380A microscope. SEM image of SrZrO3 powders calcined at 800°C is shown in Fig. 4. The SEM image clearly indicates the high homogeneity of the SrZrO3 powders.

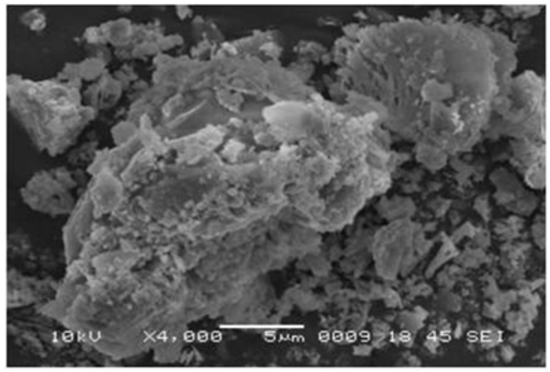

Fig.4. Scanning electron microscopy image of $SrZrO_3$

3.2. *Photocatalytic degradation studies*

3.2.1. *Effect of pH*

Employing $SrZrO_3$ as a photocatalyst the decomposition and mineralization of IC dyes in aqueous suspension of $SrZrO_3$ was studied in the pH range between 4 and 10 (Fig. 5). In this study it has been shown that the degradation rate for IC dye under investigation is strongly influenced by reaction pH where the efficiency of degradation rate for the decomposition of dye was better at pH 7.50 (Natural),8 and 10, where as it was lower at pH values 4 and 6.

3.2.2. *Effect of photocatalyst loading*

The effect of photocatalyst loading on the degradation of IC was investigated employing different concentration of $SrZrO_3$ varying from 1 to $3gl^{-1}$ shown in Fig. 6. As expected the COD of dye solution was found to decrease with increase in catalyst concentration up to $2gl^{-1}$. Further increase in catalyst concentration found constant value of COD. The increase in the efficiency seems to be due to the effective surface of catalyst area and the absorption of light. Hence, in this study catalyst loading was optimized $2gl^{-1}$ for IC at their natural pH.

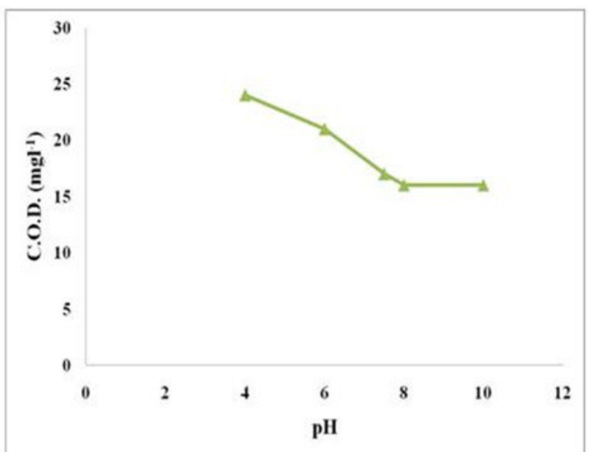

Fig.5. Effect of pH on COD removal of IC

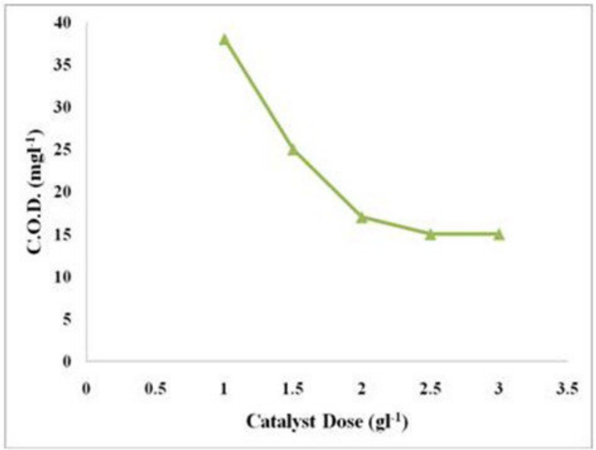

Fig.6. Effect of catalyst concentration on COD removal of IC

(Dye Concentration-50mgl^{-1}, Catalyst Dose-2g l^{-1}, Irradiation Time-60min) (Dye Concentration-50mgl^{-1}, Irradiation Time-60min, pH-7.50(Natural))

3.2.3. *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 25mgl^{-1} to 200 mgl^{-1} keeping other parameters constant (Fig. 7). It is interesting to note that the COD removal of dye solution decrease with increase in dye concentration from 25mgL^{-1} to 200 mgL^{-1}. The initial dye concentration dependence of the degradation rate of dye can be realized by the fact that the photocatalytic reaction occurs on $SrZrO_3$ particles as well as in solution. On the surface of $SrZrO_3$ 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 $SrZrO_3$ at a higher initial dye concentration. This condition can be ascribed to the increase in the initial concentration which led to less photons reaching the $SrZrO_3$ surface and resulted in a slower production of ·OH radicals. Consequently, the degradation rate is decreased.

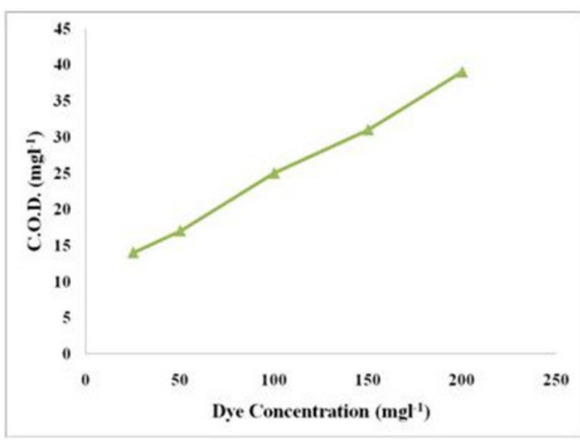

Fig.7. Effect of dye concentration on COD removal of IC

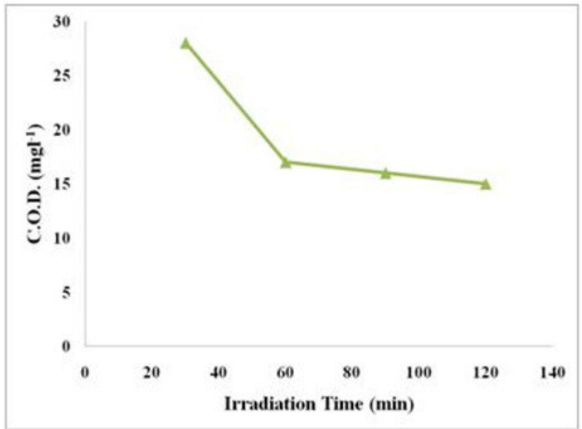

Fig.8. Effect of irradiation time on COD removal of IC

(Catalyst Dose-2.0gl^{-1}, Irradiation Time-60min, pH-7.50(Natural)) (Dye Concentration-50mgl^{-1}, Catalyst Dose-2.0gl^{-1}, pH-7.50(Natural))

3.2.4. *Effect of irradiation time*

The effect of irradiation time on degradation of IC dyes was investigated and same is shown in Fig. 8. The irradiation time was varied from 30min to 120min keeping other parameters constant. It was observed that the maximum degradation of IC dye was found up 60min after that the degradation rate was slow.

3.2.5. *Regeneration study*

Physical and Chemical properties of regenerated catalyst was found to be similar to that of original catalyst. It does not show any change in TGA and DTA. Catalyst was found to be stable in acid and alkali, no sign of degradation of regenerated $SrZrO_3$ was observed and degradation of IC dyes with regenerated $SrZrO_3$ was found to be 93 percent at their optimized parameter

4. Conclusion

Strontium Zirconate was successfully synthesized by using solution combustion synthesis method at 400°C within 15 min. time interval. Strontium Zirconate was found to be efficient photocatalyst for photodegradation of Indigo Carmine dye, nearly 94 percent COD removal was observed in 60min using Ultra Violet light as a source of irradiation. $SrZrO_3$ can regenerate and reused effectively and degradation efficiency from observation was found to be nearly similar to that of original $SrZrO_3$.

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