PHOTOCATALYTIC DEGRADATION OF COMMERCIAL DYES ON COMBUSTION SYNTHESIZED BARIUM ZIRCONATE

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ABSTRACT:

This paper reports the semiconductor assisted photocatalytic degradation of reactive dyes such as Congo Red (CR), Naphthol Blue Black (NBB) and Indigo Carmine (IC) on combustion synthesized Barium Zirconate ($BaZrO_3$) as a photocatalyst. Glycin, Urea and Ammonium Nitrate were used as fuel in fuel deficient proportion and corresponding metal nitrates were used as oxidizer for the synthesis of $BaZrO_3$. Barium zirconate was characterized by powder XRD, Brunquer-Emmett-Teller (BET) surface area, scanning electron microscopy, powder density and reflectance spectroscopy. BET surface area was found to be $35.85 m^2/g$ and had a particle size equal to 66nm. Energy gap was found to be 3.89eV as observed by reflectance spectroscopy. 94, 92 and 95 percent COD removal was observed for CR, NBB and IC dyes respectively at their natural pH. The time required for their degradation was 60, 90 and 90 min. respectively for CR, NBB and IC dyes using indoor solar light as a source of irradiation.

KEY WORDS: Photocatalysis; Combustion synthesis; COD;

INTRODUCTION:

In the present investigation BaZrO has been prepared by modified solution combustion synthesis route using mixture of fuels viz. glycine, urea and ammonium nitrate in fuel deficient proportion. It is an inexpensive technique to produce oxides and mixture of submicron and nanosized powder. The fuels employed in this method have good complexing tendency and moreover they are cheap. Generally glycine fuel gives traces of carbon in the combustion product. So ammonium nitrate, which acts as an oxidizer was used along with glycine and urea (Aruna and Rajam, 2004; Mark et al., 1967). Huge amount of waste water containing dyestuff with intensive color and toxicity is introduced into aquatic system during dye production and textile manufacturing. Some of these dyes are difficult to degrade with standard biological methods (Wang, 2000). Within the overall category of dyestuffs, some dyes consequences in terms of surrounding ecosystem. Some of the dyes are resistant to aerobic degradation (Kiriakidou et al. 1999) and under

anaerobic conditions they can be converted to potentially carcinogenic aromatic amines (Stylidi et al., 2003). Therefore, there is a need to investigate new alternative for the adequate treatment of this type of waste.

During last few years, several Advanced Oxidation Processes (AOPs) have been proposed as alternative routes for water purification (Legrini et al., 1993; Brillas et al., 1998). Among them, heterogeneous photocatalysis seems to be the most attractive method for water decontamination (Serpone, 1995; Hoffman et al., 1995) and the usefulness of this method for performing degradation reactions has been successfully tested for a large variety of pollutants (Dominguez et al., 1998; Pelizzetti and Minero, 1993; Herrmann et al., 1998; Schmelling and Gray, 1995; Fu et al., 1995; Alberici and Jardim, 1997).

Congo Red (CR) and Naphthol blue black (NBB) are azo dyes. They are toxic to many organisms and are suspected carcinogen and mutagen. CR is a benzidine-based anionic disazo dye. Benzidine and CR are, however, banned in many countries because of health concerns. But, it is still widely used in several countries. It also represents a significant effluent problem along with related dyes from textile, printing and dyeing, paper, rubber and plastic industries. Its structural stability makes it highly resistant to biodegradation and obviously its bright color and toxicity are entirely undesirable in the environment. The IC is considered as highly toxic indigoid class of dye. Contact with it 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 (Jenkins, 1978). It has also been established that the dye leads to tumours at the site of application (Yoshida et al., 1971).

Recently, semiconductor assisted photo-catalysis has been extensively investigated mainly due to its capacity to degrade a large number of recalcitrant chemicals in aqueous system. In this work, Barium Zirconate prepared by modified solution combustion method has been used as semiconducting material mainly due to its characteristic including, high photochemical reactivity, relatively low cost of production, regeneration capacity and environmentally benign material. Literature survey reveals that combustion synthesized $BaZrO_3$ have not been used as a photocatalyst for degradation of CR, NBB and IC dyes. The $BaZrO_3$ prepared by this route has large surface area and small particle size which helps in prevention of electron and whole recombination for efficient photodegradation process. In this paper, we report synthesis of $BaZrO_3$ as photocatalyst for degradation of CR, NBB and IC dyes. The results obtained are presented and discussed in this paper.

MATERIALS AND METHODS:

Chemicals: In this study all chemicals used were of AR grade. Congo red dye, naphthol blue black dye, Indigo carmine dye and zirconium nitrate were procured from LOBA Chemie Company Mumbai. Barium nitrate, glycine, urea and ammonium nitrate were purchased from Merck, India. They were used as such without further purification.

Synthesis of barium zirconate catalyst: In solution combustion synthesis method corresponding metal nitrates were used as oxidizer and glycin, urea and ammonium nitrate were used as fuels in fuel deficient proportion (O/F, 2/1). 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. $BaZrO_3$ 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 $BaZrO_3$ 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 h in air to obtain pure form of BaZrO3.

Methods for characterization of $BaZrO_3$: The crystallinity and phase identification of the powders were determined by powder XRD using Philips PW-1700 diffractometer with Ni filtered CuKa radiation. A reflectance spectrum was recorded on GBC Cintra 10e (Australia) spectrophotometer, $BaSO_4$ of A.R. grade was used as a reference and diluents. The sample to $BaSO_4$ ratio was 1:10 (w/w). Mixing was done for several minutes with agate and mortar. The sample pellet was prepared by manually pressing powdered sample in a metal sample holder and ensuring the surface to be perfectly smooth and homogeneous. The spectrum was recorded in the wavelength range 200-900nm at the data interval of 1nm. 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:

$$^{d}bet\ ^{6/s}bet* P$$

Where S is the superficial area (m^2/g) measured by BET analyses; p, the density of powders (g/cm^3); and D_{BET}, the diameter (nm) 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.

Experimental procedure: After each irradiation the sample solution were studied for chemical oxygen demand (COD). The COD test determines the oxygen required for chemical oxidation of organic matter with the help of strong chemical oxidant. The organic matter gets oxidized completely by potassium dichromate in presence of sulfuric acid to produce carbon dioxide and water. COD analysis was carried out on UNIPHOS India make COD analyser before that sample were digested (2h) at 150^0C in UNIPHOS COD digester. The color removal and degradation of dye was analyzed on UV- visible spectrophotometer (UV-1800, Shimadzu, Japan).

Catalyst regeneration: After irradiation catalyst was regenerated. Previously used catalyst was separated from dye solution, kept in muffle furnace at 600°C for 2h. Also stability of $BaZrO_3$ 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.

Results and discussions

The solution combustion synthesis of $BaZrO_3$ using glycine, urea and ammonium nitrate as fuels and corresponding metal nitrates as oxidizer was found to be successful in producing crystalline, phase pure powders at a temperature 400°C within 15min time. The fuel used, react non-violently, produce non-toxic gases and act as good complexant for metal cations.

Characterization of $BaZrO_3$: Fig 1. illustrate that the XRD pattern of $BaZrO_3$. An excellent match is observed with ICDD file 89-2486. It is observed that a single phase, crystalline nature with cubic structure has been formed. The powder XRD shows very sharp peak, which can be attributed to high exothermicity of solution combustion process. The high exothermicity of the process may be attributed to the presence of ammonium nitrate, which may act as a combustion aid as suggested by Segadaes et al (Sagadaes et al., 1998). (Biamino and Badini, 2004) observed that, when ammonium nitrate is present in the reagents, the sample temperature, sometime after ignition, increases more quickly, and the combustion rapidly reaches the end. Thus ammonium nitrate provides required temperature for the formation of pure BaZrO3 and also hinders detrimental secondary reaction of thermal decomposition.

DTA and TGA curve of $BaZrO_3$ are presented in Fig 2. It is observed that the compound is almost stable with very small weight loss. It may be observed due to structural changes taking place in compound; up to 830°C no thermal degradation was observed. DTA results of $BaZrO_3$ shows two endothermic and one exothermic peak. The endothermic break at 650°C, reaches a peak at 735°C, and end at 756°C. The second endothermic curve begins at 805°C reaches a peak at 875°C end at 950 °C, and merges with an exothermic curve. The small exothermic curve reaches a peak at 950°C and ends at 980°C. The exothermic peak in the high temperature region can be attributed to the formation of different phases in compound. The reflectance spectrum of BaZrO3 is shown in Fig 3. Diffuse reflectance spectra is an efficient tool for the determination of band gap of materials. It shows absorption in UV region. The band gap of $BaZrO_3$ was found to be 3.89eV. BET surface area was found to be $35.85m^1/g$. Powder density was calculated by pycnometer using xylene as liquid medium. Powder density was found to be 2.54 g cm^{-3}. The average particle diameter was found to be 66nm which was obtained from BET surface area measurement and density value.

The morphology of BaZrO3 samples was investigated by scanning electron microscopy (SEM) with JEOL 6380A microscope. SEM image of BaZrO3 powders calcined at 800°C is shown in Fig 4. The SEM image clearly indicates the high homogeneity of the BaZrO3 powders.

Effect of pH: Employing $BaZrO_3$ as a photocatalyst the decomposition and mineralization of CR, NBB and IC dyes in aqueous suspension of $BaZrO_3$ was studied in the pH range between 4 and 10 (Fig 5). In this study it has been revealed that the degradation rate for CR dye under investigation is strongly influenced by reaction pH where the efficiency of degradation rate for the decomposition of dye was better at pH 7.5, 8

and 10, where as it was lower at pH values 4 and 6. The efficiency of degradation of CR 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 OH radicals and thus increasing the efficiency of CR dye degradation. The efficiency of degradation of NBB and IC dye was enhanced at pH 4, 6 and 7.5 and lower at pH 8 and 10. The efficiency of degradation of NBB and IC was more in acidic and neutral pH and as the pH increases the percent COD removal decreases. At low pH value, the electrostatic interaction between positively charged surface of BaZrO and dye anions in aqueous solution leads 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.

Effect of catalyst loading: The effect of photocatalyst loading on the degradation of CR, NBB and IC was investigated employing different concentration of $BaZrO_3$ varying from 1 to 3 g/L shown in Fig 6. As expected the COD of dye solution was found to decrease with increase in catalyst concentration up to 2 g/L for CR and 2.5 g/L for NBB and IC respectively. Further increase in catalyst concentration found constant 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 $BaZrO_3$ is obtained. The large amount of photons adsorbed and the amount of dyes adsorbed on the $BaZrO_3$ surface improved the photocatalytic degradation. When the $BaZrO_3$ 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 BaZrO 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, in this study catalyst loading was optimized 2 g/L for CR and 2.5 g/L for NBB and IC at their natural pH.

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, NBB and IC was studied at varying concentration from 25 mg/L to 200 mg/L keeping other parameters constant .

It is interesting to note that the COD of dye solution increase with increase in dye concentration from 25mg/L to 200 mg/L. The initial dye concentration dependence of the degradation rate of dye can be realized by the fact that the photocatalytic reaction occurs on $BaZrO_3$ particles as well as in solution. On the surface of $BaZrO_3$ particles, the reaction occurs between the OH' radicals generated at the active OH^- sites and dye molecule from the solution. When the initial dye concentration increase, the number of available active sites was reduced for dye molecule because of their competitive adsorption on $BaZrO_3$ surface. Since the intensity of light and irradiation time were constant, the OH' radicals formed on the surface of $BaZrO_3$ remained practically the same. Thus the active OH radicals attacking the organic pollutant decrease due to the lower ratio of the OH/dye. In addition, a significant amount of light may also be absorbed by the dye molecules rather than the $BaZrO_3$ 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 $BaZrO_3$ surface and resulted in a slower production of OH radicals. Consequently, the degradation rate is decreased, since fewer OH radicals are available to degrade more dye molecules.

Effect of irradiation time: The effect of irradiation time on degradation of CR, NBB and IC dyes was investigated and same is shown in Fig 8. The irradiation time was varied from 30 min to 120 min keeping other parameters constant. It was observed that the maximum degradation of CR dye was found in 60 min after that the degradation rate was slow. For NBB and IC the rate of degradation was found higher at 90 min and further increase in irradiation time, the rate of degradation of dye was slow. Hence, the irradiation time for CR, NBB and IC was optimized to 60 min, 90 min and 90 min respectively.

Degradation and Decolourization: The irradiation process for all three dyes was carried out at optimized parameter. The UV-visible spectrum of the original dye solutions and degraded dye solution are

presented in Fig 9, 10 and 11. The full spectrum scanning pattern showed extremely obvious difference. No peak was detected in analyzed wavelength indicating complete destruction of CR dye. As a result, both an appropriate light source and catalyst are essential for photocatalytic decolorization and degradation.

Regeneration study: Physical and Chemical properties of regenerated catalyst was found to be similar to that of original catalyst. Catalyst was found to be stable in acid and alkali medium, no sign of degradation of regenerated $BaZrO_3$ was observed. Degradation of CR, NBB and IC dyes with regenerated $BaZrO_3$ was found to be 92, 90 and 90 respectively at their optimized parameter.
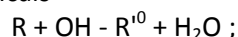
Proposed mechanism for degradation: Following is the proposed mechanism for degradation of dyes, —absorption of efficient photons (he S E = 3.89 eV) by BaZrO

$(BaZrO_3)$ + he — e''_{CB} + 11+^; —oxygen ionosorption

$(O_2)_{ads}$ + e-CB - $O°~_2$;
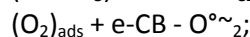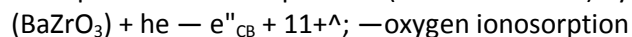
—neutralization of OH^- groups into OH by photoholes

[35T I

(H_2O « H+ + OH-)$_{ads}$ + h+vB - H+ + OH; —oxidation of the organic reactant via successive attacks by OH radicals

R + OH - R'^0 + H_2O ;

—or by direct reaction with holes

R + h+ — $R+^0$ — degradation products.

As an example of the last process, holes can react directly with

carboxylic acids, generating CO_2 according to the so called

photo-Kolbe reaction:

RCOO- + h+ — R^0 + CO,
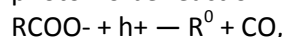
CONCLUSION

Barium Zirconate was successfully synthesized by using solution combustion synthesis method at 400°C within 15 min. time interval. Barium Zirconate was found to be efficient photocatalyst for photodegradation of commercial dyes. Nearly 94, 92 and 95 percent COD removal was observed for CR, NBB and IC dyes respectively. The time required for degradation of CR, NBB and IC dyes was 60, 90 and 90 min. respectively using indoor solar light as a source of irradiation. $BaZrO_3$ can be regenerated and reused effectively. Degradation efficiency of regenerated $BaZrO_3$ from observation was found to be nearly similar to that of original BaZrO .

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