Application of synthesized tetragonal structured zirconium oxide nanoparticle on victoria blue B and acridine orange dye

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Abstract. Zirconium oxide with the tetragonal phase was prepared from zirconium nitrate and urea by solution combustion method. Nano-photocatalyst zirconium oxide was investigated by XRD, SEM-EDAX, TEM, UV absorbance spectroscopy and specific surface area analysis. The distribution size of ZrO was found to be less than 17nm and was confirmed by XRD and TEM studies. Further the ZrO nano-photocatalyst confirms the tetragonal phase by XRD. EDAX reveals the formation of ZrO. The efficiency of ZrO nanoparticles in the photodegradation of victoria blue B and acridine orange dye under sunlight was investigated. The results reveal that the degradation efficiency was found to be 95.42% for VBB (at 0.030g/pH 6/1×10⁻⁴ mol/dm³) and 92.52% for AO (at 0.035g/pH 4/1×10⁻⁴ mol/dm³). Further the degradation efficiency shown highest in VBB dye when compare to AO dye. Therefore, the ZrO nanoparticle has been found to be suitable for the treatment of textile effluents.

Keywords: Acridine Orange, Victoria Blue B, Zirconium Oxide, Photodegradation

1. Introduction

Nanomaterials have drawn attention towards the researchers for their unique characteristics and wide applications in different areas [1]. Among these, various metal oxide nanoparticles such as ZnO, SnO₂, TiO₂, ZnO, CuO, MgO, NiO and ZrO etc. [1-3] have been used to eliminate the organic pollutants. ZrO is an eco-friendly material, non-toxic, cost effective and has high thermal and chemical stability [4]. Because of these properties, ZrO finds wide range of industrial applications such as, electronic components, electrochemical gas sensors, pigments, thermal coating, orthopedic replacements, [5] [6], catalytic applications [7] [8], explosive primers, vacuum tube getters and filaments as an alloying agent which are exposed to corrosive agents [9]. ZrO is p-type semiconductor and strong transition metal [9] [10]. ZrO exhibits three different crystal phases like cubic, tetragonal and monoclinic, depending upon the various synthesis methods and varying temperatures [11]. Different synthesis methods are reported such as, biological method, co-precipitation, solid state reaction, microwave synthesis, [12] vapor phase method, pyrolysis, spray pyrolysis, hydrolysis,[13] hydrothermal, [4] sol-gel method, arc discharge method,[5] combustion method,[14] precipitation and thermal decomposition [15]. Reddy et al., 2018 [4] reported that, some methods require specific equipments, difficult to maintain specific control system and requires huge production cost. Compared to these methods, solution combustion is a friendly method to synthesize the ZrO nanoparticles in low cost. In our study, we report the synthesis and characterization of ZrO nanoparticles. The prepared ZrO nanoparticle was characterized by XRD, SEM-EDAX, TEM, BET and UV–visible spectroscopic studies.
2. Materials and Methods
Easily available zirconium nitrate (Alpha Chemicals, Mumbai) and urea chemicals were used in the synthesis of ZrO nanoparticles. Commercially available victoria blue B (VBB) ($\lambda_{\text{max}}$ 615nm) and acridine orange (AO) ($\lambda_{\text{max}}$ 492nm) dyes were obtained from Sigma Aldrich Pvt. Ltd. Maharashtra (Figure 1).

2.1 Synthesis of ZrO Nanoparticle
Commercially available zirconium nitrate as metal nitrate and urea as a fuel are used for the synthesis of ZrO nanoparticle by solution combustion method (SCM). Stochiometric composition of zirconium nitrate (13.87g) and urea (6.05g) were dissolved in double distilled water. Further, the solution was subjected to combustion in a preheated muffle furnace (600ºC). After cooling, the obtained particles were finely ground and used for characterization and photocatalytic activity. The propellant chemistry reaction is presented below.

$$6\text{Zr(NO}_3\text{)}_2 + 10 \text{NH}_2\text{CONH}_2 \rightarrow 6\text{ZrO} + 10\text{CO}_2 + 20\text{H}_2\text{O} + 16\text{N}_2$$

(Eq. 1)

2.2 Characterization of ZrO nanoparticles
The synthesized ZrO nanoparticles were characterized by XRD (Make: Bruker AXS D8). Surface morphology and elemental analysis were measured by SEM-EDAX (Make: JEOL JSM - 6390LV). Further material crystal structure and size were analyzed during TEM (Make: JEOL JEM-2100). The optical band gap (OBG) determination was carried out using UV–visible spectrophotometer wavelength of 175 – 3300nm (Make: Varian, Cary 5000) and Brunauer–Emmett–Teller (BET) was used to measure micro-pores and specific surface area (SSA) at 77 K (Make: NOVA-1000 v3.70).

2.3 Experimental Procedure
The stock solution was prepared by dissolving 0.025g of VBB and 0.015g of AO dye in 50mL of double distilled water. For each experiment, an appropriate volume of dye from stock solution was further diluted to 50 ml using double distilled water and pH was adjusted by adding NaOH or HCl. The experimental set up was placed on a magnetic stirrer under direct sunlight between 11am to 2pm (180 min) as a batch study and the average light intensity was recorded to be 927×100 lux. During the experiment, an aliquot of 5 mL was drawn out every 30 minutes to monitor the degradation process using UV-Visible spectrophotometer. All the experiments were conducted in 100ml beakers (Borosil), and to avoid evaporation of dye solution in sunlight, we stoppered the beakers using petri plates. The percentage of degradation calculated from the equation is given below

$$D = \frac{A_0 - A_t}{A_0} \times 100$$

(Eq. 2)

3. Results and Discussion
3.1 XRD
The synthesized ZrO nanoparticle patterns are shown in figure 2a. The 2θ (degree) of ZrO nanoparticles are 30.22, 35.27, 50.73, 60.20 and 62.85, indexed to 101, 110, 200, 211 and 202 planes with lattice constant (a): 3.5957Å (space group P42/n [137]) and well defined diffraction peaks were observed. The ZrO nanoparticle confirms the tetragonal structure (JCPDS card number 01-079-1769) which indicates crystallinity of solids. However the particle size is affected by broadening of peaks. Scherer’s formula was used to calculate the size of the ZrO nanoparticle.
D=0.94λ/βcosθ  
(Eq. 3)

Where D is the average crystal size, β is the half-height width of the diffraction peak, θ is the diffraction angle, and λ is the X-ray wavelength (0.1541 nm). The size of the ZrO was 14 nm.

3.2 SEM-EDAX

The surface morphology and elemental analysis was recorded for ZrO nanoparticles are shown in figure 3. Figure 3a illustrates that particles are non-homogeneous and agglomerated in nature. Figure 3b confirms the presence of ZrO nanoparticles and weight percentage was found to be 58.27% and 41.73% respectively.

3.3 TEM

The TEM image recorded for ZrO nanoparticles are shown in figure 4. The size and shape of the particles were found to be non-homogeneous and agglomerated. The particles sizes ranged between 3nm and 17nm. Interplanar spacing (d) was determined by SAED patterns. The figure 4c illustrates the electron diffraction patterns of selected area ZrO nanoparticle. The d-space value of ZrO nanoparticle is calculated from the distance between two bright spots found to be 9.351 and the d-space value of ZrO was found to be 0.22nm. The TEM and XRD are in well agreement with the crystalline sizes.

3.4 UV-Visible Absorption Spectrum

The UV-Visible absorption of prepared tetragonal ZrO nanoparticle is shown in figure 2b and OBG was calculated using Tauc relation

(αhv)\(\cdot\)hν = (Eg)\(\cdot\)[1/2]  
(Eq. 4)
Where \( h\nu \) is the photon energy and \( \alpha \) is the optical absorption coefficient near the fundamental absorption edge. The absorption coefficients were calculated from the optical absorption spectra. The OBG of ZrO obtained by plotting \((\alpha\hbar\nu)^2\) versus \((\hbar\nu)\) in the high absorption range followed by extrapolating the linear region of the plots to \((\alpha\hbar\nu)^2=0\). The OBG of ZrO nanoparticle was found to be 3.2eV. Singh and Nakate [2014] [11] reported the wide variation in the band gap, which can be attributed to presence of the phase, morphology and defect state.

3.5 BET Surface area analysis

The SSA of ZrO was measured using BET nitrogen adsorption–desorption. \( N_2\)-adsorption/desorption isotherm plot and the Barret-Halenda (BJH) pore size distribution plot is shown in figure 5a and 5b respectively.

![Figure 5: (a) \( N_2\) adsorption and desorption isotherm plot (b) BJH plot for pore size distribution](image)

The isotherm was found similar to type IV behaviour, having micro-pores material characteristic (particle size < 2nm) confirmed by TEM image (figure 4d). Similar Type IV behaviour was reported in Reddy et al., [2018] [4]. The SSA of ZrO was found to be 0.779 m\(^2\)/g. The obtained SSA is efficient to carry out the photocatalytic activity. The multi peak pore size curve distribution reveal the presence of variation in pore size distribution within 15nm range (figure 5b) and different particle size as shown by TEM. The pore size distribution is found to be within 100nm range (figure 5b).

3.6 Effect of Catalyst Concentration

The effect of ZrO loading on VBB and AO dye removal was studied by varying catalyst dose from 0.025g to 0.045g with constant dye concentration\((1\times10^{-4}\)mol/dm\(^3\))and maintained at pH 7 (figure 6). The degradation efficiency of ZrO is shown in Table 1. A rapid degradation rate is observed before the peak degradation is achieved, after which the degradation decreases [16]. The initial rapid degradation is attributed to the availability of abundant active surface area of ZrO.

![Figure 6: Effect of catalyst concentration (a) AO (b) VBB](image)
A further increase in catalyst concentration beyond the optimum range leads to aggregation of nanoparticles and formation of turbid solution. This leads to the penetration of lesser photons, reduction in hydroxides and super oxides [17] [18] leading to decreased efficiency of degradation. Hence the optimum catalyst concentration achieved was 0.030g for VBB dye and 0.035g for AO dye.

Table 1: Effect of parameters for ZrO NPs for photodegradation of VBB and AO dye

| Catalyst Concentration | VBB Degradation (%) | AO Degradation (%) | pH | VBB Degradation (%) | AO Degradation (%) | Dye Concentration | VBB Degradation (%) | AO Degradation (%) |
|------------------------|---------------------|--------------------|----|---------------------|--------------------|-------------------|---------------------|--------------------|
| 0.025g                 | 88.05               | 79.61              | 2  | 83.24               | 86.27              | 1x10^{-4}mol/dm³ | 95.42               | 92.52              |
| 0.030g                 | 93.63               | 84.47              | 4  | 89.51               | 92.52              | 2x10^{-4}mol/dm³ | 87.91               | 88.55              |
| 0.035g                 | 89.51               | 90.67              | 6  | 95.42               | 88.95              | 3x10^{-4}mol/dm³ | 79.26               | 81.42              |
| 0.045g                 | 85.99               | 86.19              | 8  | 90.35               | 83.25              | 4x10^{-4}mol/dm³ | 69.99               | 73.87              |

3.7 Effect of pH

The pH was varied (pH 2–10) to determine the optimum pH for the photodegradation of VBB and AO dye while keeping constant catalyst concentration (0.030g for VBB and 0.035g for AO) and dye concentration (1x10^{-4}mol/dm³). The degradation efficiency of VBB and AO dyes are represented in table 1 and figure 7. The rate of degradation initially increased with increase in pH (2-6 for VBB and 2-4 AO) but decreased with the further increase in pH (> 6 for VBB and AO). The maximum rate of degradation was achieved at pH 6 for VBB and pH 4 for AO dyes respectively. Table 1 shows that, the maximum degradation was achieved in acidic medium, in acidic medium positively charged ZrO nanoparticles and negatively charged dye molecules are adsorbed on the surface by electrostatic attraction. However at the higher pH (> 6) the degradation efficacy is decreased because of domination of negatively charged molecules present on the surface of the catalyst, which blocks the negatively charged dye molecules. Further increase in the generation of OH⁻ molecules in the solution and competition between the OH⁻ ions and negatively charged dye molecules decreases the rate of degradation [18-21].

Figure 7: Effect of pH (a) AO (b) VBB

3.8 Effect of Dye Concentration

The concentration of dye is an important parameter during the treatment of textile effluent. We varied the dye concentration from 1x10^{-4}mol/dm³ to 4x10^{-4}mol/dm³ with constant catalyst loading (0.030g for VBB and 0.035g for AO) with optimum pH (pH 6 for VBB and pH 4 for AO). The degradation efficacy is shown in table 1 and figure 8. The degradation efficacy initially increases with increment in the dye concentration up to 1x10^{-4}mol/dm³. Further increase in the concentration (>2x10^{-4}mol/dm³) decreases the degradation efficacy. This is attributed to the decreased light penetration into the solution due to the huge amount of dye adsorbed on the ZrO surfaces. The increased dye concentration also increases the time required for this process. This further leads to a decline in the generation of
hydroxyl radicals [17] [22] [23] and oversaturation of dye molecules, requiring more number of active species and loses adsorption efficacy [24] [25].

![Figure 8](image1)

**Figure 8:** Effect of dye concentration (a) AO (b) VBB

3.9 Reuse of Catalyst

The efficacy of reusability of synthesized ZrO nanoparticle is shown in figure 9. The reuse of catalyst shows appreciable results 88%, 77% for VBB and 85%, 77% for AO dye respectively. The degradation loses its efficiency by increase in number of reuse cycles due to surface bleaching of nanoparticles and less availability of active surface area. Further the loss of minute quantity of nanoparticles during the separation process. Hence it can be applicable for large scale waste water treatment process [26].

![Figure 9](image2)

**Figure 9:** Reuse of Catalyst

4. Conclusion

In this present study, we have conveniently synthesized ZrO nanoparticle by SSC method. The XRD characterization revealed the tetragonal shape and average size <15 nm. The presence of zirconium and oxygen elemental composition was confirmed by EDAX. The band gap was found to be 3.2eV. The batch study of degradation efficiency was carried out under sunlight for VBB and AO in presence of ZrO nanoparticle. The highest degradation efficiency was found to be 95.42% for VBB (at 0.030g/pH 6/1×10^{-4} mol/dm^{3}) and 92.52% for AO (at 0.035g/pH 4/1×10^{-4} mol/dm^{3}). Further the degradation efficiency is found highest in VBB dye when compare to AO dye. Therefore, the ZrO nanoparticle is suitable for the treatment of textile effluents.

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