

Decolourization of Fast Red Acid dye using Photoactive Bi₂O₃ Nanoparticle under Solar Irradiation

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Abstract: The photocatalytic efficiency of prepared Bismuth Oxide (Bi₂O₃) nano catalyst was investigated against colour induced by Fast Red acid dye. The Bi₂O₃ nanoparticles were prepared by a simple solution combustion method and the average powder size of the obtained Bi₂O₃ nanoparticles was determined by SEM and XRD analysis. The research work was done to determine the influencing parameters like, optimum catalyst dosage, pH of the dye solution, effect of sunlight irradiation and effect of dye concentration. The treatment with prepared Bi₂O₃ nanoparticle proved to be very efficient in removing the colour (~ 95.02%) at pH 10 and 0.8g/100ml of catalyst dose. The Bi₂O₃ nanoparticle was found to be an effective and low cost photocatalyst by degrading Fast Red acid dye in presence of sunlight.

1 INTRODUCTION

Over the decades, an enormous interest has been developed over photocatalysis using oxide semiconductors in environmental applications. Textile processing industries are widespread and major industrial sectors in developing countries. From the most used processes in the textile industry, dyeing process consumes most of the available water for dyeing, fixing, and washing processes. The textile industry utilizes about 10000 different dyes and the worldwide annual production of dyestuffs is more than 7×10⁵ tons (2013).

Among several textile dyestuffs, the reactive dyes contribute about 50% (2007) of the total market share and the most common group used as chromophore is the azo dye (70%), followed by anthraquinone (2004). It has been a known fact and also a documentation that dye loss in wastewaters could vary up to 50% during manufacturing or processing operations. The release of the coloured wastewaters to the water bodies will bring a drastic change in the form of pollution and results in the formation of toxic and mostly non-biodegradable substances in the ecosystem. The colouration is visible even in a very low dye concentration (below 1mgL⁻¹) (2004). As a result, technological systems

for the removal of organic pollutants such as adsorption on active carbon, reverse osmosis, ion exchange on synthetic adsorbent resins, ozonation, and biological methods were examined (2001). All of them have advantages and drawbacks but these processes have very high operating costs. However, these conventional treatment methods are not so efficient in removing the dyes from effluents, so finding an alternative and effective technique is necessary (2004), (2015), (2002), (2017).

A watchful time has been spent to develop dye treatment methods at its source (ISO 14001, October 1996). An alternative to conventional methods, such as, “advanced oxidation process” (AOP) has been developed based on the generation of very reactive species such as hydroxyl radicals. The generated hydroxyl radicals can oxidize a wide range of organic pollutants quickly and non-selectively. Among the (AOPs), heterogeneous photocatalysis appears as an emerging solution to the environmental pollution for aquatic system. This process consists of the non selective destruction of organic compounds in presence of natural light and photocatalysis systems such as TiO₂, ZnO, and CdS (2015).

In this study we have synthesized bismuth oxide nanoparticles by simple solution combustion method using stoichiometric equations. Bismuth oxide is an

important metal-oxide semiconductor, having an excellent optical and electrical property such as wide band-gap, high refractive index and photoconductivity.

Therefore, it has been used widely in many fields such as solid oxide fuel cells, gas sensors, photoelectric materials, high temperature superconductor materials, catalysts and functional ceramics (2013). For the above reasons the objective of this study was to explore the possibility photocatalytic degradation on fast red dye by varying the different parameters such as, initial dye concentration, pH, catalyst loading and in different conditions with respect to UV light and dark conditions.

2 MATERIALS AND METHODS

The commercially available water soluble dye fast red (λ_{\max} 525nm) was obtained from Sisco Research Laboratory Pvt. Ltd. Maharashtra (Figure 1). The chemicals Bismuth Nitrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$) obtained from Sisco Research Laboratory Pvt. Ltd. Maharashtra and Urea (NH_2CONH_2) obtained from Hi-Media Chemicals, Mumbai. The Visible spectrophotometer (Elico, SL 177) was used for recording absorbance at λ_{\max} . Later the absorbance was recorded in visible spectrophotometer (Elico, SL 177).

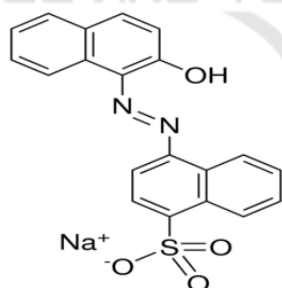
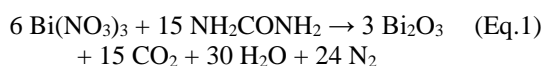


Figure 1: Structure of Fast Red Dye

2.1 Synthesis and Characterization of nanoparticles



The solution taken in a crucible was kept in a preheated muffle furnace at 600°C and the synthesized nanoparticles was crushed in a mortar to make the powder amorphous and used for further characterization. Characterization of nanoparticles by Powder X-ray diffraction (XRD) was performed

by using Rigaku diffractometer by Cu-K α radiation (1.5406 Å) in a θ -2 θ configuration. Scanning electron microscope (SEM) image was taken with a JEOL (JSM-840A). The UV-visible spectra of the photocatalysts were carried out using a UV-visible spectrophotometer in the λ range from 200 to 1200 nm. The confirmatory presence of elements was carried out using Energy Dispersive X-ray (EDX) spectrometer.

2.1.1 Experimental Procedure

Photocatalytic experiments were carried out under direct sunlight. The fast red solution was prepared by dissolving 0.02 g of dye with 1000mL double distilled water using a 1000ml volumetric flask and degradation in the presence of bismuth oxide nanoparticles at different catalyst dosages pH levels and initial dye concentration. Initially, 100ml of 20ppm dye samples were tested with different catalyst dosages (from 0.1g to 1g), by varying pH (from 2pH to 11pH), dye concentration (20ppm to 40ppm) and different conditions with respect to U.V and dark. Except U.V and dark conditions all experiments were carried out in presence of direct sunlight. The whole experimental set-up was placed under sunlight between 10 am to 2 p.m. and the average intensity of sunlight during this period was found to be 100000 to 130000 lux. After the photocatalytic degradation, the degradation percentage was estimated by recording absorbance of the dye solution using spectrophotometer (Elico, SL 177) in order to get the optimum catalyst dose. The percentage was calculated using the equation,

$$D = (A_0 - A_t / A_0 \times 100) \quad (\text{Eq. 2})$$

A_0 is initial concentration of fast red dye and A_t is the concentration of Fast Red dye at time 't'

2.2 Result and Discussion

Characterization of the Nanoparticles

2.2.1 X-ray Diffraction [XRD]

The pattern obtained from the XRD analysis of the prepared bismuth oxide nanoparticles is shown in figure 2. According to the Debye Scherrer's formula:

$$D = K\lambda/\beta \text{Cos}\theta \quad (\text{Eq. 3})$$

Where K is the Scherrer's constant, λ the X-ray wavelength, β is the peak width at half-maximum and θ is the Bragg's diffraction angle.

In the present work, the powdered sample of bismuth oxide by XRD studies found that, the size was varied from 20 nm to 55 nm and its average size was achieved at 36 nm respectively.

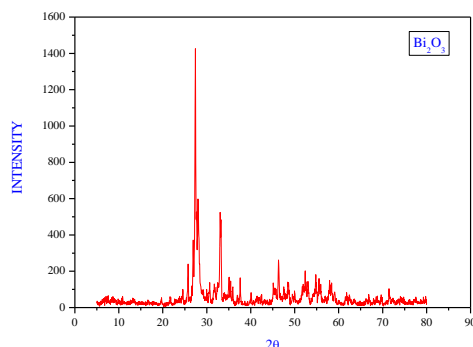


Figure 2: XRD of the synthesized Bi₂O₃ nanoparticles

2.2.2 Scanning Electron Micrograph [SEM]

Scanning Electron Microscope pictures depicts bismuth oxide nanoparticles. The photograph depicts an aggregated, cluster, foamy in nature. The enlarged image shows the agglomeration, uneven texture of the different nanoparticles and also shows strong bonding of nanoparticles over one another (Fig. 3).

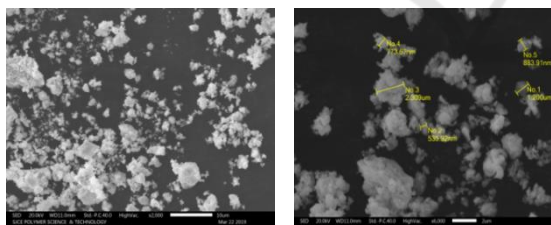


Figure 3: Scanning Electron Micrographs of synthesized Bi₂O₃ Nanoparticles

2.2.3 UV-Vis Spectroscopy

The optical absorption is a significant tool to get optical energy band gap of crystalline and amorphous materials. The elemental absorption corresponds to the electron jump from valence band to the conductivity band. The spectrum reveals that, the Bismuth oxide nanoparticle absorption in the visible radiation with an above wavelength 400 nm. The value of optical band gap (OBG) is calculated from the TAUC's relation:

$$[\alpha h\nu] = B[h\nu - E_g]^n \quad (\text{Eq. 4})$$

Where, ' $h\nu$ ' is the photon energy, ' B ' is the constant and ' n ' is the power factor and that takes 1/2, 2, 3/2 and 3 allowed direct, allowed indirect, forbidden direct and forbidden indirect transitions respectively. The OBG of the bismuth oxide nanoparticle found to be 3.6eV.

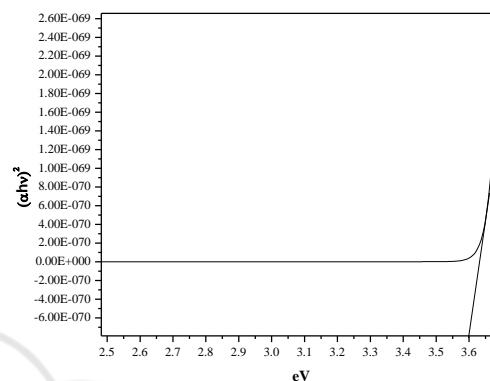


Figure 4: UV-absorption spectra of synthesized Bi₂O₃ nanoparticles

2.2.4 Energy Dispersive X-ray

The confirmatory presence of elements was carried out using Energy Dispersive X-ray [EDX] spectrometer. The presence of bismuth, Carbon and Oxygen signals from the Bismuth oxide nanoparticles (Fig. 5). The weight and atomic percentage of Carbon, Oxygen, and Bismuth was found to be 22.82, 16.23, 60.95 and 58.26, 31.11, 10.63 these corresponds, the spectrum without impurities peaks.

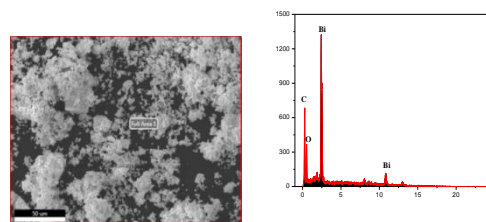


Figure 5: Energy Dispersive X-ray of synthesized Bi₂O₃ nanoparticles

2.2.5 Effect of Catalyst Concentration

The effect of catalyst concentration on the photocatalytic degradation was studied at the range of catalyst amount from 0.1 to 1g/100ml for fast red

dye. The synthesized nanoparticle shows appreciable results. The bismuth oxide (urea) with the nanoparticle size 36 nm has shown 92.62 % degradation. Since, the photodegradation was very efficient at 0.8g/100ml in 120 minutes for Bi_2O_3 nanoparticles concentration showed in (Figure-6) (Photo-1).

The increase in degradation rate can be determined in terms of availability of active sites on the catalyst surface and sunlight penetration into the suspension as a result of increased screening effect and scattering of light. A further increase in the catalyst amount beyond the optimum dosage for the obtained nanoparticles decreases the photodegradation by some margin. This may be due to overlapping of adsorption sites as a result of overcrowding owing to collision with ground state catalyst (2018), (2007). Since, the photodegradation was very effective at 92.62% 0.8g/100ml for Bi_2O_3 nanoparticle dosages, further experiments were continued with the obtained dosage.

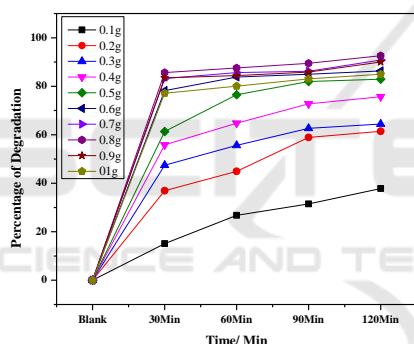


Figure 6: Effect of catalyst concentration on dye solution at 120 minutes=20 ppm, pH=7



Photo 1. Effect of catalyst concentration on Fast Red dye at 120 minutes=20 ppm, pH=7

2.2.6 Effect of pH

To study the effect of pH on the degradation efficiency of Bi_2O_3 catalyst, the experiments were carried out at pH ranging from 2 to 11. The results showed that pH significantly affected the degradation efficiency. The percentage of degradation of fast red for Bi_2O_3 (Fig.7) (Photo 2) nanoparticles was achieved at 76.11% to 95.32% from pH 2 to 10, similarly, the degradation decreases to 93.33% at pH 11 in 120 minutes for

0.8g/100ml. The maximum degradation was found at pH 10. The results from the experiment show that, the degradation was effectively in pH 10 due to the interaction between the dye and nanoparticles leads to generation of OH^\cdot in the alkaline medium which are responsible for the photodegradation. Above pH 10 the degradation decreases due to amphoteric nature of the catalyst and electrostatic repulsion between negatively charged dye molecules and the catalyst (*Journal of Photochemistry and Photobiology A: Chemistry*.vol. 158, no. 1, pp. 27-36), (2012), (2016), (*Solar Energy Materials & Solar Cells*.vol. 77, no. 1, pp. 65-82.). Thus, the adsorption is mainly depends on the pH of the solution.

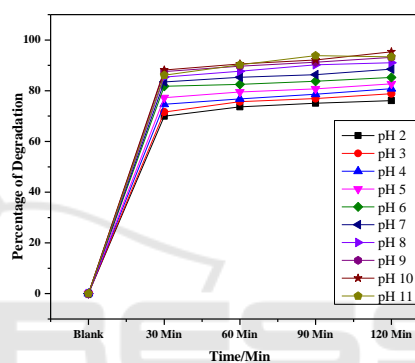


Figure 7: Effect of pH on dye at 120 minutes



Photo. 2. Effect of pH on dye at 120 minutes

2.2.7 Effect of Initial Dye Concentration

For effect of (Fast Red) initial dye concentration, the dye solution concentration was varied from 20 ppm to 40 ppm. The results obtained for Bi_2O_3 (Fig. 8) (Photo 3) is 95.32% for 20ppm, 78.70% for 30ppm and 54% for 40ppm, these experiments illustrated that the degradation efficiency was directly affected by the concentration. The decrease in the degradation with an increase in dye concentration was ascribed to the equilibrium adsorption of dye on the catalyst surface which results in a decrease in the active sites. This phenomenon results in the lower formation of OH^\cdot radicals which were considered as primary oxidizing agents of the organic dye (2012), (*Journal of Iranian Chemical Society*.vol. 6, no. 3, pp. 578-587). According to Beer Lambert's law, as the initial dye concentration increases, the path

length of photons entering the solution decreases. This results in the lower photon adsorption of the catalyst particles, and consequently decreases photocatalytic reaction rate (2006).

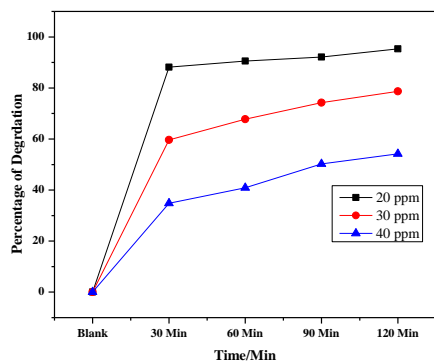


Figure 8: Effect of initial dye concentration on the photocatalytic degradation of Fast Red dye, Bi₂O₃ g/pH=0.8/10



Photo 3. Effect of initial dye concentration on the photocatalytic degradation of Fast Red dye, Bi₂O₃ g/pH=0.8/10

2.2.8 Effect of Sunlight Irradiation on Fast Red Dye

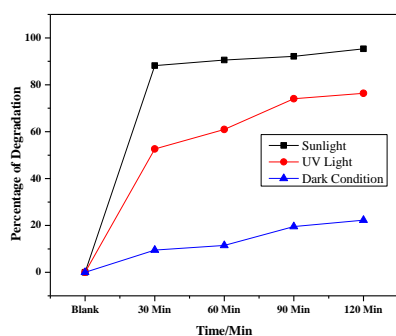


Figure 9: Effect of sunlight irradiation with respect to Dark condition and UV condition on photocatalytic degradation of Fast Red dye in 120 minutes



Photo 4. Effect of sunlight irradiation with respect to Dark condition and UV condition on photocatalytic degradation of Fast Red dye, in 120 minutes

The photocatalytic degradation of fast red dye (20mg/L) under three different experimental conditions were examined, *i.e.*, through dye/dark/catalyst, dye/UV/catalyst and dye/sunlight/catalyst. Fast red dye solution when exposed directly to the sunlight without the catalyst, the degradation was found to be zero during the entire experiments. The degradation rate was found to be increased with increase in irradiation time, for dye/sunlight/Bi₂O₃ showed 95.32%, dye/UV/Bi₂O₃ found to be 76.34% and for dye/dark/Bi₂O₃ 22.25% was recorded (Fig. 9). The obtained results show that photodegradation occurs most efficiently in the presence of sunlight (Photo 4). Under sunlight, excitation of electrons from the catalyst surface takes place more rapidly than in the absence of light (2010), (2009).

4 CONCLUSIONS

In the present study, solar photocatalytic degradation of textile dye, Fast Red dye has been investigated by using synthesized Bi₂O₃ nanoparticles and found that, Bi₂O₃ nanoparticles synthesized economically, conveniently and quickly with the available cost effective metal nitrates. At lower catalyst concentration, the catalyst surface and adsorption of dye on the catalyst surface are the limiting factors. Thus, an increase in catalyst concentration greatly enhances the efficiency of the process. On the other hand, at very high concentration, overlapping of adsorption site and deactivation of activated catalyst reduces the process efficiency. The degradation efficiency increased with an increase in pH, attaining maximum decolourization at pH 10.

In the present study, it is found that synthesized Bi₂O₃ nanoparticles exhibit excellent photocatalytic activity against Fast Red dye and can be used in water purification systems and dye effluent treatment.

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