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A Comparative Study on Photocatalytic Efficiency of TiO_2 and $BiVO_4$ Nanomaterial for Degradation of Methylene Blue Dye under Sunlight Irradiation

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ABSTRACT

The photocatalytic activity of synthesised $BiVO_4$ nanomaterial has been investigated and compared with that of anatase TiO_2 powder. Laboratory experiments with Methylene Blue as the model organic pollutant have been carried out to evaluate the performance of both $BiVO_4$ and TiO_2 nanomaterials. Both nanomaterials were characterized by SEM, XRD, FT-IR and UV-DRS analysis. The effect of various operational parameters like concentration, time, dose and pH were also investigated. A possible photocatalytic mechanism were also schematically investigated.

1. Introduction

Most of the synthetic dyes used for Paper, Printing and Textiles are released into the environment [1]. Most of the dyestuffs are complicated aromatic compounds and are chemically stable [2]. For the treatment of dye-containing waste water, traditional methods such as flocculation, carbon adsorption, reverse osmosis and activated sludge process has difficulties in the complete destruction of dye pollutants [3], and has the further disadvantage of potentially secondary pollution [4]. In recent review articles it has been suggested that photosensitized degradation on semiconductor surfaces can be a remediation of coloured organic pollutants [5]. Semiconductors are inexpensive, non-toxic and capable of extended use without substantial loss of photocatalytic activity [6].

TiO_2 is well- known as an effective photocatalyst for the degradation of organic compounds because of its characteristic relative functions [7]. However, TiO_2 can only be excited by ultraviolet light (<387nm) (which is less than 5% in solar light to produce photo-induced hole electron pairs. In addition photoinduced hole- electron pairs in the semiconductor particles are inclined to recombination very quickly [8,9] which is eliminate these drawbacks of TiO_2, recently the development of visible light driven photocatalyst has attracted more attention. Among these, one of the promising non-titania based visible-light driven semiconductor photocatalyst is $BiVO_4$ [10-12].

In this present paper we prepared visible light $BiVO_4$ nanomaterial for photodegradation of methylene blue dye under sunlight irradiation. The morphology, structure and particle size were also studied in this work.

2. Experimental Methods

2.1 Materials

TiO_2 nanoparticles (~21 nm) was purchased from Sigma-Aldrich company. Bismuth nitrate penta hydrate and Ammonium meta vanadate were purchased from Merck. Methylene Blue was supplied by Qualigens Fine Chemicals. All the reagents were of analytical purity grade, and were used as received without further purification.

2.2 Preparation of $BiVO_4$ Nanomaterial

0.1M Bi (NO_3). $5H_20$ and 0.1 M NH_4VO_3 were mixed together in 100 mL solvent containing ethylene glycol and deionized water. Then the mixture was then stirred for 1h at room temperature to get a solution. Afterwards, the mixture was exposed to high-intensity ultrasonic irradiation (PCI 80, 60W, Model: 1.5 L 50H) at room temperature in ambient air for 2h. The yellow precipitate was centrifuged, washed with DD water and absolute ethanol and then dried at 343 K for 10h in the air.

2.3 Characterization Studies

The powder X-ray diffraction data was recorded using X-ray diffractometer (model: RICH SIEFRT & CO with Cu as the X-ray source (λ=1.5406×10^{-10}m). The surface morphology of the sample was recorded using Scanning Electron Microscopy (SEM) (Model: FEG Quantum 250 EDAX). UV-Visible absorbance studies were carried out to estimate the photodegradation efficiency using a UV-Visible (DRS) spectrophotometer (model: SHIMADZU, UV 2450). The presence of functional groups was detected with the help of Fourier Transform Infrared Spectroscopy. The photoluminescence (PL) measurements were carried out on a fluorescence spectrophotometer (model: PERKIN ELMER, LS 45).

2.4 Photocatalytic Studies

The photocatalytic activity of the sample have been determined by measuring degradation rate of Methylene Blue dye in an aqueous solution under sunlight irradiation. 0.01 g of each sample was dispersed in 50 mL aqueous solution of Methylene Blue dye. Before exposing to light, the suspension was stirred vigorously for 30 min in dark for adsorption, desorption equilibrium. The reaction mixture of Methylene Blue dye and nanocatalyst was irradiated to the light illumination. To check the photodegradation activity, the decomposed dye solution was measured using UV-Visible absorption spectra. The collected suspension was centriguged and filtered before the UV-Visible absorption measurements. The degradation rate of methylene blue dye (665nm) is estimated by the following equation,

$$\text{Percentage removal (\% R)} = \left[\frac{C_i - C_f}{C_i}\right] \times 100 \quad (1)$$

where, C_i & C_f is the initial & final concentration of dye (ppm) at a given time.

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3. Results and Discussion

3.1 Characterization of $BiVO_4$ and TiO_2 Nanomaterial

Fig. 1 represents the XRD pattern of $BiVO_4$ and TiO_2 nanoparticles, respectively. The diffraction lines of $BiVO_4$ corresponds to the monoclinic BiVO4 (JCPDS 14-0688) [13-15]. In the patterns anatase TiO_2 diffraction peaks at 25.3°, 37.8° and 48.1° appeared which are attributed to the 101, 004 and 200 reflections respectively. This indicates that only anatase phase of TiO2 can be indexed from the patterns, and that the rutile and brookite phases of TiO2 are not observed [16-17]. The crystal size was determined from the diffraction peak broadening by the following equation,

$$D = K\lambda \ /\beta \ COS \ \theta \qquad (2)$$

The mean crystallite size estimated using Scherrer's equation is around 6.66 nm for $BiVO_4$ nanoparticle.

Fig. 2 shows the surface morphology of the $BiVO_4$ and TiO_2 photocatalyst. Fig.2a shows the $BiVO_4$ sample was prepared at room temperature consisted of irregular particles and the particles are well aggregated. The close observation indicates that BiVO4 sample was composed of smaller primary crystals [18-20]. Fig. 2b shows the TiO_2 particles are microspheres and they are well aggregated [21-24].

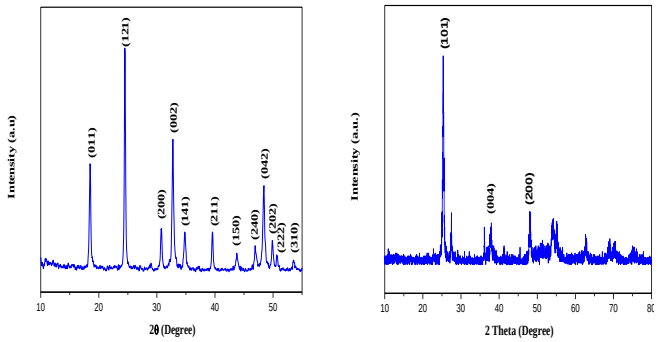

Fig. 1 XRD pattern of a) $BiVO_4$ and b) TiO_2 nanoparticles

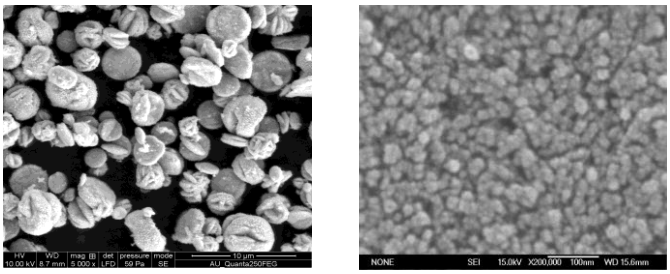

Fig. 2 Surface morphology of a) $BiVO_4$ and b) TiO_2 photocatalyst

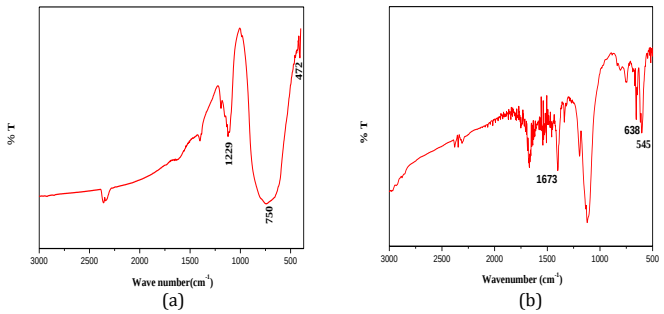

Fig. 3 FT-IR spectra of a) $BiVO_4$ and b) TiO_2 nanoparticles.

Fig. 3 shows the FT-IR spectra of $BiVO_4$ and TiO_2 nanoparticles. The broad pattern observed between 650 to 850 cm^{-1} consists of multiple characteristic bands which corresponds to the stretching and bending vibration bands of V-O and Bi-O [25,26]. The band at 545cm^{-1} which corresponds to the Ti-O stretching [27].

Fig. 4 shows the UV-DRS spectra for $BiVO_4$ and TiO_2 nanoparticles. The different absorption range corresponding to 480 nm was observe in the case of $BiVO_4$ nanoparticles. Therefore with the use of $BiVO_4$ nanoparticles enhanced photocatalytic activity in the visible light region [28,29]. Fig. 4b shows the intense absorption of TiO_2 nanoparticles. The maximum absorption capacity for TiO_2 is < 400 nm. This results shows that TiO_2 nanoparticles only active under UV light region [30, 31]. The Eg value can be estimated by using the formula $Eg = 1240/\lambda$. The obtained Eg value for $BiVO_4$ is 2.58eV.

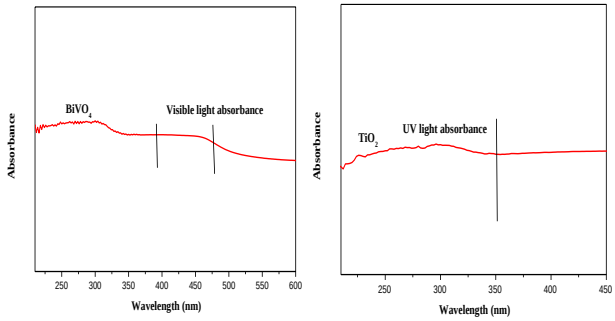

Fig. 4 UV-DRS spectra of a) BiVO4 and b) TiO_2 nanoparticles

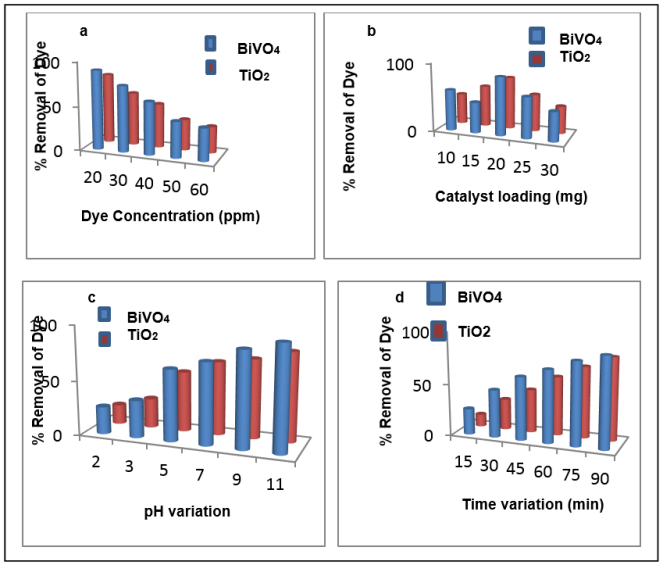

Fig. 5 Effect of various operational parameters

3.2 Effect of Initial Dye Concentration

The effect of initial concentration of the dye on the rate of dye degradation was performed by varying the initial dye concentration from 2×10^{-4} to 6×10^{-4} mol L^{-1} with constant catalyst loading (0.01 g/50mL) and the results are reported in Fig. 5a. The observed results in Fig. 5a reveals that the initial concentration influences the rate of degradation of the dye. When the dye concentration increases from 20 ppm to 60 ppm, the rate of degradation decreases because more number of dye molecules which are adsorbed at the surface of the catalyst. The photon entering path will be reduced by the adsorbed dye molecules. This proves that the rate of decolourisation and degradation decreases considerably with increase in dye concentration [32-35].

3.3 Effect of Catalyst Loading

The increase in the amount of catalyst increased the number of active sites on the photocatalyst surface, which in turn, increased the number of hydroxyl and superoxide radicals. When the concentration of TiO_2 and $BiVO_4$ catalyst increased from 10 mg to 20 mg the % removal of dye increases above the limiting value, ie) 25 and 30 mg the degradation rate decreased due to the interception of the light by the suspension [36-38] as shown in Fig. 5b

3.4 Effect of pH

The effect of pH is one of the important parameter for photodgradation of dyes. Since it influences the surface charge properties of the photocatalysts. The zero point charge for $BiVO_4$ is 3.0 and for TiO_2 is 6.25. $BiVO_4$ surface is positively charged in acidic media (pH< 3) where it is negatively charged under alkaline condition (p H>3). The pH increases from 3 to 11 the surface of the $BiVO_4$ is become negatively charged. So, the cationic Methylene Blue dye easily attracted by the negatively charged $BiVO_4$ catalyst. The rate of degradation increases gradually with increase of pH [39-41] as shown in Fig. 5c

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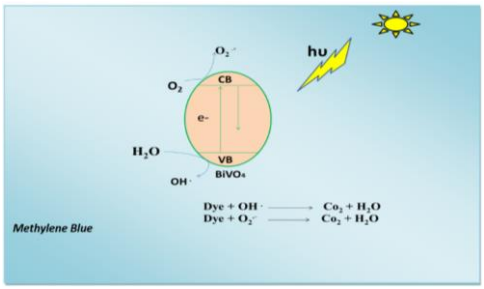
3.5 Effect of Time variation

The percentage of photodegradation increases with increase in irradiation time and complete degradation was obtained with 90 minutes for Sunlight irradiations. This may be due to with increase in irradiation time from 15 to 90minutes, dye molecules and catalysts have enough time to take part in photocatalytic degradation process and hence percentage of degradation increases [42,43] as shown in Fig. 5d.

3.6 Mechanism



Scheme 1 Mechanism of $BiVO_4$ nanoparticle to enhance the photocatalytic activity under sunlight irradaition

4. Conclusion

Sunlight induced degradation of Methylene Blue has been completely degraded by both $BiVO_4$ and TiO_2 catalysts. The main reason for this greater activity of $BiVO_4$ is that it absorbs large fraction of the visible spectrum. Therefore, it may be concluded that for sun light applications $BiVO_4$ will be the best catalyst for the pollutants degradation.

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