SYNTHESIS OF POLYMER MODIFIED NANOCATALYST FOR THE DEGRADATION OF ORGANIC DYE UNDER SUNLIGHT IRRADIATION

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Abstract

The textile industry consumes considerable amounts of water during the dyeing and finishing operations. Dyes are extensively used and hence wastewaters discharged in rivers or public sewage treatment plants are highly contaminated. In this work, The photoactivated degradation reaction of organic dye was studied using Polymer modified metaloxide as Nanocatalyst. The nanomaterial are synthesized by Chemical Oxidative Polymerization method. The as prepared material was further characterized by TEM, SEM, XRD and UV-DRS analysis. The effects of various parameters such as catalyst loading, pH, and initial concentration of the dye on degradation have been determined. The percentage removal of dye was calculated by using UV-Vis spectrophotometer.

Key Words: Polymer, Chemical Oxidative Polymerization, Sunlight, Dyes, Metal oxides, Nanomaterials

1. INTRODUCTION

Dyes are introduced into the environment as a result of several man-made activities. Over 70000 tons(about 10000 types) of dyes and pigments are produced annually worldwide, of which about 20% are assumed to be discharged as industrial effluent during the textile dyeing processes [1]. Due to the high concentration of organics in the effluents and the higher stability of modern synthetic dyes, the conventional biological methods are ineffective for the complete colour removal and degradation of organics and dyes [2]. Therefore, many physicochemical methods such as adsorption, coagulation, precipitation, filtration and oxidation have been attempted for dye removal. The adsorption process has been found to be the most effective [3]. In order to decrease damage caused by organic dye pollution to environment and humans, the use of photocatalyst to degrade organic compounds in contaminated air or water or to convert them into harmless chemicals has been extensively studied [4]. The content ratio of UV light in solar spectrum is only 5 % and moreover those in fluorescent lights and white light emitting diodes are much less. To raise photocatalytic activity and use photocatalysts indoors, it is indispensable to develop their visible light responses. However, the mismatch between the large band gap and the sunlight spectra limits the utilization of solar energy. Therefore, new visible light responsive photocatalyst with narrow band gap is highly desired [5].

At present, conductive polymers such as polyaniline and polypyrrole (PPy) have attracted considerable attention due to their high absorption coefficients in the visible part of the spectrum, high

mobility of charge carriers, and good environmental stability [6]. These conductive polymers act as a stabilizer or surface capping agents when combined with metals or semiconductor nanoparticles [7].

In this paper, we have prepared Polymer modified metaloxide nanocatalyst for the degradation of organic dye under Sunlight irradiation.

2. EXPERIMENTAL

2.1. Materials

Pyrrole (Py) monomer (AR Grade) was purified twice under reduced pressure and stored at 0-4° C prior to use. TiO_2 nanoparticles, Bismuth nitrate pentahydrate ($Bi(NO_3)_3.5H_2O$), Ammonium metavanadate (NH_4VO_3), Ammonium persulphate, Methylene Blue (MB). All the chemicals in this work were purchased from Alfa Aesar Chemical Reagent Company, and were of analytical grade and used without further purification.

2.2. Synthesis of BiVO$_4$ nanoparticles
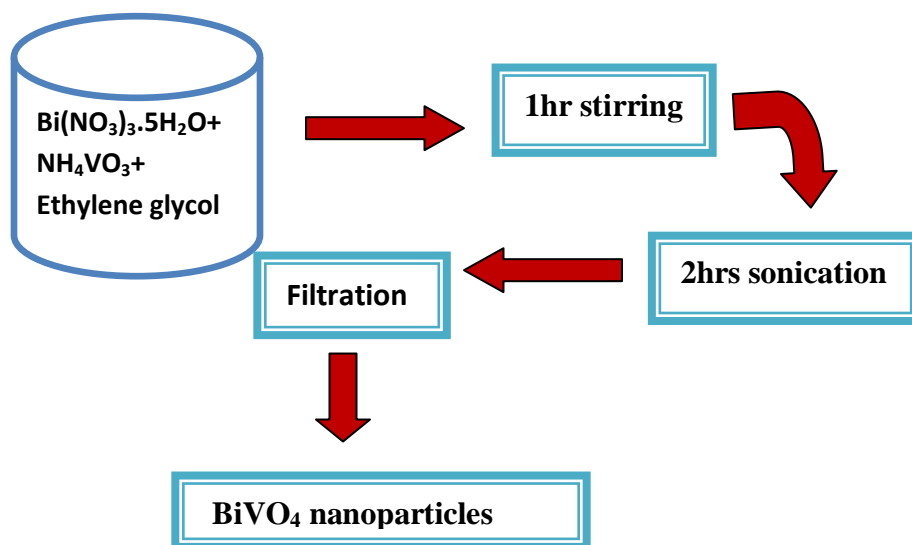
2.3.   Synthesis of Polymer modified Metaloxide Nanoparticles

The Photo catalyst materials were synthesized by Chemical Oxidative Polymerization method. A typical procedure is outlined: Pyrrole (5mmol) was added to 500ml of 0.1M Sulphuric acid solution. Then the metal oxides both TiO_2 and $BiVO_4$ nanoparticles were added in 100ml pyrrole solution containing beakers with continuous stirring. Then it was kept under 5^0C cooled condition. Then 20ml of Ammonium persulfate solution were added drop by drop. The green coloured solution was obtained. After constant stirring, the precipitation occurred dark colour. The obtained product was washed with distilled water to remove the remaining ammonia solution. Finally the product were dried out at room temperature at overnight.

2.4.   Characterization Studies

The optical density was measured by using UV-visible spectrophotometer "SHIMADZU" model: UV 2450. The Crystallographic structures of the materials were determined by High resolution powder 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 and Energy Dispersive X-ray Analysis (SEM-EDAX) (Model: FEG Quantum 250 EDAX). TEM analysis was done by High Resolution Transmission Electron Microscopy (HRTEM) and Small Area Electron Diffraction (SAED) using FEI Tecnai F20 Transmission Electron microscope.

2.5.   Photo catalytic Activity

Photo catalytic activities of the synthesized Polymer modified TiO_2 and Polymer modified $BiVO_4$ nanoparticles were evaluated by the degradation of MB under Sunlight irradiation. In each experiment, a 0.020g of photo catalyst was added into 100ml MB solution with a concentration of 20 mg L^{-1}. Prior to irradiation, the suspensions were stirred in the dark for 1 h to reach an adsorption/desorption equilibrium between the pollutant and photo catalyst. Under irradiation, the suspensions were stirred continually and open to air. After irradiation time intervals of 1 h, 4ml of the suspensions were collected, and then centrifuged to remove the photo catalyst particles. The solutions were analyzed by UV–vis spectrophotometer at 665 nm. The percentage of degradation of MB dye was estimated by the following equation,

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

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

3.0.   RESULTS AND DISCUSSION
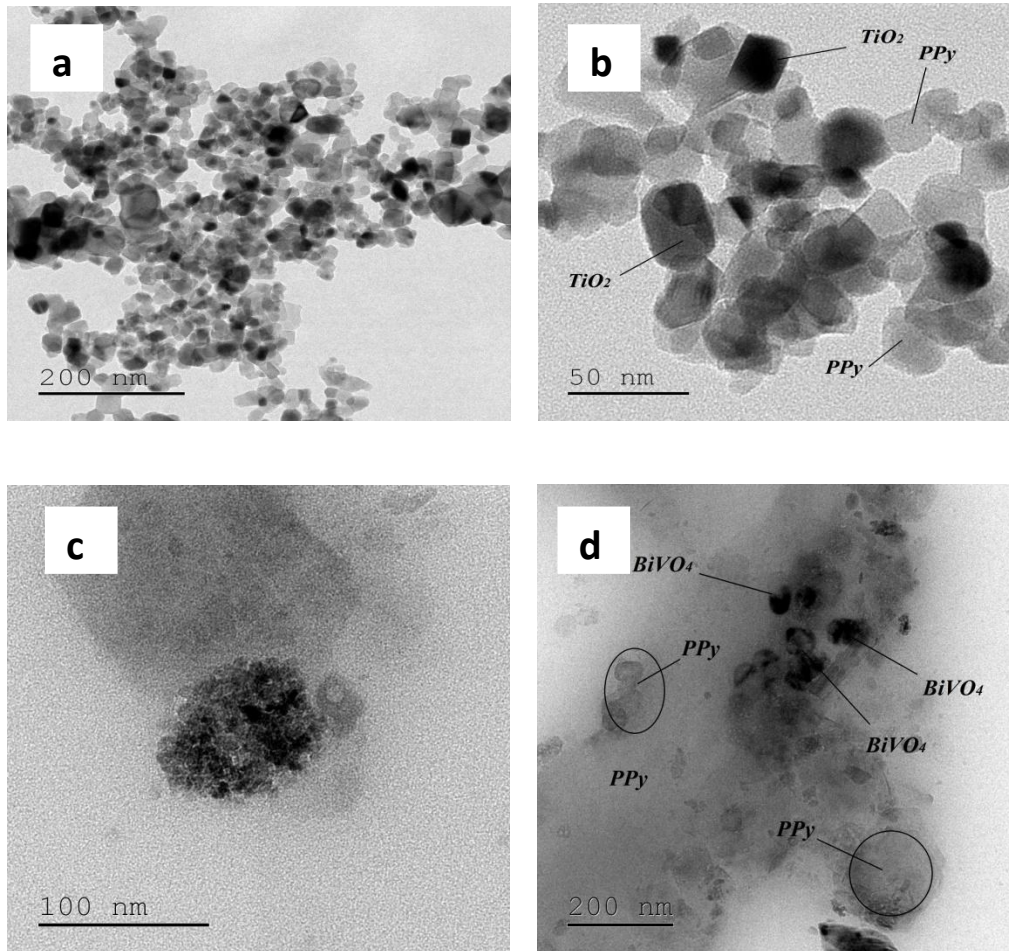
3.1.   Morphological Studies (TEM and SEM)

Fig. 1 TEM images of Polymer modified TiO$_2$ (a, b); TEM images of Polymer modified BiVO$_4$ (c, d)

The surface morphology of the polymer modified metaloxide nanocomposite was characterized by TEM analysis. Fig. 1(a, b) shows the surface morphology of Polymer modified TiO$_2$ nanoparticles. The TiO$_2$ particles are distributed on Polypyrrole surface. When the size of the TiO$_2$ particle is very small, the ratio of the atoms on the surface to all of the atoms in the particle increases. In this situation, the surface atoms can affect the morphology of the particle. When the particle size grows, ratio of the atoms on the surface to all of the atoms in the particle decreases. Fig. 2(c, d) shows the surface morphology of polymer modified BiVO$_4$ nanoparticles. The BiVO$_4$ particles are agglomerized on Polypyrrole surface [8-10].
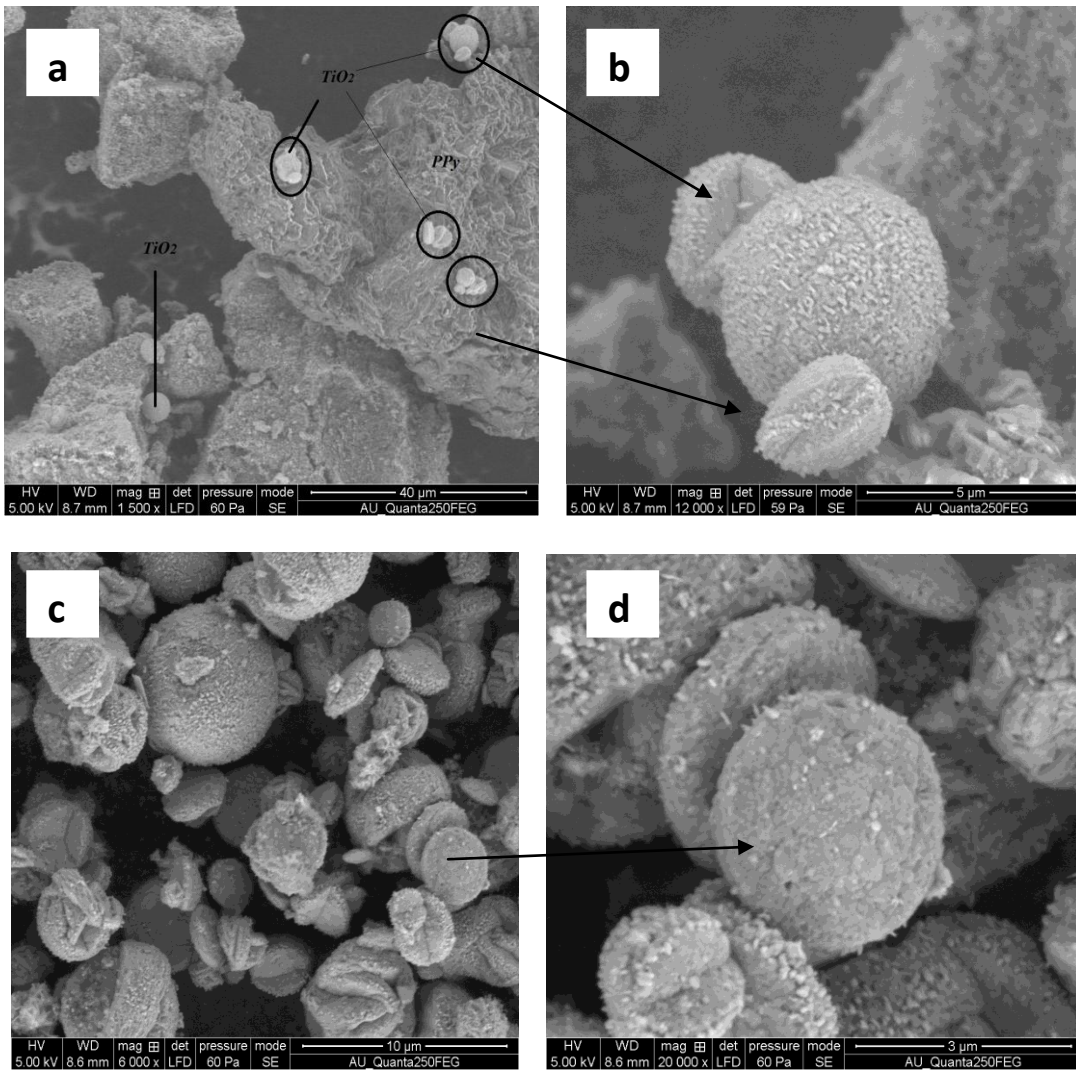
Fig. 2 SEM images of Polymer modified TiO$_2$ (a, b); TEM images of Polymer modified BiVO$_4$ (c, d)

The surface morphology of the prepared nanocomposite was analysed by Scanning Electron Microscopy techniques. Fig. 2(a, b) shows the surface morphology of the polymer modified TiO$_2$ nanoparticles. The TiO$_2$ nanoparticles are ball like sphere shape. They are deposited on polymer surface. Fig. 2(c, d) shows the surface morphology of polymer modified BiVO$_4$ nanoparticles. The particles are seed and plate like structure. The surfaces of the particles are very loose. This kind of surface structure can provide a better adsorption environment and more active sites for the photocatalytic reaction [11-13].
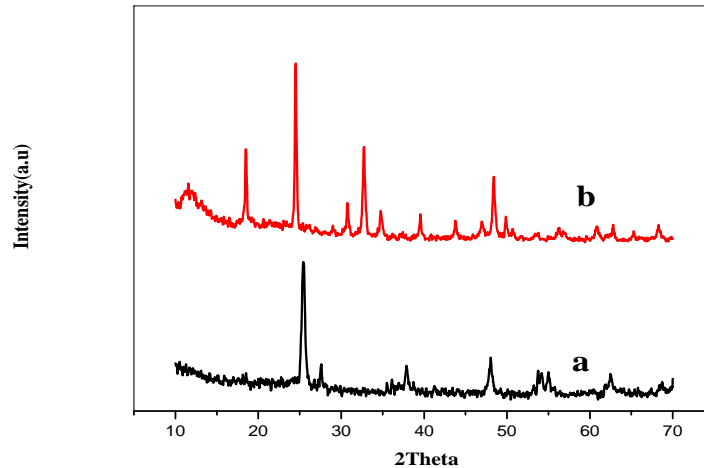
3.2.   Powder XRD analysis

Fig. 3 XRD for Polymer modified TiO_2 (a); XRD for Polymer modified $BiVO_4$ (b)

Powder XRD patterns of the prepared photo catalysts are displayed in Fig. 3. In Fig. 3a shows the diffraction peaks at 2θ = 25.6°, 26.2°, 36.0°, 38.2°, 48.9°, 54.3°, 56.6°, 63.1° and 69.9° confirms the formation of Polymer modified TiO_2 nanocomposite In Fig. 3b the presence of diffraction peaks at 2θ = 18.98°, 35.45°, 39.9°, 47.2°, 50.26° and 53.7° confirms the formation of polymer modified $BiVO_4$ nanocomposite. These low intensity peaks represents the less crystalline nature of TiO_2 and $BiVO_4$. The sharp peak at 2θ of 25.6° indicates Polymer doping of PPy. This indicated the existence of smaller particle size in the nanocomposite containing high PPy content. The mean sizes of Polymer modified TiO_2 and $BiVO_4$ nanocomposites was calculated by Scherrer's formula,

$$D \text{ scherrer} = k\lambda/\beta \cos\theta \quad \text{--------------------}\quad (2)$$

Where, λ is the wavelength of the X-ray radiation (λ= 1.54×10^{-9}nm)

k is the Scherrer constant (k =0.89)

θ is the diffraction angle and β is the line width at half-maximum height of the most intense peak. Based on the XRD results, the crystalline size of both nanocatalyst are 8.31nm and 7.92nm   respectively. The results are in good agreement with the SEM images [14-17].

3.3.   UV-DRS analysis
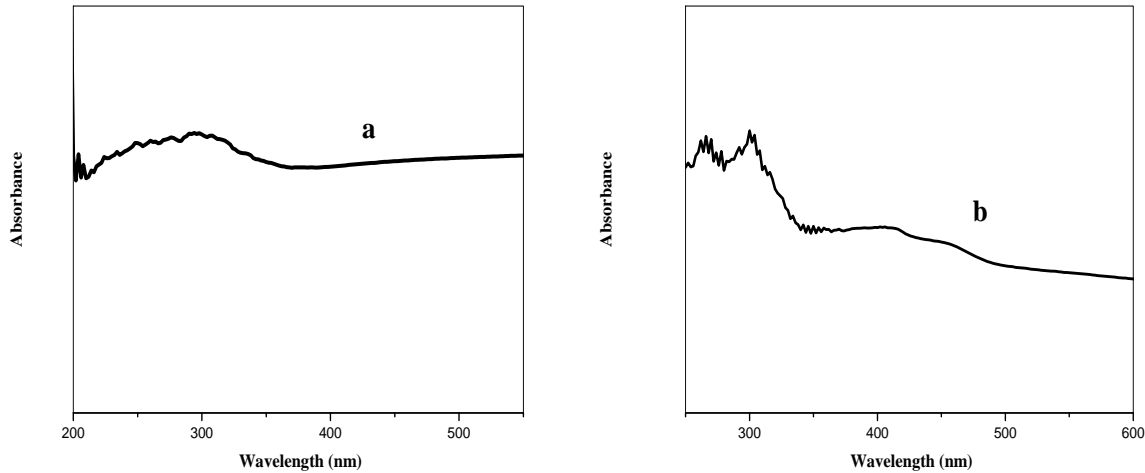
The optical properties of Polymer modified metal oxide nanocomposites investigated by UV-DRS spectroscopy as shown in Fig. 4(a, b). From the UV-DRS analysis we can measure band gap of the synthesized   nanocomposite. The position of fundamental absorption edge of the prepared nanocomposite is determined using equation,

$$(\alpha h\upsilon)^2 = A\,(h\upsilon - Eg)^n \text{ --------(3)}$$

Where α, h, υ, Eg and A are the absorption coefficients, Plank constant, light frequency, band gap and a constant, respectively. The n value depends on the transition characteristics. The Eg value can be estimated by extrapolating the straight portion of the $(\alpha h\upsilon)^2$ - $(h\upsilon)$ plot. The band gap energy (Eg) values given in Table 1 are the average of both direct and indirect band gap energies. .

Catalyst	Band Gap (Eg)
TiO_2	**3.2**
Polymer modified TiO_2	**2.1**
$BiVO_4$	**3.0**
Polymer modified $BiVO_4$	**2.75**

4.0.   PHOTODEGRADATION STUDIES

4.1.   Effect of initial concentration of dye

The initial concentration of dye varied from 2ppm to 12ppm. It was observed that the rate constant decreases from 2ppm to 12ppm dye concentration. This is due to the fact that more dye molecules are available in the photoactive volume for the degradation process. Rate constant decreases with further increase in concentration of dye above the optimal value. The decrease is attributed to fact that the dye itself will start acting as a filter for the incident irradiation, reducing the photoactive volume. At low concentration, the reverse effect is observed [18] as shown in Fig.5.
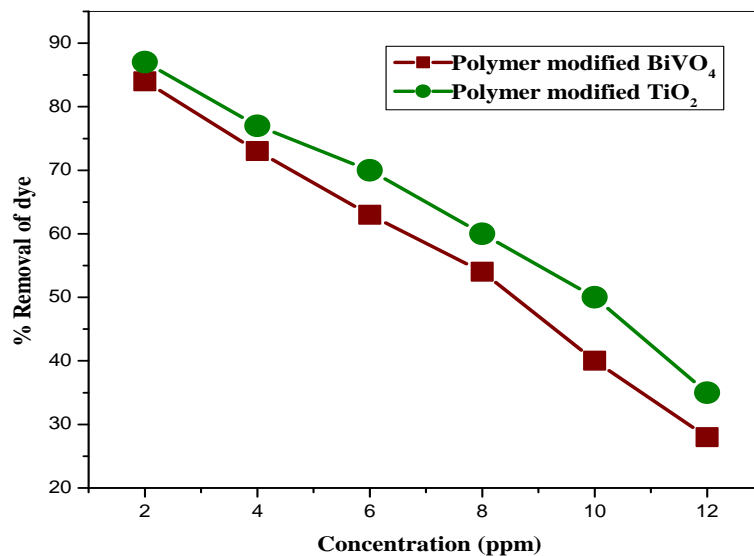

Fig. 5 Effect of Concentration of Dye

4.2.   Effect of catalyst loading

The percentage of removal was found to enhance linearly with increase in the dose of the catalyst indicating the heterogeneous regime. This may probably be due to: (i) increase in the extent of dye adsorption molecules on the catalyst surface; (ii) increase in the number of surface active sites; (iii) enhanced generation of hydroxyl radicals due to increase in the concentration of charge carriers [19-23] as shown in Fig. 6. However, at higher catalyst loadings (beyond 18mg/50mL), the reaction rate

decreased which may be attributed to; (i) the deactivation of activated molecules by collision with ground state molecules; (ii) the agglomeration of the catalyst particles at higher loading which covers the part of photosensitive area retarding the photon absorption and also the dye adsorption; (iii) turbidity at higher catalyst loading results in the shadowing effect thus decreasing the penetration depth of light irradiation; (iv) high degree of scattering by the catalyst particles and increase in the opacity [24]. Hence above a certain level, the additional catalyst amount does not get involved in catalytic activity and further increment in the reaction rate was not observed.
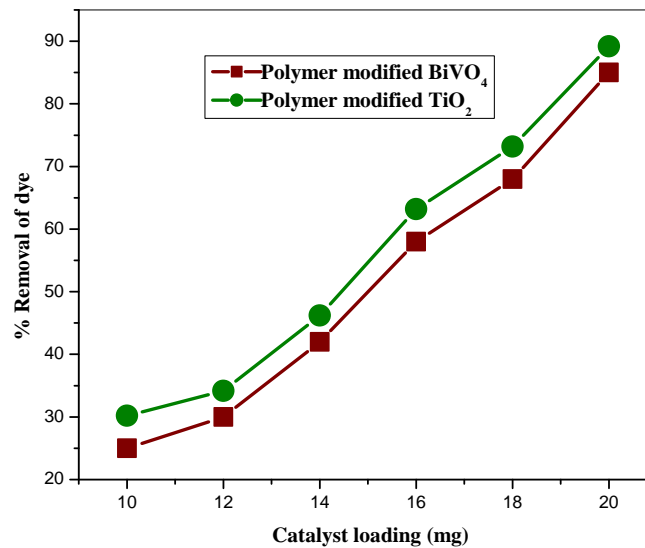

Fig. 6 Effect of Dose of catalyst

4.3.   Effect of time variation

Irradiation time plays an important role in the photocatalytic degradation process of MB dye. Effect of irradiation time with constant dose of the catalysts (20mg/50 mL) and initial concentration (2ppm) of MB dye. It has been observed from the Fig.7,   that the percentage of photodegradation increases with increase in irradiation time and complete degradation was obtained with 105 minutes for both UV and solar irradiations. This may be due to with increase in irradiation time dye molecules and catalysts have enough time to take part in photocatalytic degradation process and hence percentage of degradation increases [25]. The results of experiments showed that the photocatalytic degradation of MB dye obey apparently pseudo first order kinetics and the rate expression is given by the following equation,

$$\ln (Co/Ct) = kt \quad \text{-------- (4)}$$

Where,

Co = initial concentration of dye solution

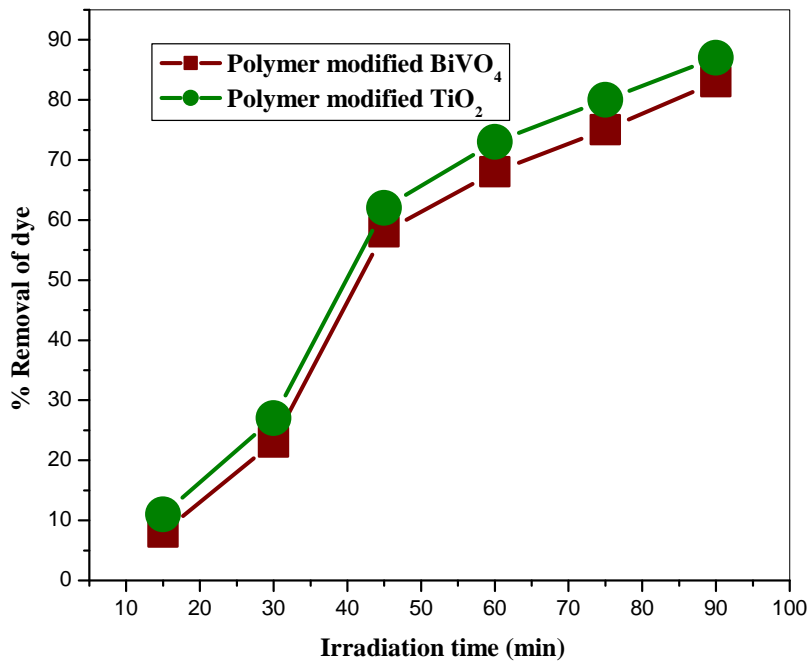Ct = final concentration of dye solution in various time interval

Fig. 7 Effect of Time variation

4.4.   Effect of pH variation

The wastewater from textile industries usually has a wide range of pH values. Further, the generation of hydroxyl radicals is also a function of pH. The pH values increases from 2 to 11 for MB dye. The zero point charge for TiO_2 is 6.25. In MB dye the pH values 8, 9, 10 and 11 higher percentage (70%, 73%, 80 and 90%) removal was occur because at this basic condition the surface of the catalyst will become negatively charged so the cationic dye (MB) easily attracted by the catalyst. So higher percentage

removal occur in basic condition. In contrast, the zero point charge for the $BiVO_4$ nanoparticles is 3.0. At pH 4, 5, 6, 7……11 higher percentage removal was occurred as shown in Fig.8 [26].
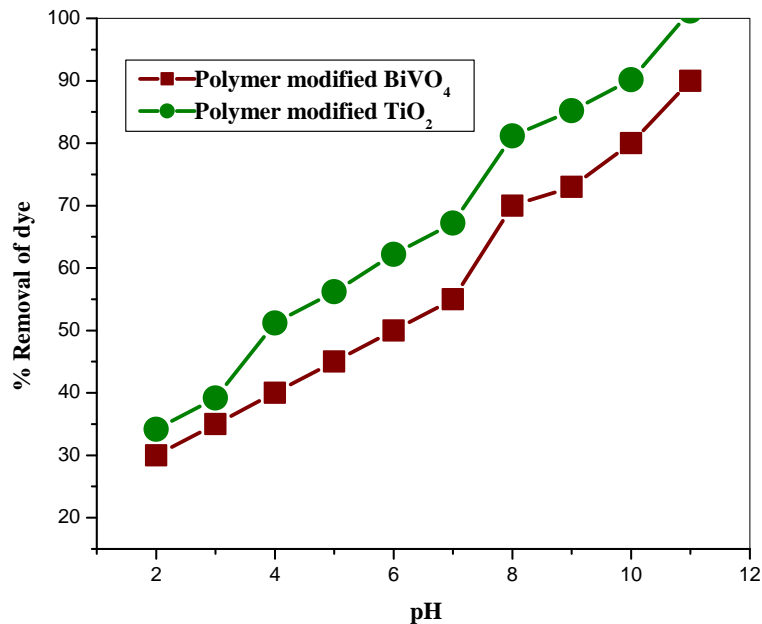

Fig. 8 Effect of pH

4.5.   Reuse of Catalyst

The reuse of the photocatalytic degradation activity of a 0.02 g of polymer modified TiO_2 nanocomposite performed on a 2 ppm MB solution (50 mL) is expressed as the number of cycles. Where the photocatalytic degradation of the nanocomposite was reduced from 85% on the first usage to 75%, 70% and 600% after the second, third and fourth cycles of reuse, respectively. This reduced dye photodegradation activity is in accord with the appearance of polymer modified TiO_2 nanocomposite, which was clearly changed in the morphology of the Polymer modified TiO_2 nanocomposites due to the Photodegradation.

5.0 Conclusion

The polymer modified metaloxide nanocomposite was successfully prepared by Chemical Oxidative Polymerization Method. The results from the SEM and TEM analysis indicates that the metal oxide nanopartilces were deposited on Pyrrole surface. From the XRD measurements the peaks were

confirmed the formation of polymer modified material. The synthesized nanocomposite could be used for removal of waste water which contributes to the environmental pollution.

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