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Photodegradation of reactive black 5 Azo dye (RB5) By Nb₂O₅ photocatalyst synthesized by modified sol-gel method

MJ Pawar and MD Gaonar**Abstract**

Niobium pentaoxide (Nb₂O₅) was synthesized from niobium ethoxide by using modified sol-gel method. The physical and photophysical properties of the as-obtained samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), BET analysis and UV-Vis diffusion reflectance spectroscopy (UV-Vis). The degradation efficiency for reactive black 5 (RB5) dye over synthesized photocatalyst nanoparticles was systematically investigated.

Keywords: Sol-gel Method, Nb₂O₅, reactive black 5 dye, Photocatalysis

1. Introduction

Niobia (Nb₂O₅) has attracted a great deal of interests due to its many remarkable properties suitable for a wide range of applications such as for gas sensing, catalysis, electrochromics, photoelectrodes as well as in field-emission displays and microelectronics [1-5]. In recent years replacement of stoichiometric reagents with solid catalysts in industrial chemical synthesis becomes a new environmental remediation technology. Nb₂O₅ shows a great promise in providing strong surface acidity and stability in aqueous medium for various acid-catalyzed reactions. In addition, pure or doped Nb₂O₅ are the focuses of growing attention for the photodegradation of organic contaminants [6, 7]. Particularly, the preparations of Nb₂O₅ with different nanostructures and morphologies by chemical synthesis could enable detailed elucidation of structure-activity relationships.

Nb₂O₅ nano powder has potential applications in optical, chemical, ceramics, magnetic, gas sensor, catalyst, ferroelectric and electronic devices due to its good mechanical, electronic, conductive and thermal properties [8-12]. The comprehension of synthesis method and the employed post-thermal conditions are essential to control the influence of defects and their dependent physical properties. In the literature, there are many synthesis pathways described to prepare Nb₂O₅ nano powder, such as hydrothermal, solvothermal, anodization and the other physical and chemical methods [13-16].

In the present study, Nb₂O₅ nano-powders were prepared by modified sol-gel method. This method is a homogeneous process which results in a continuous transformation of solution into a hydrogel. Synthesis of nano size crystallized powder of high purity at relatively low temperature, possibility of stoichiometry controlling process, preparation of composite materials, and production of homogeneous materials are some of advantages related with a sol-gel method of preparation. These advantages have driven many researchers to the use sol-gel method for the preparation of photo catalysts.

The powders obtained were characterized by X-ray diffraction (XRD) to evaluate the influence of heat treatment on the Nb₂O₅ phases. All of the materials were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), UV-Vis diffusion reflectance spectroscopy (UV-Vis) and BET techniques. In this study, the photocatalytic decolorization of a textile azo dye; Reactive Black 5 azo dye (as the model dye compound) was investigated to demonstrate the performance and behaviors of synthesized Nb₂O₅ nanoparticles under various conditions. The effects of various key parameters such as catalyst loading, initial dye concentration, pH, and hydrogen peroxide concentration (H₂O₂) were investigated on the photocatalytic treatment of RB5 dye under the irradiation of UV light.

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2. Experimental

2.1 Materials used

For synthesis of nanostructured Nb₂O₅, niobium ethoxide obtained from Sigma Aldrich, Germany was used as a source of Nb. Absolute ethanol ammonium hydroxide and glacial acetic acid were supplied by Merck Germany. Reactive Black 5 azo dye obtained from Sigma Aldrich, Germany was used.

2.2 Preparation of Nb₂O₅ nano powders

A calculated quantity of niobium ethoxide was added to the mixture of absolute ethanol (25 mL) and glacial acetic acid (5 mL, 10%) followed by the continuous stirring at 60°C for 3 h. To this mixture, 10 mL of ammonium hydroxide solution was added and the mixture was kept for vigorous stirring for 2 h at the same thermal conditions. After shaking, the obtained gel was transferred to china dishes and was allowed to dry in oven at 150°C for 4 h. The dry mass obtained was then calcined at 500, 550 and 600°C. Nb₂O₅ nano powders calcined at 500, 550 and 600°C were labeled as Nb-I, Nb-II and Nb-III respectively (Table 1).

3. Result and discussion

3.1 X-ray diffraction analysis

Information about the crystallization and phase purity of calcined powder was obtained with X-ray diffraction studies at room temperature. XRD results indicate that the degree of crystallization increases by increasing processing temperature. The diffraction spectrum of as synthesized Nb₂O₅ nanoparticles is presented in Figure 1, where sharp and intense peaks indicate the crystalline nature of the calcined powder. It was observed that at calcination temperature 500°C, Nb₂O₅ particles crystallize in a hexagonal structure with resolved peaks at: $2\theta = 22.42^\circ$, 28.33° , 36.71° , 46.24° and 56.18° , as reported in JCPDS028-0317. The particle size estimated by using Scherrer equation is in the range of 12-44 nm. We observed from the Figure 1, that the calcination temperature is an important parameter during the Nb₂O₅ synthesis. On calcination the peak intensities increases with crystallinity with removal of impurities.

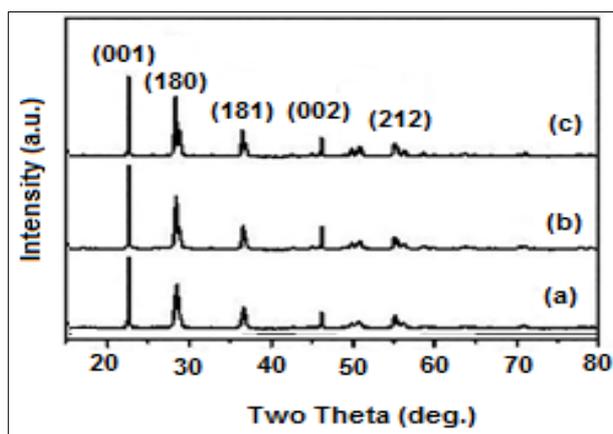


Fig 1: XRD of Nb₂O₅ samples calcined at 500, 550 and 600°C.

Table 1: Two theta angle, FWHM and particle size (nm) calculated from XRD data of Nb₂O₅ samples calcined at 500°C.

2θ (deg.)	FWHM	Particle size (nm)
22.39	0.44061	22.01
28.33	0.54010	15.80
36.71	0.20859	43.55
46.21	0.52799	15.25
56.20	0.61619	12.00

3.2 BET analysis

Specific surface areas of samples that prepared by modified sol-gel method at 500, 550 and 600°C are 324, 126, and, 90 m²/g, respectively. The specific surface area decreases with increasing heat treatment. Those data are consistent with XRD data that shows the degree of crystallinity increase with increasing processing temperature. The surface area 324 m²/g of the sample processed at 500°C is very close to the value.

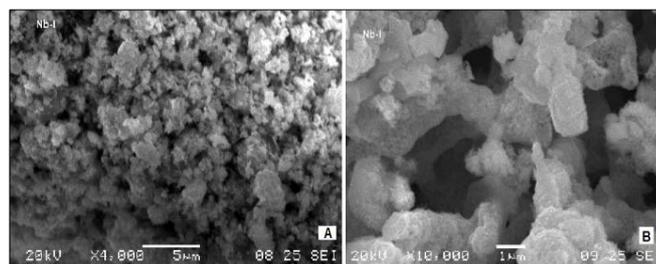


Fig 2: SEM images of Nb₂O₅ obtained at 500°C at different magnifications.

3.3. SEM analysis

SEM analysis was carried out to find the surface morphology of as synthesized Nb₂O₅ samples using scanning electron microscope at different magnification levels and results were shown in Figure 2. The micrographs (Figures 2A and 2B) showed that the network formation occurred at the Nb₂O₅ nanoparticles. It was clearly indicated that the agglomeration had been taken place. From the images it was confirmed that the synthesized Nb₂O₅ nanoparticles were in well agreement with the result obtained from XRD. Moreover the synthesized Nb₂O₅ nanoparticles had a spherical shape with rough surface.

3.4 Photocatalytic activity

Photocatalytic activity of as synthesized niobia nanoparticles was evaluated by the degradation of Reactive Black 5 (RB5) dye at room temperature under UV light irradiation. In a typical experiment, initially 50 mg of as prepared photocatalyst was dispersed in 50 ml of dye solution with an initial concentration of 10 mg/L. In order to attain adsorption/desorption equilibrium between the dye molecules and catalyst surface, the prepared solution was stirred for about 30 min in the dark, prior to irradiation. A 400 W (Philips) high-pressure mercury vapor lamp ($\lambda_{\max} = 365$ nm) was used as a light source. During irradiation, about 2 ml of the suspension was taken out at the regular intervals and centrifuged to separate the photocatalyst particles. The supernatants were analyzed by using a UV-Vis absorption spectroscopy to determine the RB5 dye concentration by measuring the absorbance at its maximum absorption wavelength. The % photo degradation efficiency (%P.D.E.) for each of sample was computed using the following equation (equation no.):

$$\%P.D.E. = \frac{C_0 - C_t}{C_0} \times 100$$

Where: C_0 and C_t are the initial concentrations of the RB5 dye before and after t /min UV irradiation, respectively.

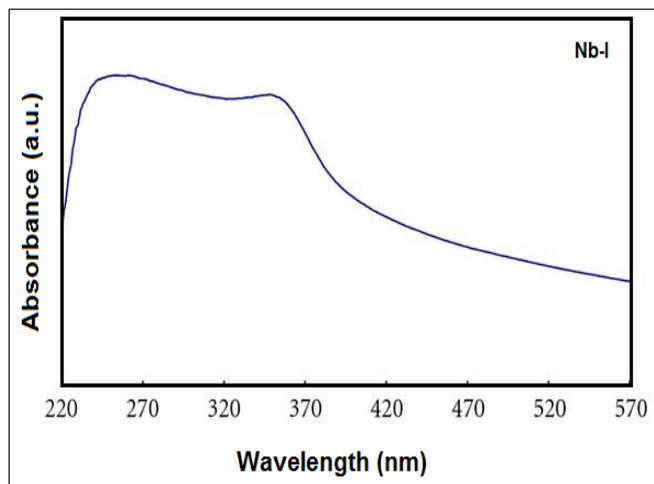


Fig 3: UV-vis absorption spectrum of Nb_2O_5 nanoparticles calcined at 500°C (Sample Nb-I).

3.4 UV-Vis Absorption Spectrum

UV-Visible spectrum of sample Nb-I over the range 200-600 nm presented in Figure 3 showed photo absorption properties no longer than 240 nm suggesting that the catalyst is photo active under UV light irradiation. UV-visible absorption spectroscopy is being used to examine the optical properties of nanosized particles. The absorption spectrum of Nb_2O_5 nano powder is shown in Fig 3. It exhibits a strong absorption band at about 405 nm. The size of the nanoparticles plays a crucial role in changing the entire properties of materials. Thus, size evolution of semiconducting nanoparticles becomes very essential to explore the properties of the materials. However, the increase of surface area is likely not the main factor affecting the photocatalytic activity of photocatalyst. Other factor that could affect photocatalytic efficiency is such as availability of active sites, crystalline structure and pore size.

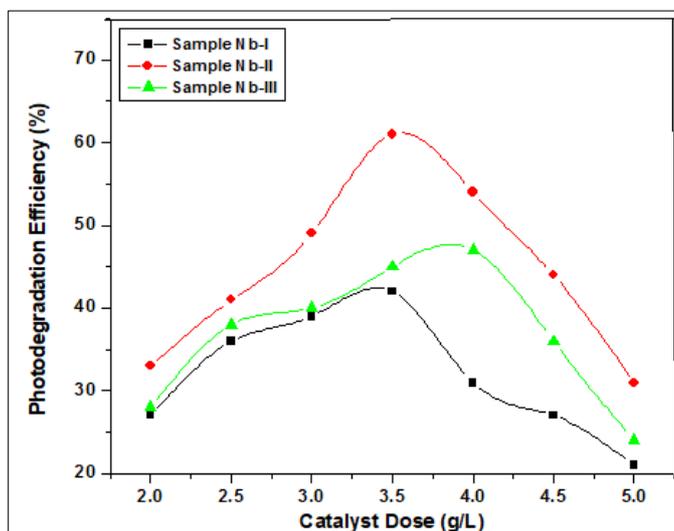


Fig 4: Effect of catalyst dose on photo degradation efficiency of RB5 dye

[UV Irradiation time: 90 min, Dye concentration: 15 mg/L]

3.4.1 Effect of photocatalyst dose

To find the optimum amount of photocatalyst load for efficient degradation, the wastewater degradation efficiency was studied by varying the amount of photocatalyst load from 2-5 gm/L. Fig 4 describes the effect of reaction conditions on

the performance of the catalyst. Initial rise in photo degradation capacity is observed with increase in the amount of catalyst weight, which then attains saturation at a catalyst dosage of 4 g/L and suddenly falls to less than 25%. Thus a catalyst weight of 4 g/L was selected for further studies. The dye concentration is varied, and from the results, it is observed that the catalyst showed about 55% degradation of the dye pollutant at low concentrations in 90 min.

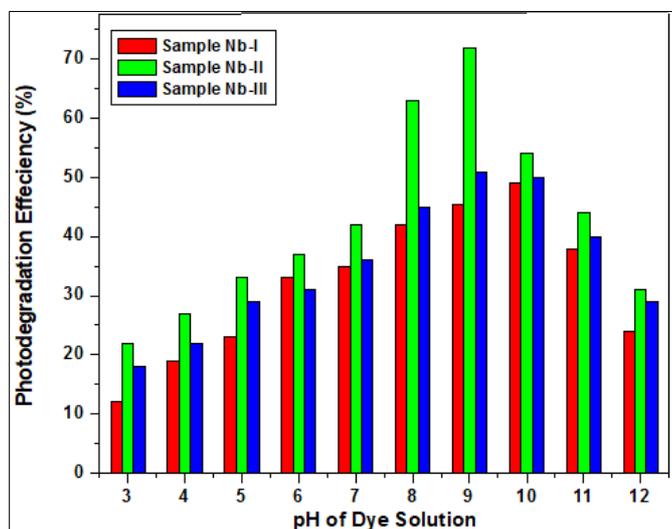


Fig 5: Effect of pH on photo degradation efficiency of RB5 dye

[UV Irradiation time: 90 min, Catalyst dose: 4g/L, Dye concentration: 15 mg/L]

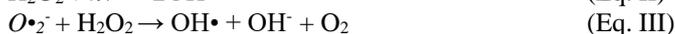
3.4.2 Effect of pH

The pH is one of the significant parameters for the photocatalytic dye degradation as it can influence dye reaction rates in multiple ways. Since photo catalysis occurs at the surface, therefore the effect of pH on the degradation rate of RB5 using the as synthesized samples was investigated in the pH range 3.0 to 13.0. The pH of the dye solution was varied from acidic to alkaline range, since the dye pollutant effluent from the industry may be of different pH. The catalysts worked well in higher pH values. Under acidic pH, activity is reduced and the percentage dye degradation decreased to about 25% at a low pH value of 3. Still, the activity is better since the percentage dye degradation is more than 90% at pH 10 as observed in the results shown in Fig 5. The pH of dye solution has an important role, since it starts the photo degradation process by initiating the photolysis process of the used solution, which produces the very reactive OH radical ($\bullet\text{OH}$) that is responsible for attacking the pollutant to start degradation of dye molecules. The interpretation of the pH effect on the degradation process is difficult as it comprises various factors such as electrostatic interactions between the catalyst surface and reaction of charged radicals such as superoxide, hydroxyl radicals, etc. aggregated on the catalyst surface with pollutant molecules.

3.4.3 Effect of H_2O_2 concentration

The addition of oxidizing species, such as H_2O_2 , during photo catalysis often leads to an increase in the rate of photo-oxidation [17, 18]. In photochemical reactions, H_2O_2 is considered to act as an alternative electron acceptor to oxygen because hydrogen peroxide is a better electron acceptor than molecular oxygen, thereby promoting the charge separation (Eq. (I)). Moreover, H_2O_2 also produces hydroxyl radicals via photodecomposition and inhibits the electron-hole (e^-h^+)

recombination according to the equations (Eq. II and III) [19, 20].



As shown in Eq. (3), the illumination of Nb_2O_5 with UV light generates holes in the valence bands (h^+), and the electrons in the conduction band (e^-). However, the hole-electron recombination limits the use of Nb_2O_5 photo catalysis system in wastewater treatment. Whereas the electrons are consumed during the reaction with oxygen (O_2) to convert it to the superoxide radical ($O_2^{\bullet -}$) (Eq. V)), the holes can react with hydroxide ion on the Nb_2O_5 surface to form hydroxyl radicals (Eq. (IV)). Therefore, the photocatalytic reaction needs sufficient oxygen (O_2) to suppress the electron-hole recombination process.

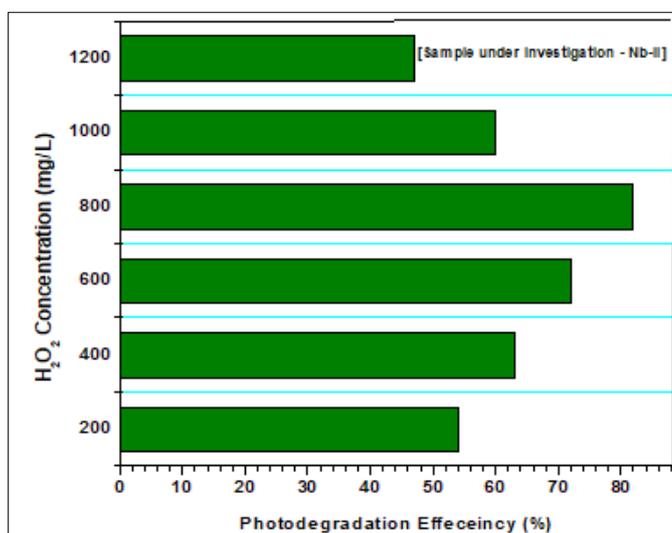


Fig 6: Effect of H_2O_2 concentration on photo degradation of RB5 dye

[UV Irradiation time: 90 min, Catalyst dose: 4g/L, Dye concentration: 15 mg/L].

The catalytic oxidation runs for different H_2O_2 concentrations were carried out using the following operational conditions: Initial pH of 9, catalyst amount of 4 g L^{-1} , initial concentration of RB5 of 15 mg/L, H_2O_2 concentration ranging from 200 to 1,000 mg/L. The percentage decolorization of RB5 dye without addition of H_2O_2 was 43% and after addition of H_2O_2 from 100 to 800 mg/L it reached 63% but as the amount of H_2O_2 was further increased to 1,000 mg/L, the percentage decolorization was 31% with a drop in the decolorization efficiency after 90 min irradiation of UV light. The decrease in the photo degradation may be explained in terms of the fact that H_2O_2 scavenges the photo-generated valence band holes and hydroxyl radicals that are responsible for oxidation of dye molecule (Eqs. (IV) and (V)).



4. Conclusion

Nb_2O_5 photocatalyst was synthesized and changed into nanoscale by the hydrothermal method. The crystallite size of the Nb_2O_5 photocatalyst was estimated to be about 12.44 nm. The degradation efficiency of Nb_2O_5 photocatalyst indicated that the low initial dye concentration and high catalyst dose

are more favorable for the degradation process. The experimental results of this study show that the Nb_2O_5 photocatalyst degrade RB5 dye up to 65%. Therefore, Nb_2O_5 could be a very promising catalyst for the degradation of azo dyes and need further studies for the enhancement of photocatalytic efficiency.

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