Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2014.993721

57 (2016) 4652–4658
February

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Taylor & Francis Group

Removal of textile dye Reactive Blue 59 by using Nb_2O_5 as a photocatalyst

Sunil D. Marathe, Vinod S. Shrivastava*

Nano Chemistry Research Laboratory, G.T.P. College, Nandurbar 425412, India, emails: sunilmarathe86@gmail.com (S.D. Marathe), drvinod_shrivastava@yahoo.com (V.S. Shrivastava)

Received 27 May 2014; Accepted 26 November 2014

ABSTRACT

In this work, photocatalytic degradation of textile dye Reactive Blue 59 in aqueous suspension was examined using Nb_2O_5 as a photocatalyst in the presence of UV light in photocatalytic reactor. The Nb_2O_5 photocatalyst was characterized by X-ray diffraction, scanning electron microscopy, and energy dispersive X-ray spectrometry techniques. The photocatalytic experiments were carried out to optimize the various parameters like effect of amount of catalyst, initial dye concentration, irradiation time, and pH. The effect of UV light and Nb_2O_5 photocatalyst on the rate of removal of dye was studied. In addition to this, the changes in the chemical oxygen demand of the dye solution after photocatalytic irradiation in the presence of Nb_2O_5 were studied. The maximum photocatalytic removal of reactive blue achieved using Nb_2O_5 was 88.97% with 15 mg/L optimum dye concentration.

Keywords: Nb_2O_5; Reactive Blue 59; Photocatalytic degradation; SEM

1. Introduction

Textile industries are the major source of pollution due to the large amount of dyestuffs that they release to water sources. Dyes are coloring matter with highly complex structure. Thousands of different dyes and pigments are used industrially and million tons of synthetic dyes are produced annually, worldwide [1]. About 1–15% of the dye is lost during the dyeing process in textile industry process and is released in wastewaters [2].

Most of the dyes are very difficult to degrade because of their complex structure and synthetic origin. Many researchers are working on treatments of textile effluents to remove pollutants and decolourization of dye effluents [3,4]. Different methods have been reported for the removal of textile dyes [5]. There are some conventional biological treatment methods, but these are ineffective for the complete degradation of organics and dyes [6,7]. The textile dyes have been successfully removed from aqueous solution by various researchers [8–11]. Reactive Blue 59 belongs to the class of azo dyes and is used as textile dyes in India in large amount. Similar to other reactive dyes, Reactive Blue 59 can cause allergic dermatitis and respiratory diseases [12–15], contact dermatitis, and asthma [16].

In recent years, the use of semiconductor materials for the degradation of dyes is gaining importance. In this method, dye solution is irradiated with light in presence of semiconductor photocatalyst. This method is known as photocatalytic degradation or advanced oxidation process (AOP). The photocatalytic oxidation process is an important process for the effective removal of various organic compounds, particularly textile dyes [17]. The AOP is of great importance for the removal of various organic compounds [18–21].

*Corresponding author.

The nanosized semiconducting materials used for photocatalytic degradation include TiO_2, ZnO, PbO, CdS, Nb_2O_5, etc. In this work, we have chosen Nb_2O_5 as a semiconductor photocatalyst because very little work is reported using this material as compared with other materials. The band gap of Nb_2O_5 is about 3.4 eV. Nb_2O_5 and its composites have been used successfully as a photocatalyst for the degradation of various organic compounds by using photocatalytic degradation process [22–29].

2. Experimental

2.1. Materials and methods

All the chemicals were of analytical grade. The water soluble Reactive Blue 59 and Nb_2O_5 were used for photocatalytic study. The photocatalyst Nb_2O_5 used in this work was purchased from HIMEDIA chemicals. The structure of reactive blue dye is shown in Fig. 1. A stock solution of 60 mg/L of Reactive Blue 59 dye was prepared in distilled water. Different concentrations (15, 30, 45, and 60 mg/L) of Reactive Blue 59 dye were prepared from stock solution. The pH of Reactive Blue 59 dye solution was adjusted by adding HCl and NaOH. The rate of photocatalytic degradation was followed by measuring the absorbance of the sample after a different interval of time using UV–visible spectrophotometer (Systronics-2203) using a quartz cell of 1 cm path length at max 585 nm. The removal percentage of Reactive Blue 59 was calculated using following Eq. (1).

$$\text{Removal percentage} = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

where C_0 = initial concentration, C_t = concentration at time t.

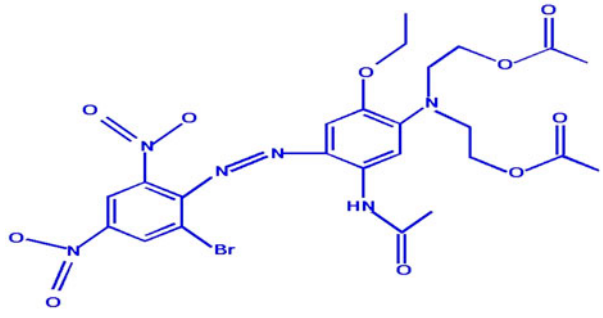

Fig. 1. Structure of Reactive Blue 59 dye.

The X-ray diffraction measurements for Nb_2O_5 powder were carried out at room temperature on X-ray diffractometer model D8 ADVANCE (BRUKER) over a 2θ range 10–80° using Cu-Kα radiations of wavelength 1.54060 Å. The scanning electron microscopy (SEM) micrographs were recorded using Hitachi s-4800 FE-SEM equipment.

2.2. Instrumentation

The photocatalytic degradation of Reactive Blue 59 dye was carried out in a photocatalytic reactor with a 400 W medium pressure mercury lamp with nominal wavelength range 220–1,400 nm. The reactor consists of a cylindrical Pyrex glass reactor, a double-walled quartz cooling water jacket to maintain the temperature and prevent the reactor from excessive heating. The reaction solution was stirred with a magnetic stirrer at a constant speed. The changes in the dye concentration are followed using a spectrophotometer (Systronics 2203). The pH measurements are carried out using an equiptronics digital pH meter (Model-E610).

3. Mechanism

The process is initiated when the solution in presence of Nb_2O_5 photocatalyst is exposed to UV radiations with the formation of electron–hole (e^-/h^+) pairs. Illumination of semiconductor photocatalyst (Nb_2O_5) with energy greater than the band-gap energy promotes the transition of electrons from the valence band to the conduction band, leaving positive holes behind. The oxygen molecules act as electron acceptors and form superoxide radicals, OH^- ions act as an electron donor to form hydroxyl radicals. The superoxide radical ions and hydroxyl radicals are responsible for oxidative degradation of dye.

$$Nb_2O_5 \xrightarrow{UV-light} Nb_2O_5(e^-) + Nb_2O_5(h^+)$$

$$O_2 + Nb_2O_5(e^-) \xrightarrow{Electron-holepair} O_2^- + Nb_2O_5$$

$$H_2O \longrightarrow H^+ + OH^-$$

$$OH^- + Nb_2O_5(h^+) \longrightarrow OH + Nb_2O_5$$

4. Results and discussion

4.1. X-ray diffraction

X-ray diffraction (XRD) is an important technique used for quantitative and qualitative analysis of

crystalline materials. Fig. 2 shows XRD patterns of Nb_2O_5 photocatalyst recorded using [model: D8 ADVANCE (BRUKER)] X-ray diffractometer over a 2θ range 10–80° using Cu-Kα radiations of wavelength 1.54060 Å. XRD pattern for synthesized Nb_2O_5 shows defined peaks around 22.20, 27.97, 36.30, 45.62, 57.75, and 70.55 which are indexed to the diffraction from (100), (004), (104), (200), (008), (119), and (126), respectively. This confirms monoclinic niobium oxide (JCPDS card No. 74-0312). The average grain size can be calculated from XRD data using Scherer's formula shown in Eq. (2). The particle size for Nb_2O_5 calculated using Scherrer's equation was 18.29 nm.

$$D = \frac{K \times \lambda}{\beta \times cos\theta} \quad (2)$$

where D = crystal size in nm, K = constant = 0.94, λ = wavelength of X-ray in nm = 154,060 nm, β = FWHM in degree, θ = angle in degree.

4.2. SEM

SEM is a characterization technique for studying the morphological features and surface characteristics of materials. The SEM micrographs were recorded using Hitachi S-4800 FE-SEM. The SEM micrographs of Nb_2O_5 material are shown in Fig. 3. It can be seen from the SEM micrographs that Nb_2O_5 photocatalyst has well-defined crystals of uniform size.

4.3. Energy dispersive X-ray spectrometry (EDX)

EDX is used for the elemental analysis or chemical characterization of the sample. The chemical stoichiometry of Nb_2O_5 was investigated with EDX which confirms the presence of elements Nb and O and their atomic ratio of Nb: O ≅ 2:5 (i.e. The compound is Nb_2O_5). The EDS pattern for Nb_2O_5 is shown in Fig. 4.

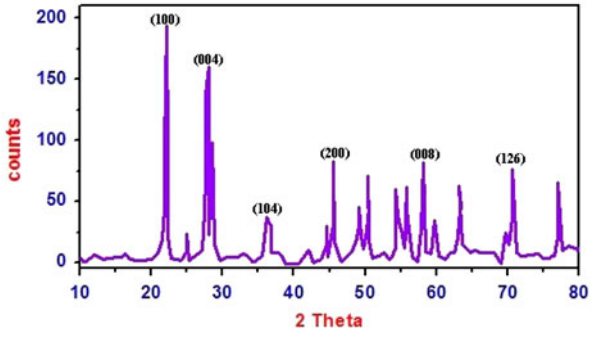

Fig. 2. XRD pattern of Nb_2O_5.

4.4. Photocatalytic behaviours

4.4.1. Effect of initial dye concentration and contact time

The effect of initial dye concentration and contact time on the rate of removal of Reactive Blue 59 was studied with initial dye concentration of 15, 30, 45, and 60 mg/L by keeping a constant Nb_2O_5 photocatalyst dose of 1 g at pH 9. The absorbance was measured at 15 min interval, and percentage of removal was calculated for different dye concentrations (15, 30, 45, and 60 mg/L) from 0 to 150 min. The plot of percentage of removal against time is shown in Fig. 5. It was observed that the removal percentage decreases with increasing initial concentration of Reactive Blue 59 and increases with increasing time.

4.4.2. Effect of catalyst dose

In this work, effect of Nb_2O_5 photocatalyst dose on the removal of Reactive Blue 59 was studied by carrying out a series of reaction with different catalyst dose (i.e. 0.5, 1.0, and 1.5 g) at pH 9 .The results are shown in Fig. 6. The rate of removal of Reactive Blue 59 was found to be increased rapidly with the increasing amount of photocatalyst Nb_2O_5. The increase in the removal rate of dye can be attributed to the increase in active sites on the Nb_2O_5 photocatalyst surface with increasing catalyst dose.

4.4.3. Effect of pH

The rate of photocatalytic degradation of Reactive Blue 59 using Nb_2O_5 photocatalyst was studied to optimize the pH. The pH of the solution is an important parameter during the photocatalytic study. The effect of pH on the removal of reactive blue using Nb_2O_5 was studied in the pH range 2–10, with 1 g catalyst dose and 30 mg/L dye concentration, the results are shown in Fig. 7. The maximum removal rate was obtained at pH of 8.

4.4.4. Effect of UV light and catalyst

The rate of removal of Reactive Blue 59 using Nb_2O_5 photocatalyst was studied at three different conditions i.e. in presence of only UV light, in presence of only catalyst, and in presence of both UV light and catalyst. The results for the study are shown in

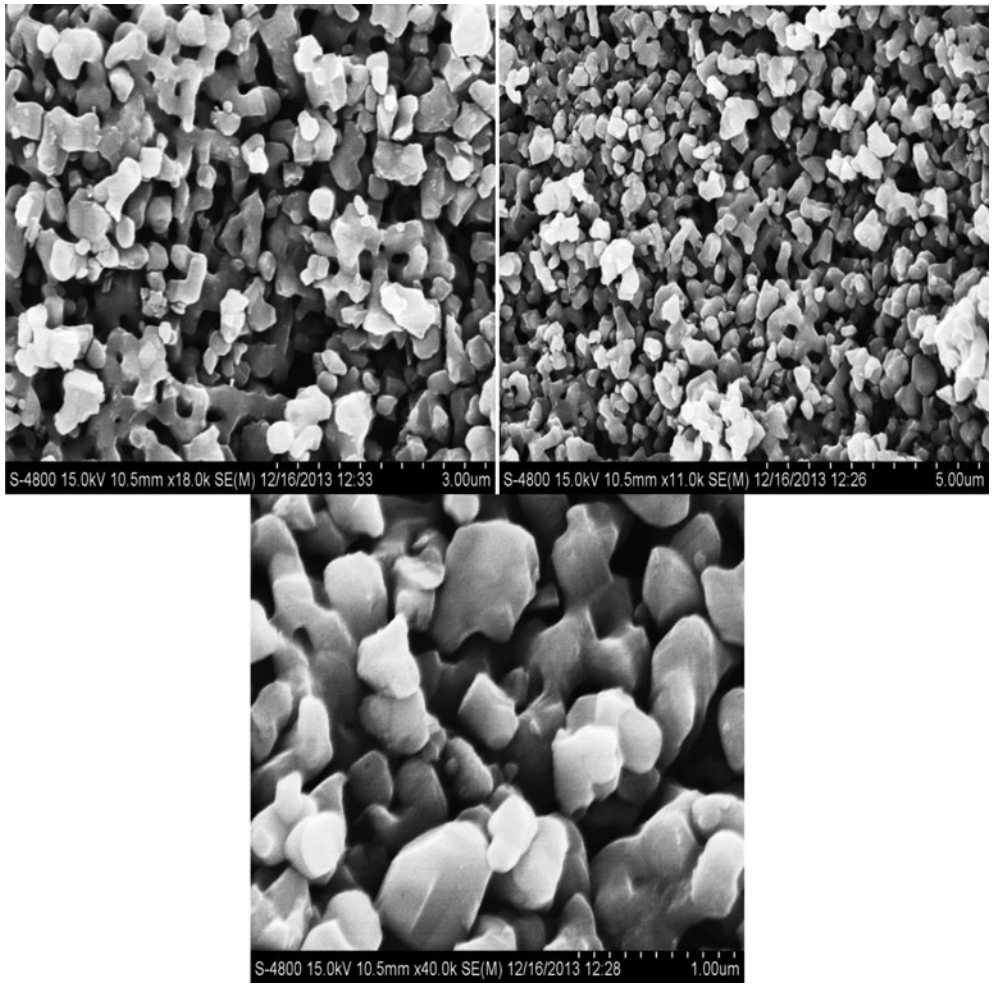

Fig. 3. SEM images of Nb_2O_5.

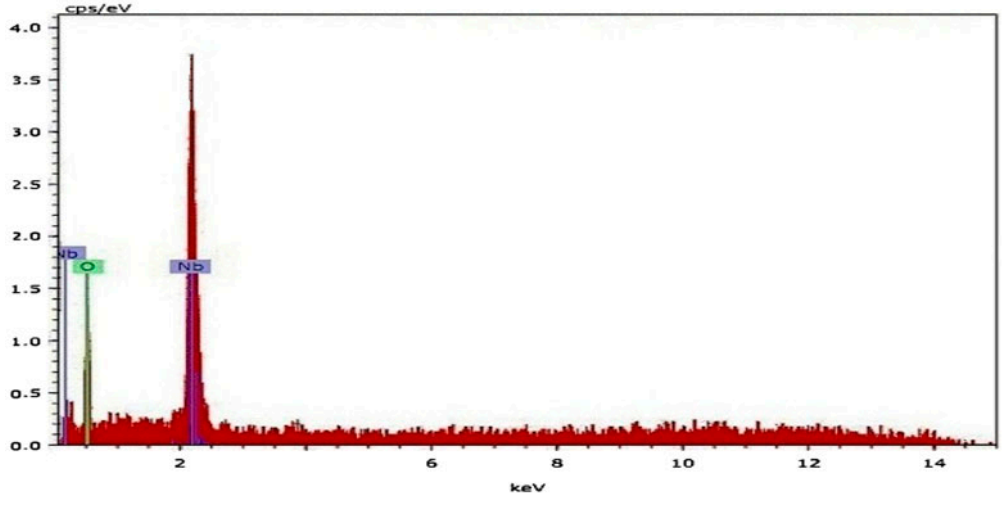

Fig. 4. EDS of Nb_2O_5.

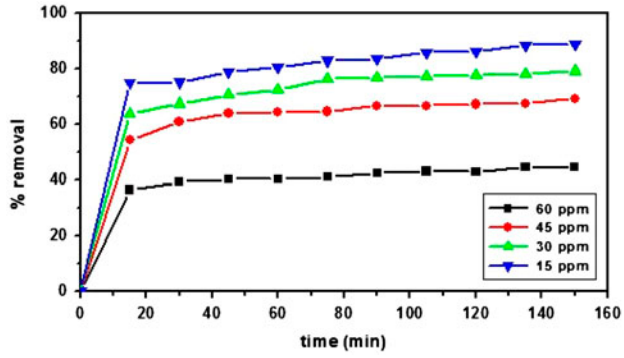

Fig. 5. The effect of initial dye concentration and contact time on the rate of removal of Reactive Blue 59 using Nb_2O_5 photocatalyst with 1 g dose and pH 9.

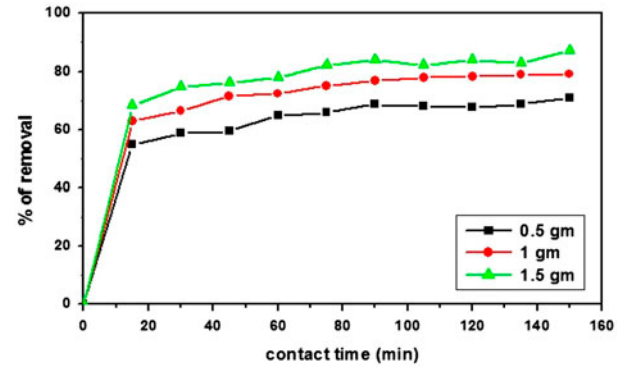

Fig. 6. The effect of catalyst dose on the rate of removal of Reactive Blue 59 using Nb_2O_5 photocatalyst with constant initial dye concentration 30 mg/L and pH 9.

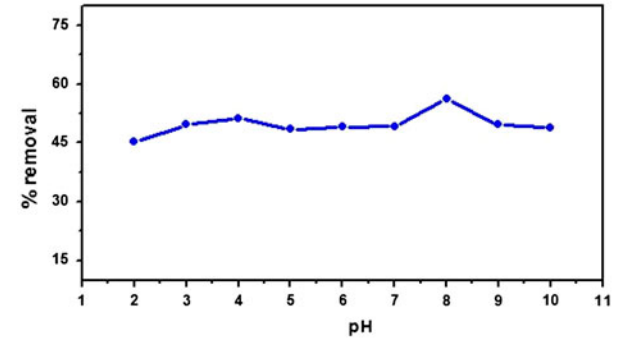

Fig. 7. The effect of pH on the rate of removal of Reactive Blue 59 using Nb_2O_5 photocatalyst with 1 g dose and dye conc. 30 mg/L.

Fig. 8. It was observed that the rate of removal of dye in the presence of both UV light and catalyst was highest.

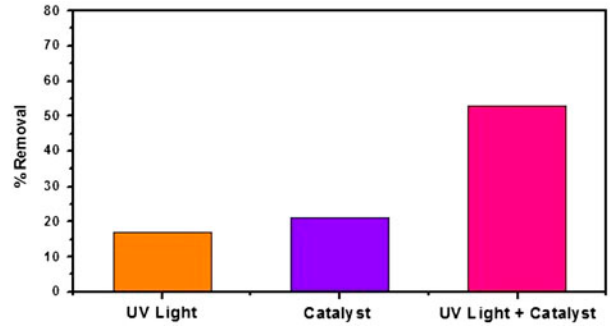

Fig. 8. The effect UV light and catalyst conditions on the rate of removal of Reactive Blue 59 using Nb_2O_5 at 30 mg/L dye concentration and 1 g catalyst dose.

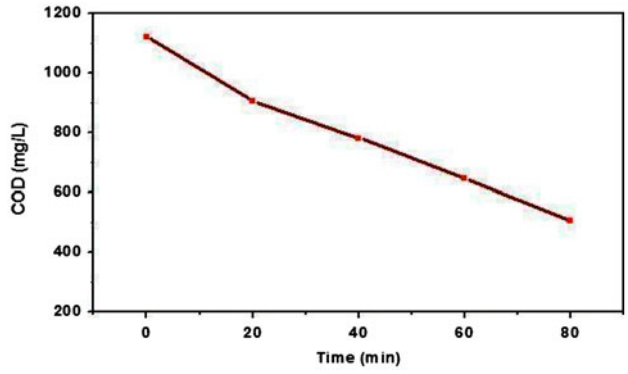

Fig. 9. The effect of photocatalytic treatment on COD.

4.4.5. Chemical oxygen demand (COD)

The COD is a measure of the amount of organic compound in wastewater. This test allows measurement of waste in terms of the total quantity of oxygen required for the oxidation of organic material to CO_2 and water. In the present work, the changes in the COD of the dye solution after photocatalytic irradiation were followed by measuring the COD of the solution at different intervals of time.

In this work Reactive Blue 59 dye after measurement of initial COD was irradiated with UV light in a photocatalytic reactor in presence of Nb_2O_5, and the changes in COD were measured by withdrawing few ml of sample at regular interval of time from the photocatalytic reactor. The results are shown in Fig. 9.

5. Conclusion

The degradation and mineralization of textile dye Reactive Blue 59 were successfully carried out using Nb_2O_5 photocatalyst in the presence of UV light. The

rate of removal of dye decreases with increasing initial dye concentration and increases with increasing time. The highest removal rate was obtained at pH 8. The present study shows that Nb_2O_5 can be used as A photocatalyst for removal of Reactive Blue 59 in the presence of UV light and highest removal is obtained in the presence of both UV light and catalyst than that obtained in the presence of only UV light. A rapid decrease in COD was observed upon the photocatalytic treatment of Reactive Blue 59 solutions in the presence of Nb_2O_5 and UV light. The maximum photocatalytic removal percentage was 88.97% in 150 min with 15 mg/L initial dye concentration of Reactive Blue 59 and 1 g Nb_2O_5 catalyst dose.

Acknowledgment

Authors are gratefully acknowledged to North Maharashtra University, Jalgaon for XRD, SEM, and EDX. Nano chemistry research laboratory, G.T.P. College, Nandurbar for FTIR studies. Authors are also thankful to the Principal G.T.P. College, Nandurbar for providing necessary laboratory facilities. Thanks to Dr. Vijay Agrawal Foundation, Surat, for financial help during our work. Thanks to Anil N. Kulkarni for his guidance.

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