

Photocatalytic Degradation of Malachite Green Dye Over Naked Niobium Oxide as a Photocatalyst

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Abstract

This study is one application of Advanced Oxidation Process (AOPs) that is using Naked Niobium Oxide (Nb_2O_5) as a photocatalyst to degrade the industrial Malachite Green dye. Malachite Green is used in many industries such as leather, silk, paper, plastic and others. This research involved Study different factors of photodegradation [weight of catalyst (0.03 – 0.3) g, initial concentration of dye (5 – 15) ppm, temperature (5 – 25) °C, light intensity (2.3 – 3.5) mW / cm², pH (2 – 8), adding of hydrogen peroxide (0.5 – 2) mL and type of gas (air, N₂)].

Key words: Niobium oxide, Malachite Green dye, Photocatalytic degradation, Advanced Oxidation Processes.

الخلاصة

تعتبر هذه الدراسة أحد تطبيقات عمليات الأكسدة المتقدمة (AOPs) باستخدام العامل المساعد المجرّد أوكسيد النيوبيوم (Nb_2O_5) كعامل مساعد ضوئي لتكسير صبغة المالاخيت الأخضر.

تستخدم صبغة المالاخيت الأخضر في عدة صناعات منها صناعة الجلود، الحرير، الورق، البلاستيك بالإضافة الى صناعات أخرى. تضمن البحث دراسة تأثير الظروف المختلفة على عملية التفسير الضوئي لتأثير وزن العامل المساعد (0.03 – 0.3) غم، التركيز الابتدائي للصبغة (5 – 15) جزء بالمليون، درجة الحرارة (5 – 25) درجة سيليزية، شدة الضوء المستخدم (2.3 – 3.5) ملي واط/سم²، الدالة الحامضية (2–8)، إضافة بيروكسيد الهيدروجين (0.5 – 2.0) مليلتر ونوع الغاز المستخدم (هواء، غاز النتروجين).
الكلمات المفتاحية: أوكسيد النيوبيوم، صبغة المالاخيت الأخضر، التفسير الضوئي المحفز، عمليات الأكسدة المتقدمة.

Introduction

Photocatalysis, in recent years, has many developments in relationship between energy and environment (Ibhadon *et al.*, 2013). It represents the combination of photochemistry with catalysis. Light with catalyst are necessary to accelerate a chemical reaction (Galves *et al.*, 2003).

Different types of industries caused different types of pollution in environment; Advanced Oxidation Processes (AOPs) are chemical treatments to remove pollution from different industries (Bokhari *et al.*, 2013). AOPs depends on the generation of hydroxyl radicals that have high oxidation potential ($E^\circ = 2.8$ V), high reactive and non-selective substances used to degrade toxic organic compounds found in wastes of different industries and convert toxic compounds to carbon di oxide, water and inorganic salt or convert to less harm products (Mota *et al.*, 2008).

AOPs are used for the removing of Malachite Green dye from wastewater as a promising option (Tolia *et al.*, 2012).

Dyes are chemical compounds, which are divided into different types according to functional groups: azo, anthraquinone, heterocyclic polymers and tri phenyl methane dyes. Malachite Green is a tri methyl dye (Rai *et al.*, 2014).

Malachite Green has the chemical formula of $C_{23}H_{26}N_2O$ and it is found in many forms Malachite Green and Leucomalachite Green (Srivastava *et al.*, 2004 and Sudova *et al.*, 2007). Malachite Green has many applications; it is used as industrial dye in dying of leather, silk, paper, plastic and other (Baek *et al.*, 2010). It can be found in waste of these industries so it must be removed by using different methods (Hema *et al.*, 2008).

Niobium Oxide Nb_2O_5 is a semiconductor with high band gap energy (3.4 eV) (Desa et al., 2006, Pehlivan et al., 2005 and Shimizu et al., 2005) Niobium Oxide has lower photocatalytic activity than Titanium Oxide TiO_2 and Zinc Oxide ZnO (Habibi et al., 2011). It is used as a photocatalyst in photo degradation of contaminants (Collazzo et al., 2012 and Qi et al., 2013).

The aim of the work use naked Niobium Oxide as photocatalyst to degrade the industrial dye Malachite Green, Which is used in leather industry.

Experimental part

Materials

Niobium Oxide (Nb_2O_5) (Fluka, 99.9 %), Malachite Green (BDH, 99 %), Hydrochloric acid (HCl) (GCC, 98 %), Sodium hydroxide (NaOH) (Scharlau, 99 %), Hydrogen peroxide (H_2O_2) (Appli chem. GmbH, 30 %).

Procedure for photocatalytic degradation of Malachite Green dye

The aqueous solution (100 mL) of Malachite Green (5ppm) was prepared from stock solution (1000 ppm) of Malachite Green that it was prepared from dissolving (1 gm.) of dye in (1 Liter) of distilled water. Then (0.10 g) of naked Niobium Oxide was added to solution of dye in photo reactor. A 125 Watt of High Pressure Mercury Lamp (SYLVANIA, Germany) was used for irradiation. Adsorption time was 30 min. after adsorption the irradiation time was 1 hour and measured absorbance every 10 min by taking 2 mL of irradiated solution and centrifugation for 15 min in centrifuge (Hettich, EBA20) and measured absorbance of filtrate.

The intensity of light at various distances was measured by honle (UV. technology). A T80 UV-VIS spectrophotometer double beam (PG Instruments Ltd) was used for measuring absorbance at different time intervals.

Results and discussion

UV. Vis. Spectrum of Malachite Green is shown in figure 1 to obtain λ_{max} of dye (615 nm).

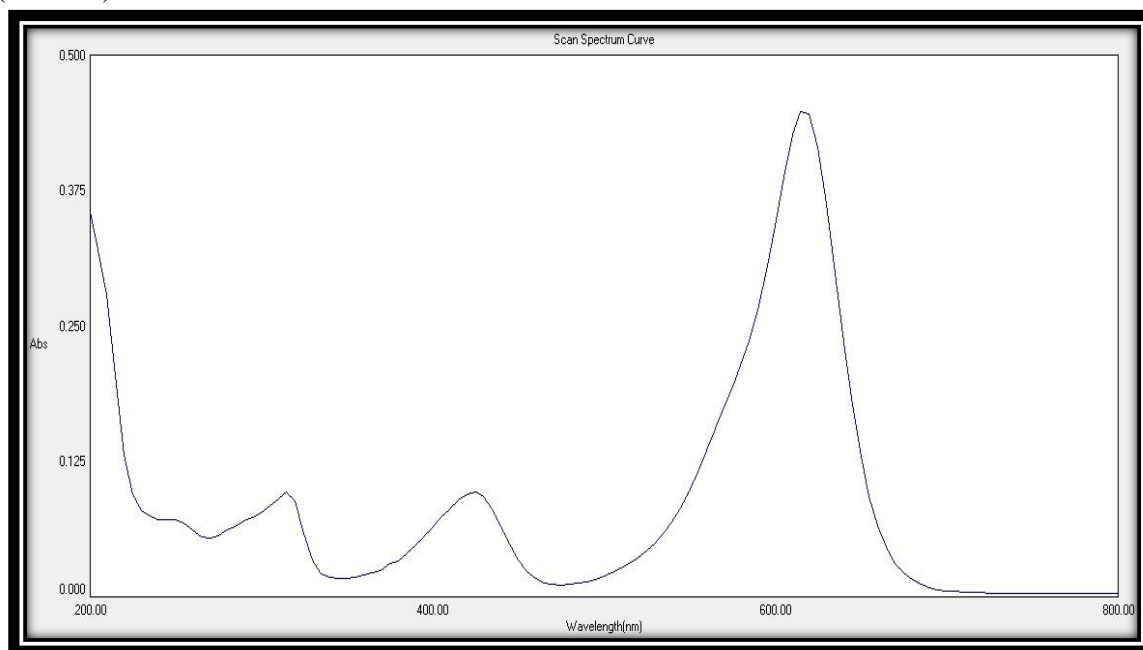


Figure 1: UV. Vis. Spectrum of (5 ppm) Malachite Green, λ_{max} 615 nm.

In figure 2 Calibration curve of Malachite Green that is represented from 1 ppm to 15 ppm.

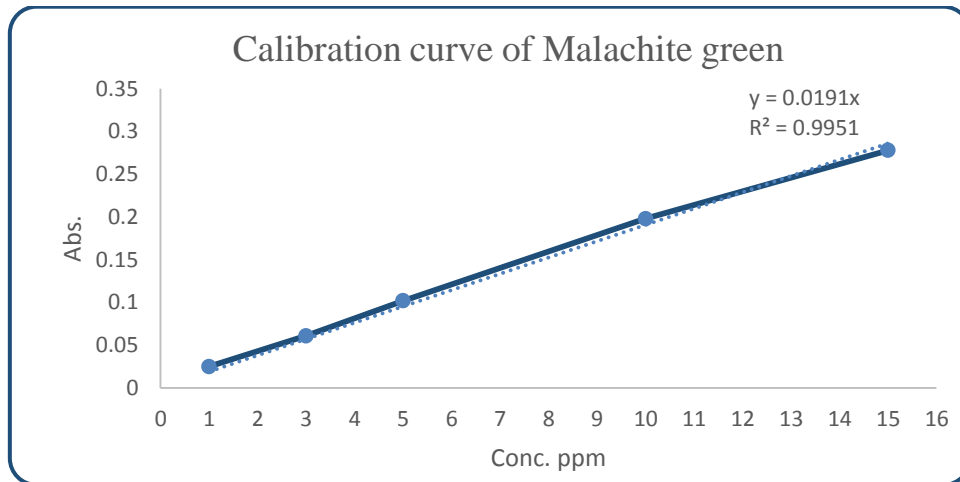


Figure 2: Calibration curve of Malachite green (1 – 15) ppm

Effect of weight of catalyst

The effect of Weight of catalyst was studied at the range (0.03 – 0.3) g. of Nb_2O_5 as shown in figure 3. The initial degradation rate of the dye was increased with increase in amount of catalyst. Further increase in catalyst weight decreased the reaction rate. Initially with increasing amount of Nb_2O_5 , the availability of semiconductor particle for absorption of photon increases, thereby producing more number of oxidizing sites, which increase the rate of the reaction. The decrease of degradation rate at higher amount of Nb_2O_5 may be related to the decrease of light penetration through the catalyst suspension and scattering of light by the catalyst particles. Therefore, optimum weight of catalyst for the reactor system was 0.1 g.

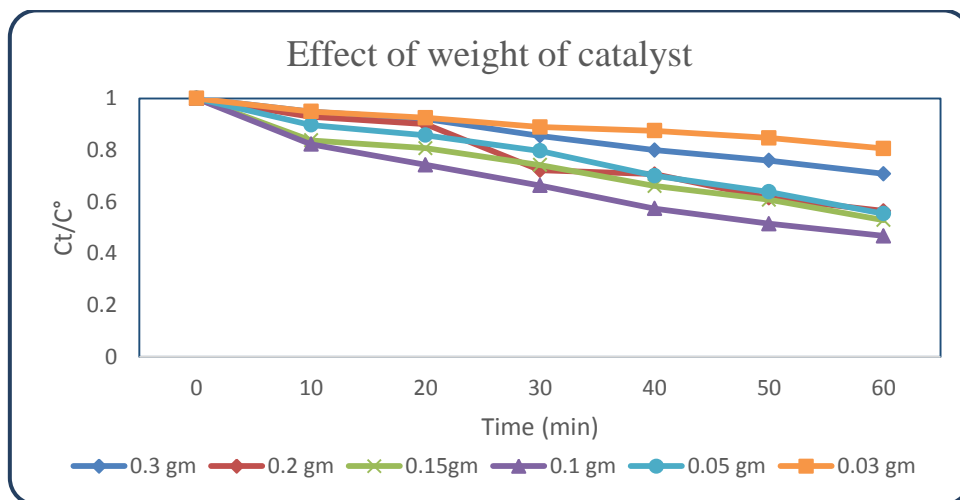


Figure 3: Effect of weight of catalyst (0.03 – 0.3) g and (5 ppm) dye at 25°C

Effect of concentration of dye

Effect of concentration of dye was studied from 5 ppm to 15 ppm according to calibration curve of dye. It can be seen in figure 4. Therefore, the optimum concentration of dye was 5 ppm.

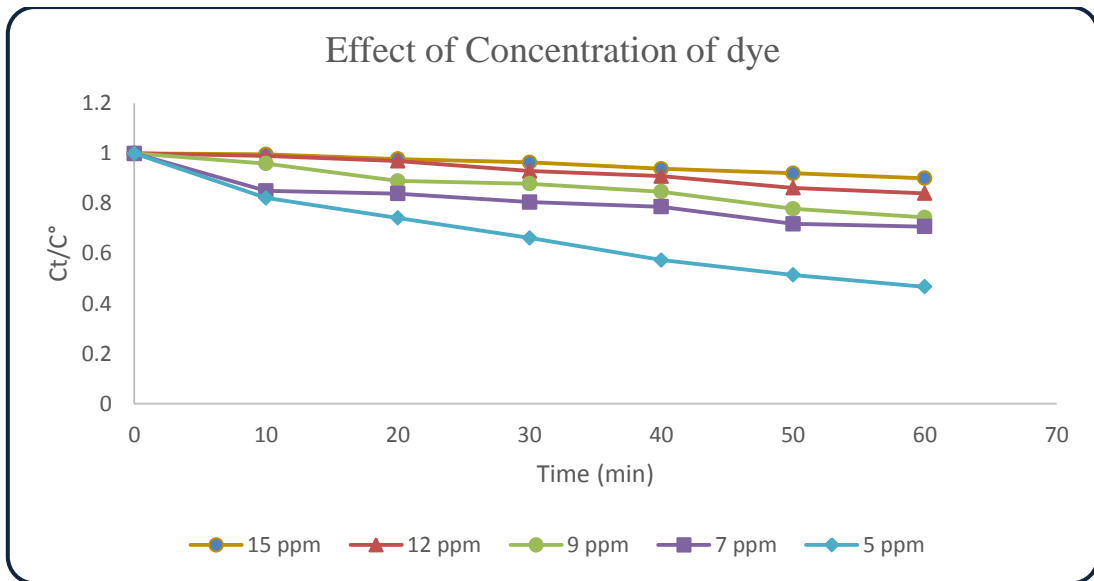


Figure 4: Effect of Concentration of dye (5 – 15) ppm. And 0.1 g of catalyst

Effect of temperature

Effect of temperature was studied from 5 °C to 25 °C that it is shown in figure 5. The optimum temperature is 25 °C that refers to increasing of rate of transfer of electron from valance band to conductive band with increasing temperature.

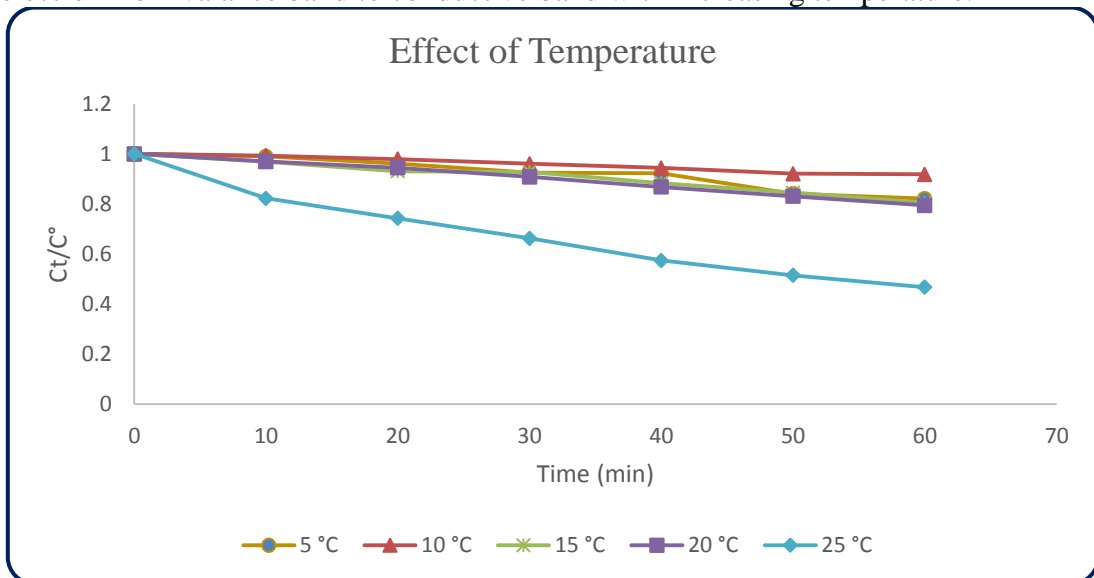


Figure 5: Effect of temperature (5 – 25) °C, (0.1 g) catalyst and (5ppm) of dye

Effect of light intensity

Effect of light intensity was studied at different height of lamp and measured light intensity by using UV. Meter that is shown in table 1.

Table 1: light intensity at different height

Height of lamp (cm)	Intensity (mw/cm ²)
5	3.5
7	3.0
10	2.5
15	2.3

Photodegradation of dye at different height of lamp can be seen in Figure 6 that is refer to increasing of degradation with decrease of height of lamp.

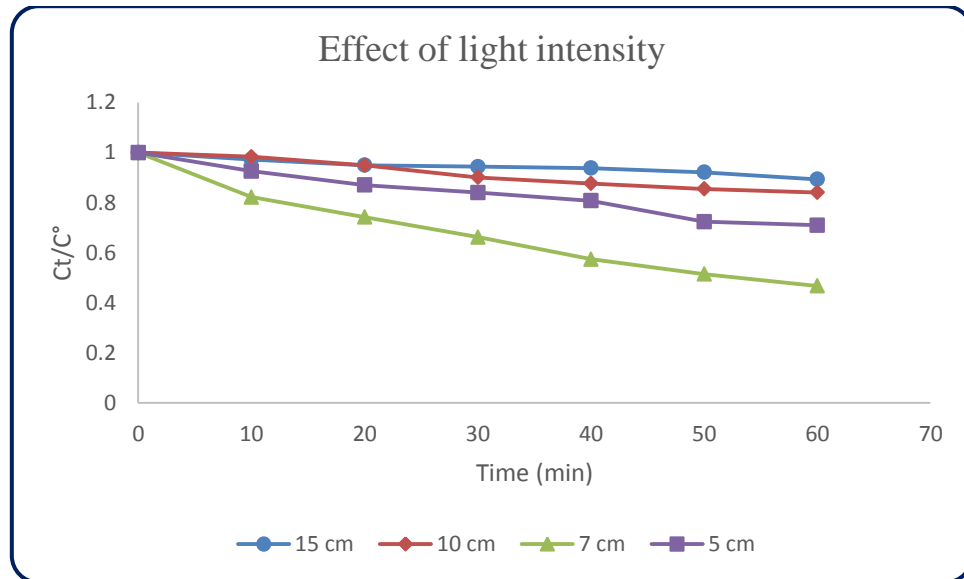


Figure 6: Effect of light intensity (2.3 – 3.5) mW / cm², (0.1 g) catalyst and (5 ppm) dye at 25 °C

Effect of pH

The effect of pH of Malachite Green is 6, so effect of pH was studied in range (2–8) by using Hydrochloric acid and Sodium hydroxide to adjust pH of dye solution, in acidic media photodegradation decreased due to decreased hydroxyl radical (important part of AOPs) while increase in basic media due to release of hydroxyl radical. Effect of pH can be seen in Figure 7.

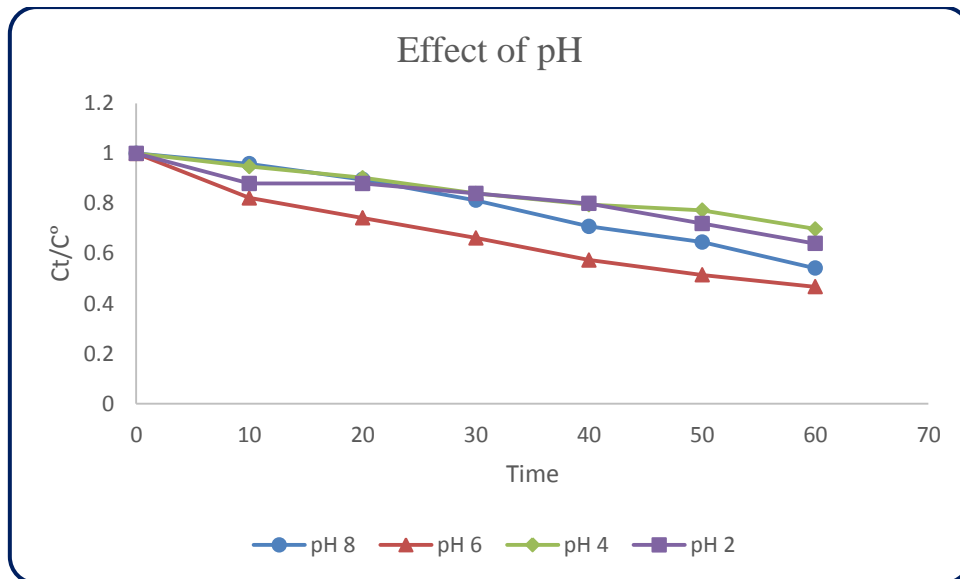


Figure 7: Effect of pH (2 – 8) on photodegradation of (5 ppm) dye and (0.1 g) at 25 °C

Effect of adding hydrogen peroxide

Effect of adding hydrogen peroxide was shown in Figure 8 that is adding (0.5 – 2) mL of H₂O₂. Adding oxidizing agent H₂O₂ increased photodegradation of dye because releasing hydroxyl radical to degrade the dye. When adding 2 mL of H₂O₂ photodegradation decreased because formed OH₂[·] Radical that hindered the photodegradation process.

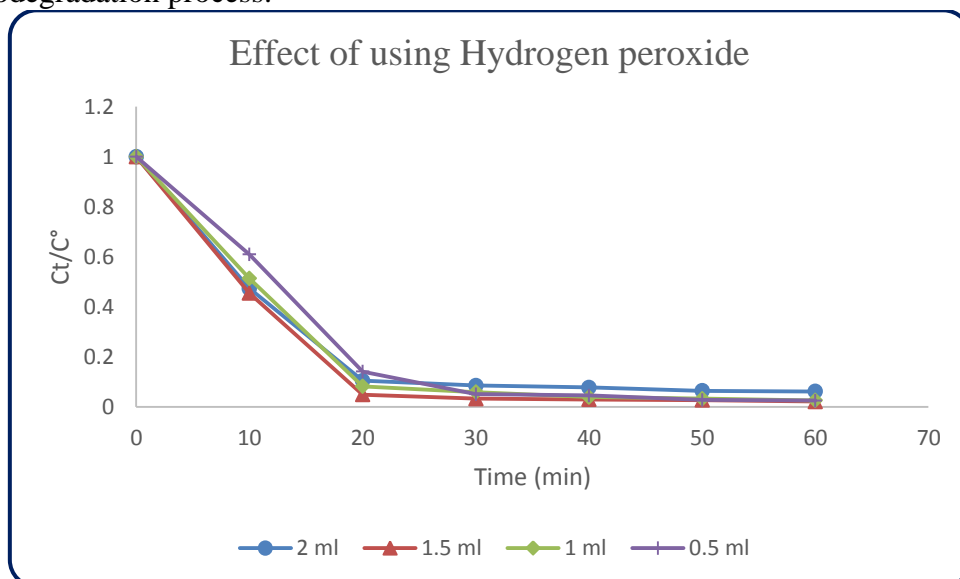


Figure 8: Effect of adding hydrogen peroxide (0.5 – 2) mL on photodegradation of (5 ppm) dye and (0.1 g) at 25 °C

Effect of type of gas

Air and Nitrogen gas were used in photodegradation of dye, it can be seen in Figure 9 that showed decreasing of photodegradation when used nitrogen gas because it is an inert gas and does not release hydroxyl radical.

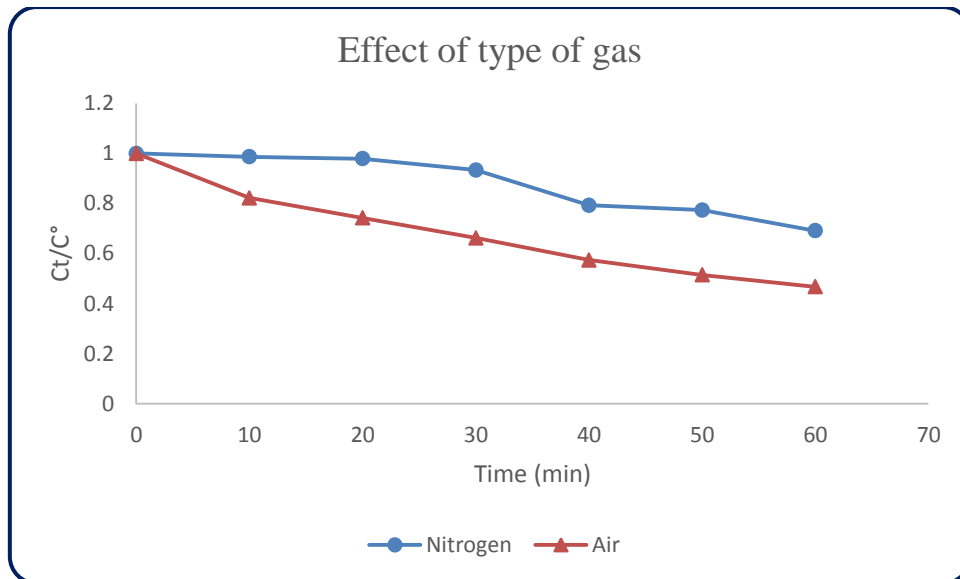


Figure 9: Effect of type of gas (Air and N₂) on photodegradation of (5ppm) dye and (0.1 g) at 25 °C

At optimum condition of this study after 1 hour of irradiation 53.25 % of dye was removed, Figure 10 shows the photodegradation process spectrums at optimum condition (0.1 g. of catalyst, 5 ppm of dye, 25 °C, 3 mW / cm² light intensity on 7 cm height of lamp and pH = 6). While when completed the photodegradation of dye, dye degraded after 3 hours shown in figure 11.

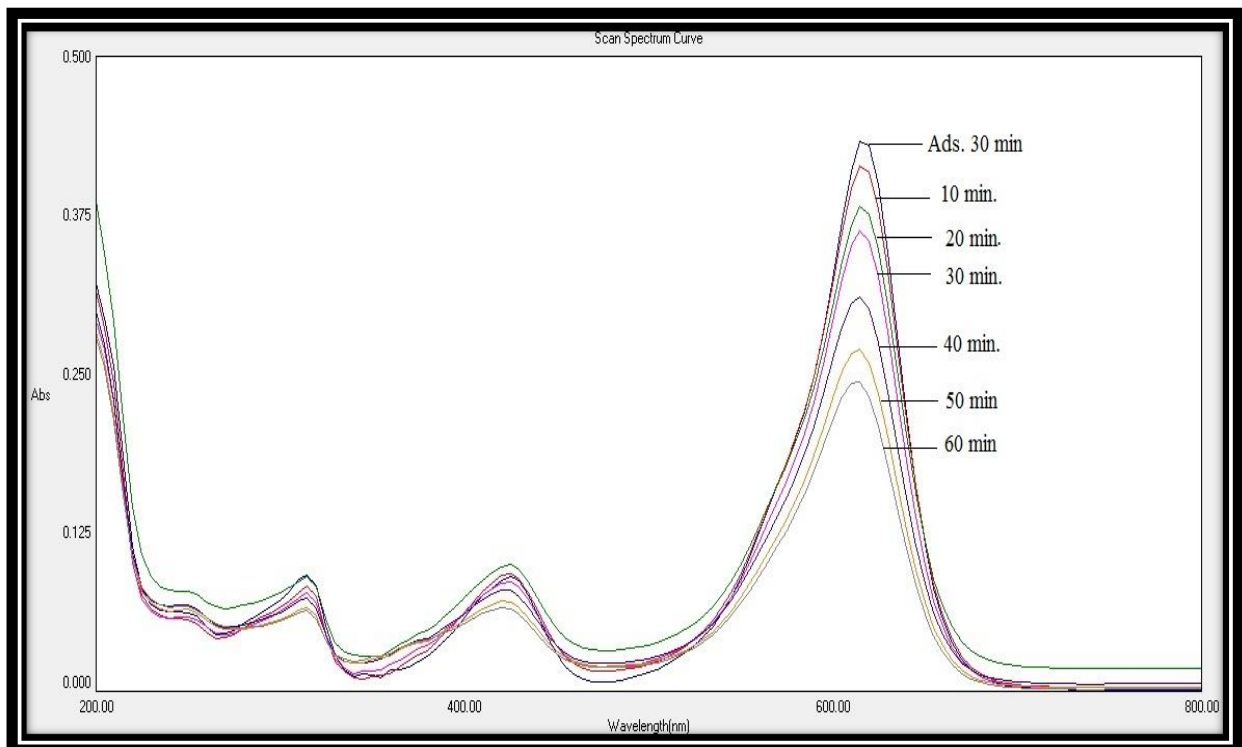


Figure 10: Spectra show photodegradation process at optimum condition (0.1g of catalyst, 5 ppm of dye, 25 °C, 3 mW / cm² light intensity on 7cm height of lamp and pH = 6)

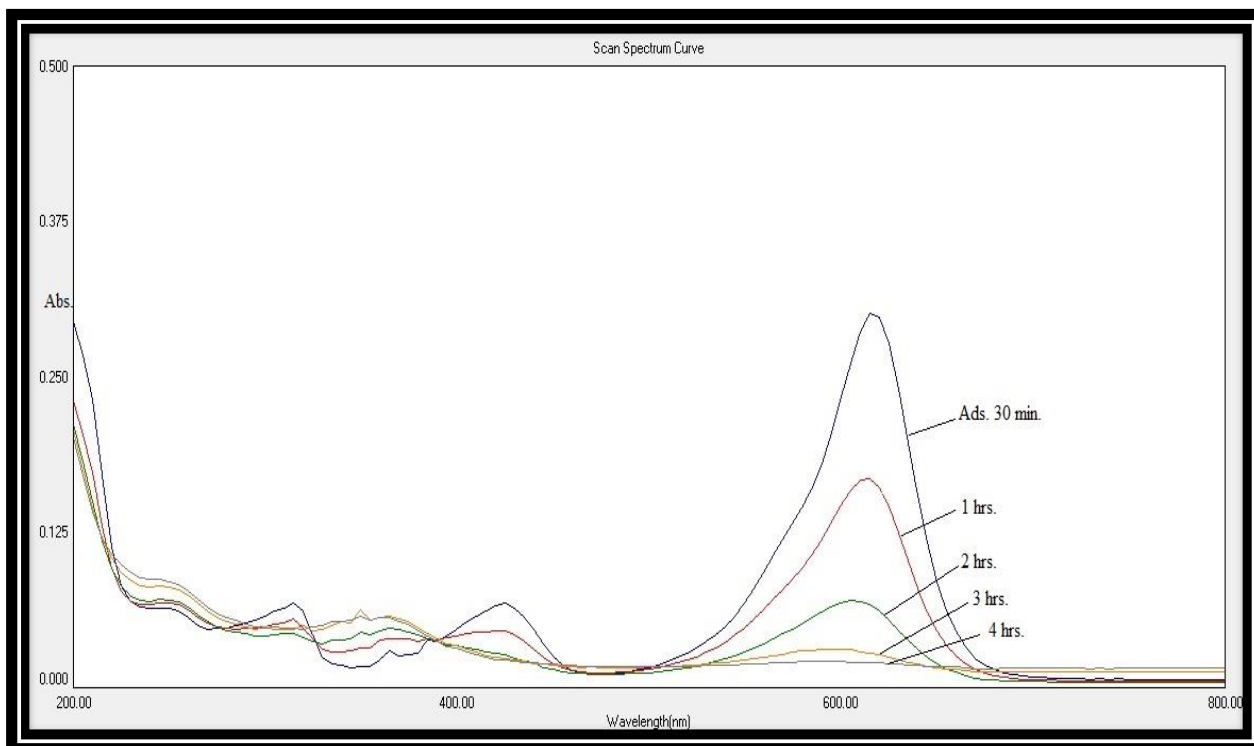


Figure 11: completed photodegradation of dye at optimum condition

Conclusions

From the results, we can conclude that the optimum conditions of this study are (0.1 g of catalyst, 5 ppm of dye, 25 °C, 3 mW / cm² light intensity on 7 cm height of lamp and pH 6). The percentage of removal dye at optimum conditions of Naked Niobium Oxide is 53.25 % and this percentage increases with using sensitized Niobium Oxide. The activity of Niobium Oxide can be increased by sensitizing with other oxides such as Zinc Oxide.

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