

## Synthesis and Characterization of Nitrogen-Doped TiO<sub>2</sub>/WO<sub>3</sub> Nano-Composite Material and its Photocatalytic Activity for Photo-degradation of Phenol Red in Aqueous Solution

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**ABSTRACT:** Crystal form of N-TiO<sub>2</sub>/WO<sub>3</sub> Nano-Composite material was prepared from urea, commercial TiO<sub>2</sub> and WO<sub>3</sub> by simple solid phase reaction followed by calcinations at a temperature of 400 °C for four hours at each step. The as-synthesized photocatalyst was characterized using XRD and Uv-Visible diffuse reflectance spectra. It was found that the absorption edge of N-TiO<sub>2</sub>/WO<sub>3</sub> was well extended to visible light. Dark experiment has been done to know the degree of photodegradation of adsorption of PR over the studied photocatalyst under non-irradiation. The result obtained was for photocatalytic degradation of adsorbed PR was only about 6.32%. The as-synthesized photocatalyst was highly active under visible irradiation (93.87%) than under UV irradiations (75.74%). This may be due to the fact that the absorption edge of the modified TiO<sub>2</sub> particle shifts to visible light range.

**KEYWORDS:** Advanced oxidation processes, degradation, visible and UV radiations.

### 1 INTRODUCTION

Nowadays Environmental pollution is proposed to be the greatest problem that chemical scientists will face in the 21st century and an increasing number of scientists are looking for new systems to solve this problem [1]. Even if chemical industries make products with much beneficial usage; they do also have negative impacts on human health and the environment. They release hazardous, calcitrant and toxic chemical substances such as phenolic compounds, high molecular weight polymeric surfactants, herbicides and pesticides from industrial wastewater effluent which are well known to be not easily biodegradable [2]. These effects have become major concern within the international community because of the environmental issues addressed by the Environmental Protection Agency (EPA) to prevent pollution and contamination of groundwater and surface waters [3]. Traditionally, industrial wastewater treatments for these effluents include different techniques such as biological treatment, reverse osmosis and activated carbon adsorption. These techniques often utilize potentially hazardous or polluting materials and even most of them are non-biodegradable.

Therefore, the development of an effective treatment technique that can convert pollutants into non-toxic or less harmful materials is highly required. In recent years, there has been the emergence of voluminous literatures on the development of novel effective photocatalytic processes for the treatment of industrial wastewater effluents and municipal wastes that contain toxic and recalcitrant pollutants. Photocatalysis is among the rapidly evolving and efficient technologies for purification of water. With this approach, harmful organic compounds are broken down in the presence of catalyst and ultraviolet (UV) irradiation without generating secondary harmful pollutants [4]. Semiconductors such as TiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, ZnO, ZnS and WO<sub>3</sub> have been known to possess Photocatalytic character [5]. Among them, titanium dioxide has been extensively studied throughout the world and considered as reference photocatalyst in the degradation of organic pollutants, sewage treatment, air purification and disinfection due to its superior photocatalytic performance, non-selective degradation of various organics, deep mineralization rate, and low cost, inert and non-toxic properties [6]. However, the wide band of TiO<sub>2</sub> (anatase of 3.2 eV, rutile of 3.0 eV) limits the absorption wavelength less than 387 nm, which is only 3–5% of the sunlight energy and holds back the practical applications [7]. In addition, the high rate of electron–hole recombination on the surface

and in the bulk phase of the catalysts and the low photoelectric conversion efficiency hamper the practical applications of TiO<sub>2</sub> as photo catalytic materials.

Therefore, doping TiO<sub>2</sub> with some transition-metal elements such as Co and Cu was used as the initial approach to shift the optical response of TiO<sub>2</sub> from the UV band to the visible band [8]. But even these metal-doped TiO<sub>2</sub> materials suffered from thermal instability and low-quantum efficiency because of increased carrier trapping after doping or require expensive facilities in the ion implantation case [9]. In contrast, better visible optical response of TiO<sub>2</sub> could be achieved by using nonmetal doping [10]. Kinds of nonmetal elements, including phosphorus, carbon, chlorine, and bromine were found to be capable of making doped TiO<sub>2</sub> respond to visible light [11].

Therefore, the proposed project was aimed at studying the Synthesis and Characterization of Nitrogen-Doped TiO<sub>2</sub>/WO<sub>3</sub> Nano-Composite material and its photocatalytic efficiency for photo-degradation of phenol Red in aqueous solution under visible and uv radiation.

## **2 MATERIALS AND METHODS**

### **2.1 EXPERIMENTAL SITE**

The synthesis of Nitrogen-Doped TiO<sub>2</sub>/WO<sub>3</sub> Nano-Composite material ,the degradation experiments and part of the characterization of the as-synthesized photocatalysts (Uv-Vis) were carried out at Haramaya University Research Laboratory (HURL). XRD characterization was done in Addis Ababa Ethiopia Geological Survey Laboratory.

### **2.2 EQUIPMENT AND APPARATUS**

The equipment and apparatus used in this study were: UV/vis spectrophotometer (Gullen kamp model SP 62), X-ray diffraction (Bruker D8 Advance XRD, AXS GMBH, Karlsruhe, West Germany X-ray defractometre), glass reactor, , tungsten lamp (TORCH 40W) as visible light source, Uv lamp (254 nm) as Uv-light source , air (oxygen) pumper, , furnace, centrifuge, magnetic stirrer

### **2.3 CHEMICALS AND REAGENTS**

In this study the following chemicals were used: commercial titanium dioxide (TiO<sub>2</sub>) (scientific park, N.Y,U.S.A.), tungsten trioxide(WO<sub>3</sub>) (MW 231.84 gmol<sup>-1</sup>, SD fine chemicals, 99%), Phenol red (C<sub>19</sub>H<sub>14</sub>O<sub>5</sub>S) (MW. 354.38 g/mol. 1, BLULUX), Ethanol (CH<sub>3</sub>CH<sub>2</sub>OH) (MW. 58.03 g mol<sup>-1</sup>, Park scientific, 99.8), Urea (MW 60.06 gmol<sup>-1</sup>, extra pure BLULUX)), 0.1M NaOH (MW. 40 g mol<sup>-1</sup> Assay: 98%) and 0.1M H<sub>2</sub>SO<sub>4</sub> (MW. 98.08 g mol<sup>-1</sup> Assay: 98%). All were analytical grade and used with no further purification.

### **2.4 EXPERIMENTAL METHODS**

#### **2.4.1 PREPARATION OF PHOTOCATALYSTS**

##### **2.4.1.1 PREPARATION OF N-DOPED TiO<sub>2</sub>**

20 g of TiO<sub>2</sub> and 60 g of urea (TiO<sub>2</sub>: urea = 1:3) were mixed and transferred to a mortar and well crushed using pestle. The obtained powder was then calcined at 400oC for four hours for solid phase reaction [3].

##### **2.4.1.2 PREPARATION OF N-DOPED TiO<sub>2</sub>/WO<sub>3</sub> NANO-COMPOSITE MATERIAL**

10 g of N-TiO<sub>2</sub>, which was synthesized in section 3.4.1.1.was mixed with 0.75 g of WO<sub>3</sub> using 1:1 (v/v) of water and ethanol as solvent. This mixture was subjected to heating at a temperature of 110°C for drying. After cooling to room temperature, it was subjected to calcinations temperature of 400oC for 4 hours [3].

#### **2.4.2 CHARACTERIZATION METHODS**

The as-synthesized composite photocatalyst was characterized using XRD and Uv-Vis spectrophotometer. The crystal phase and crystallite size of the entire obtained composite was measured by Bruker D8 Advance XRD, AXS GMBH, Karlsruhe,

West Germany X-ray diffractometer. The sample was measured in the angular range ( $2\theta$ ) of 40-640 at a scan rate of 0.020 min<sup>-1</sup> using Cu K $\alpha$  radiation ( $\lambda = 0.154056$  nm) operating at 40 kV and 40 mA accelerated voltage and applied current respectively. A Uv-visible spectrophotometer (Gullenkamp model SP 62) was used to obtain the optical absorbance spectra of the sample.

### 2.4.3 PHOTOCATALYTIC DEGRADATION EXPERIMENT

Photocatalytic degradation of phenol red was carried out in a reactor tube made of glass with an effective volume of 500 ml and having an internal diameter of 8 cm with provision for air purging during photocatalysis and an outlet for the collection of samples from the reactor.

A known amount of the synthesized photocatalyst and 250 ml of PR (50 ppm) was taken in a reactor tube with a capacity of 500 ml and the suspension was stirred in dark for one hour in each experiment to obtain adsorption equilibrium before illumination of the reactor. Prior to illumination of the sample by visible or by UV, air (oxygen) was purged using hand purge into the solution in order to have homogeneous composition. During the reaction, the solution was maintained at room temperature and the distance of the lamp from the solution was kept to 9 cm and its light intensity was recorded to be 8.25mW/cm<sup>2</sup>. 10ml of the sample was withdrawn each time at 20 minutes time interval for over the irradiation time of 3 hours. The suspension was centrifuged at 3500 rpm in order to settle down the catalyst particles at the bottom of the test tube before analysis. The absorbance of the clear solution was measured at a  $\lambda$  max of 432 nm for quantitative analysis using optimum amounts of catalysts and pH values.

To check whether the PR is easily degradable or not blank experiment (without addition of any catalyst) has also been done. Photocatalytic degradation experiment was conducted using the as-synthesized photocatalysts (N-doped TiO<sub>2</sub>/WO<sub>3</sub> nano-composite material).

#### 2.4.3.1 COMPARISON OF THE EFFICIENCY OF THE ASSYNTHESIZED PHOTOCATALYSTS UNDER VISIBLE AND UV RADIATIONS

##### EFFECT OF VARYING AMOUNT OF CATALYST ON THE PHOTODEGRADATION OF PHENOL RED

To evaluate the effect of the as-synthesized catalyst (N-doped TiO<sub>2</sub>/WO<sub>3</sub> nano-composite material) on the degradation of phenol red under UV and visible light; the experiment was carried out by taking optimal amount of catalyst 0.45 g and pH of 3 [16] and other conditions were also kept constant throughout the experiment. The percentage degradation was calculated.

## 3 RESULTS AND DISCUSSION

### 3.1 CHARACTERIZATION OF THE PHOTOCATALYSTS

A fine powder of N-TiO<sub>2</sub>/WO<sub>3</sub> was obtained following the above procedures and was characterized as follows.

#### 3.1.1 X-RAY DIFFRACTION (XRD)

Calcinations of the sample at 400°C for 4 hours brings transformation of the composite photocatalyst phase from amorphous to anatase as the XRD spectra shows maximum peak at average angle of 25.59° for N-TiO<sub>2</sub>/WO<sub>3</sub>. There are also minor peaks at around 38°, 48°, 54° and 55° for the anatase phase. Similar result has been reported by other researchers for N-TiO<sub>2</sub> [2]. For WO<sub>3</sub> peaks at 130, 180 and 190 are observed. The XRD pattern of the as-synthesized sample shows only anatase form of TiO<sub>2</sub> and monoclinic form of WO<sub>3</sub> indicating that WO<sub>3</sub> is well incorporated into TiO<sub>2</sub>. As an XRD spectroscopic technique mimics about the structure of crystals, it can be confirmed from (Appendix Figure 1) that the crystallographic shape of the as-synthesized anatase is tetragonal, as studied by many scholars. This is because calcinations of TiO<sub>2</sub> at 400°C for 4 hrs lead to the formation of anatase which is tetragonal [13]. As can be confirmed from the XRD spectra of the sample, the incorporation of the impurities into the crystal lattice of TiO<sub>2</sub> doesn't alter its crystal structure. The average crystallite size of the as-synthesized catalyst was estimated using Debye Scherrer equation which is given as:

$$d = \frac{\kappa\lambda}{\beta\cos\theta} \quad (3.1)$$

Where,  $d$  is crystallite size in nanometer  $K$  is shape factor constant, which is 0.9,  $\beta$  is the full width at half maximum in radians,  $\lambda$  is the wave length of the X-ray and  $\theta$  is the Bragg angle.

Therefore the average crystallite size of the photocatalyst (N-TiO<sub>2</sub>/WO<sub>3</sub>) was calculated based on Dubye Scherer equation at 2 $\theta$  (degree) value of 25.59 and  $\beta$  (radian) value of 0.0133 and found to be approximately 10.61 nm. As shown in Figure1, throughout the crystal of N-TiO<sub>2</sub>/WO<sub>3</sub> appears to have no other phase other than anatase phase of TiO<sub>2</sub> and the monoclinic phase of WO<sub>3</sub>. There was no particular peak resulted from nitrogen impurity in the composite catalyst (N-TiO<sub>2</sub>/WO<sub>3</sub>). This may be due to the uniform distribution of nitrogen possibly in the form of atom within the as-synthesized material [14].

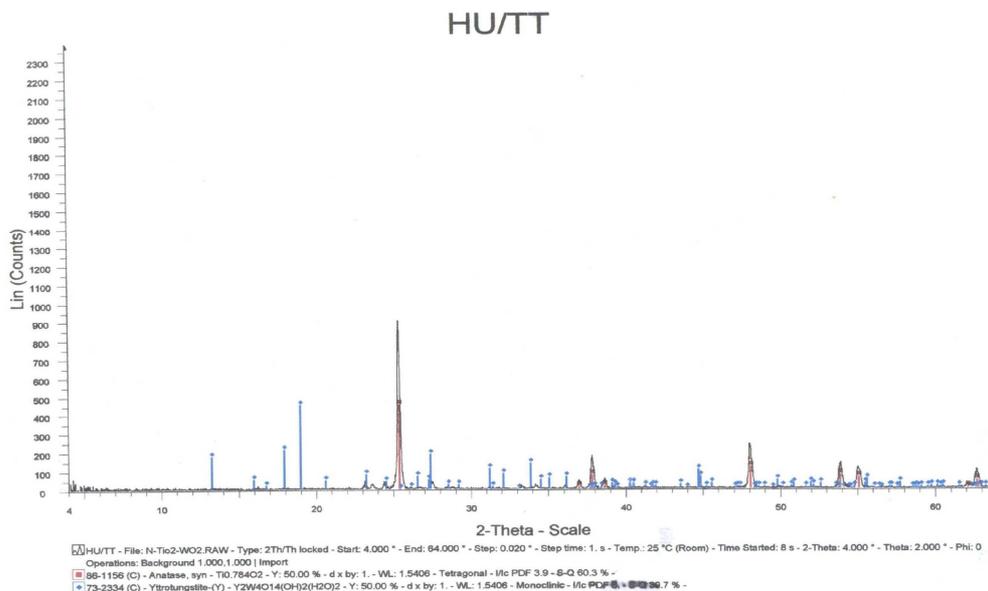


Figure1: XRD pattern of N-TiO<sub>2</sub>/WO<sub>3</sub>

### 3.1.2 UV/VIS DIFFUSE ABSORBANCE

The Uv-Visible diffuse reflectance spectrum of the prepared N-TiO<sub>2</sub>/WO<sub>3</sub> nano-composite material is given in Figure 2. The diffuse absorbance is found to be at  $\lambda$  max of 538 nm and almost similar result was reported. But the UV-Visible diffuse reflectance spectrum of the calcined TiO<sub>2</sub> was reported to be at  $\lambda$  max of 397 nm [9]. From this measurement it can be seen that the absorption edge of N-TiO<sub>2</sub>/WO<sub>3</sub> has shifted to the visible side compared to the non-doped calcined TiO<sub>2</sub>. This indicates that in the Uv-vis diffuse reflectance of NTiO<sub>2</sub>/WO<sub>3</sub>, the absorption edge of the calcined TiO<sub>2</sub> can extend from 397 nm to 538 nm. This may be due to band narrowing of the calcined TiO<sub>2</sub> upon doping N and coupling it with WO<sub>3</sub>.

Accordingly the bang gap energy of the as-synthesized photocatalyst can be calculated by the following equation:  $E_g$  (eV) = 1240/ $\lambda$  Where,  $E_g$  is band gap energy in electron volts and  $\lambda$  is the wavelength (nm) at the intercept of tangent line to the x-axis. Thus from Equation (3.2), the absorption edge of N-TiO<sub>2</sub>/WO<sub>3</sub>, can be calculated and was found to be 2.30 eV.

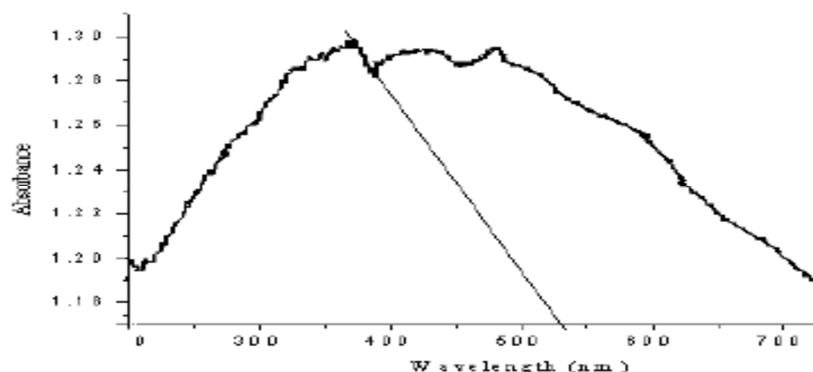


Figure.2. Uv- Visible absorbance of N-TiO<sub>2</sub>/WO<sub>3</sub>

### 3.2 PHOTOCATALYTIC ACTIVITY OF THE PHOTOCATALYST

To test the photocatalytic efficiency of the prepared nano-materials, photocatalytic degradation of PR was carried out both under UV and visible irradiations as well as in dark. The percentage degradation of PR was measured at every 20 minutes interval for over 3 hours. The percent degradation was calculated for each case using the following equation.

**Degradation (%) =  $[A_0 - A_t / A_0] \times 100$**  Where,  $A_0$  is the initial absorbance of the solution,  $A_t$  is the absorbance of the solution at time  $t$  in minutes

#### 3.2.1 COMPARISON OF THE EFFICIENCY OF THE ASSYNTHESIZED PHOTOCATALYSTS UNDER VISIBLE AND UV RADIATIONS

##### EFFECT OF VARYING AMOUNT OF CATALYST ON THE PHOTO-DEGRADATION OF PHENOL RED

Since there are various dyes which are degraded when exposed to direct UV or visible light in a short period of time even without the presence of catalyst, initial investigation ("blank" experiment without addition of any photocatalyst on to the solution of PR) was done in order to determine whether the PR solution is resistant to degradation under UV and Visible irradiation or not. However, insignificant changes were observed for the duration of 180 minutes (< 1%) both under UV and Visible light sources. This showed that the organic compound in the solution was very stable and do not have self-destruct mechanism even if it was irradiated under UV or visible light for 3 hours [15].

Dark experiment has also been done to know the degree of photodegradation of adsorption of PR over the studied photocatalyst under non-irradiation. The result obtained was for photocatalytic degradation of adsorbed PR was only about 6.32%.

The as-synthesized photocatalyst was highly active under visible irradiation (93.87%) than under UV irradiations (75.74%). This may be due to the fact that the absorption edge of the modified TiO<sub>2</sub> particle shifts to visible light range [5]. This may be because of the presence of substitutional Nitrogen atoms in the TiO<sub>2</sub> matrix enhanced the absorption in the visible band and then led to a corresponding photocatalytic activity. This may be due to that nitrogen doping could reduce the band gap of TiO<sub>2</sub> and improve its photocatalytic activity in the visible light region [2].

## 4 CONCLUSION

In this piece of work, a nano-crystalline modified anatase TiO<sub>2</sub> photocatalyst (N-TiO<sub>2</sub>/WO<sub>3</sub>) initiated from commercial TiO<sub>2</sub> has been synthesized in order to have efficient TiO<sub>2</sub> based photocatalyst that works in visible light.

Therefore, it is important to dope catalysts and prepare in composite form in order to harvest solar radiation/visible radiation.

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