Effect of Selected Operating Parameters on the Photocatalytic Efficiency of Nitrogen-Doped TiO₂/WO₃ Nano-Composite Material for Photodegradation of Phenol Red in Aqueous Solution

Tesfaye Teka¹ and Abi Tadesse²

¹Chemistry,
Adigrat University P.O. Box 50, Adigrat, Ethiopia,
Adigrat, Tigray, Ethiopia

²Chemistry, Haramaya University, P.O. Box 138, Dire dawa, Ethiopia, Harer, Hareri, Ethiopia

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ABSTRACT: Crystal form of N-TiO₂/WO₃ Nano-Composite material was prepared from urea, commercial TiO₂ and WO₃ by simple solid phase reaction followed by calcination 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-TiO₂/WO₃ was well extended to visible light. The effect of catalyst loading and initial pH on the photocatalytic efficiency of the sample was tested using phenol red as a target pollutant. The photocatalytic degradation efficiency of the catalyst for the adsorbed phenol red was increased from 61.75-93.87% under visible and 48.01-75.74% under UV as the amount of the catalyst increase from 0.15 to 0.45 gram. Further increase in concentration was found to decrease the degradation efficiency. The photocatalytic degradation efficiency of adsorbed phenol red was increased from 55.88-95.23%, under visible and 44.18 -77.32%, under UV as the pH of the solution decreased from 5 to 3. But further decrease in pH was found to decrease the degradation efficiency. The assynthesized photocatalyst was highly efficient under visible irradiation than under UV irradiations.

KEYWORDS: Advanced oxidation processes, Catalyst loading, Operational-parameters, Photocatalysis, pH of solution.

1 Introduction

Environmental pollution on a global scale 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]. The chemical industries make products with much beneficial usage; however, 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 [20]. 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 [48]. 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

Corresponding Author: Tesfaye Teka

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 [16]. Semiconductors such as TiO2, Fe2O3, ZnO, ZnS and WO3 have been known to possess Photocatalytic character [15]. 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, low cost, inert and non-toxic properties [7]. However, the wide band of TiO2 (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 [26]. 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_2 as photo catalytic materials.

Therefore, doping TiO_2 with some transition-metal elements such as Co and Cu was used as the initial approach to shift the optical response of TiO_2 from the UV band to the visible band [46]. But even these metal-doped TiO_2 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 [2].

In contrast, better visible optical response of TiO_2 could be achieved by using nonmetal doping [24]. Kinds of nonmetal elements, including nitrogen, phosphorus, carbon, chlorine, and bromine were found to be capable of making doped TiO_2 respond to visible light [23]. In particular, the presence of substitutional Nitrogen atoms in the TiO_2 matrix enhanced the absorption in the visible band and then led to a corresponding photocatalytic activity [45]. It is found that nitrogen doping could reduce the band gap of TiO_2 and improve its photocatalytic activity in the visible light region [2].

The efficiency for photocatalytic degradation of pesticides and phenolic compounds is also largely dependent on parameters such as the solution pH, catalyst loading, types of catalyst and composition, organic substrate type and concentration, light intensity and wave length, types of solvent and calcinations temperature [38]. From both application and economic point of view for operational effectiveness of a photocatalyst, the effects of such parameters should be studied.

So, understanding the impacts of various parameters on the photocatalytic degradation efficiency of nitrogen-doped TiO_2/WO_3 nano-composite materials is of paramount importance from the design and the operational points of view. The photocatalytic degradation activity of $NTiO_2/WO_3$ nano-composite materials have been reported (16]. But the effects of operating parameters on the photocatalytic degradation efficiency of $N-TiO_2/WO_3$ nanocomposite Materials have not been reported yet.

Therefore, the proposed project was aimed at studying the impacts of pH and catalyst loading on the photocatalytic efficiency of N-TiO₂/WO₃ nano-composite materials for photodegradation of phenol red in aqueous solution.

2 MATERIALS AND METHODS

2.1 EXPERIMENTAL SITE

The experiments such as synthesis of photocatalyst and the effect of parameters (pH and catalyst loading on the photodegradation efficiency of the samples) 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, Karisruhe, West Germany X-ray defractometre), glass reactor, pH meter (Mettler Tuledo MP220), tungsten lamp (TORCH 40W) as visible light source, Uv lamp (254 nm) as Uv-light source, air (oxygen) pumper, , furnace, centrifuge, magnetic stirrer, and analytical balance.

2.3 CHEMICALS AND REAGENTS

In this study the following chemicals were used: commercial titanium dioxide (TiO_2) (scientific park, N.Y,U.S.A.), tungsten trioxide(WO3) (MW 231.84 gmol-1, SD fine chemicals, 99%), Phenol red ($C_{19}H_{14}O_5S$) (MW. 354.38 g/mol. 1, BLULUX), Ethanol (CH3CH2OH) (MW. 58.03 g mol-1, Park scientific, 99.8), Urea (MW 60.06 gmol-1, extra pure BLULUX)), 0.1M NaOH (MW. 40 g

mol-1 Assay: 98%) and 0.1M H2SO4 (MW. 98.08 g mol-1 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 TIO2

20 g of TiO_2 and 60 g of urea (TiO_2 : 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 [6].

3.4.1.2. Preparation of N-doped TiO2/WO3 Nano-composite Material

10 g of N-TiO₂, which was synthesized in section 3.4.1.1.was mixed with 0.75 g of WO3 using 1:1 (v/v) of water and ethanol as solvent. This mixture was subjected to heating at a temperature of 110oC for drying. After cooling to room temperature, it was subjected to calcinations temperature of 400oC for four hours [6].

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, Karisruhe, West Germany X-ray defractometre. The sample was measured in the angular range (2 Θ) of 40-640 at a scan rate of 0.020 min-1 using Cu K α radiation (λ = 0.154056 nm) operating at 40 kV and 40 mA accelerated voltage and applied current respectively. A Uv-visible spectrophotometer (Gullen kamp 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^2 . 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 λ max of 432 nm for quantitative analysis using different amounts of catalysts and at different 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 assynthesized photocatalysts (N-doped TiO2/WO3 nano-composite material).

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

To evaluate the effect of the amount of catalyst loading on the photocatalytic efficiency of the prepared N-doped TiO2/WO3 nano-composite material on the degradation of phenol red under

UV and visible light; the experiment was carried out by varying the amount of catalyst to be loaded from 0.15-0.65 g. Similar range was taken to study the effect of the amount of catalyst loading on the photocatalytic efficiency of N-TiO₂ for the degradation of methyl orange in waste water [30]. The percentage degradation was calculated and other parameters were kept constant.

2.4.3.2 EFFECT OF VARYING PH OF SOLUTION ON THE PHOTODEGRADATION OF PHENOL RED

Some organic compounds are photocatalytically degraded at lower pH, while others do so at higher pH. Therefore to evaluate the influence of pH of the solution on the photocatalytic efficiency of the as-synthesized N-doped TiO2/WO3 nanocomposite material on the degradation of phenol red under UV and visible light; the experiment was carried out by varying the pH within the range of 2-5.5 and at neutral pH .This pH range was limited by considering the nature of the dye (anionic) and Pzc of the catalyst [4]. Percentage degradation was calculated and other parameters were kept constant.

3 RESULTS AND DISCUSSION

3.1 CHARACTERIZATION OF THE PHOTOCATALYSTS

A fine powder of N-TiO₂/WO₃ 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 25.590 for N-TiO₂/WO₃[2]. There are also minor peaks at around 380, 480, 540 and 550 for the anatase phase. Similar result has been reported by other researchers for N-TiO2 [2]. For WO3 peaks at 130, 180 and 190 are observed.

The XRD pattern of the as-synthesized sample shows only anatase form of TiO_2 and monoclinic form of WO_3 indicating that WO_3 is well incorporated into TiO_2 [19]. As an XRD spectroscopic technique mimic 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 calcination of TiO_2 at 400oC for 4 hrs leads to the formation of anatase which is tetragonal [19]. As can be confirmed from the XRD spectra of the sample, the incorporation of the impurities into the crystal lattice of TiO_2 doesn't alter its crystal structure. The average crystallite size of the as-synthesized catalyst was estimated using Dubye Scherere equation which is given as:

$d = \kappa \lambda / \beta \cos \theta (3.1)$

Where, d is crystallite size in nanometer K is shape factor constant, which is 0.9, β is the full width at half maximum in radians, λ is the wave length of the X-ray and Θ is the Bragg angle.

Therefore the average crystallite size of the photocatalyst $(N-TiO_2/WO_3)$ was calculated based on Dubye Scherer equation at 20 (degree) value of 25.59 and β (radian) value of 0.0133 and found to be approximately 10.61 nm. As shown in Figure 1, throughout the crystal of $N-TiO_2/WO_3$ appears to have no other phase other than anatase phase of TiO_2 and the monoclinic phase of WO_3 . There was no particular peak resulted from nitrogen impurity in the composite catalyst ($N-TiO_2/WO_3$). This may be due to the uniform distribution of nitrogen possibly in the form of atom within the as-synthesized material [22].

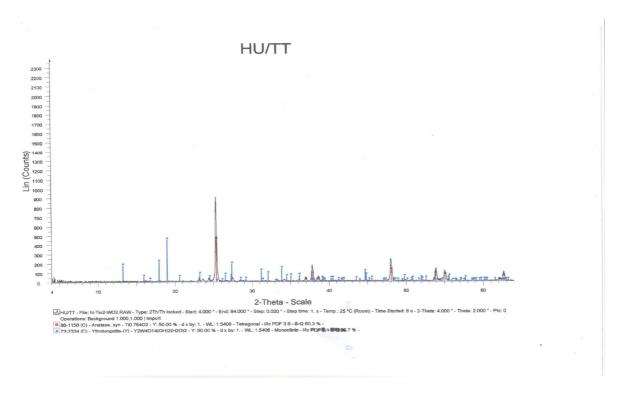


Figure 1: XRD pattern of N-TiO₂/WO₃

3.1.2 UV/VIS DIFFUSE ABSORBANCE

The Uv–Visible diffuse reflectance spectrum of the prepared N-TiO2/WO3 nano-composite material is given in Figure 2. The diffuse absorbance is found to be at λ max of 538 nm and almost similar result was reported [19]. But the UV–Visible diffuse reflectance spectrum of the calcined TiO2 was reported to be at λ max of 397 nm [19]. From this measurement it can be seen that the absorption edge of N-TiO2/WO3 has shifted to the visible side compared to the non-doped calcined TiO2. This indicates that in the Uv-vis diffuse reflectance of NTiO2/WO3, the absorption edge of the calcined TiO2 can extend from 397 nm to 538 nm. This may be due to band narrowing of the calcined TiO2 upon doping N and coupling it with WO3.

Accordingly the bang gap energy of the as-synthesized photocatalyst can be calculated by the following equation:

Eg (eV) =
$$1240/\lambda$$
 (3.2)

Where, Eg is band gap energy in electron volts and λ is the wavelength (nm) at the intercept of tangent line to the x-axis. Thus from Equation (3.2), the absorption edge of N-TiO₂/WO₃, can be calculated and was found to be 2.30 eV.

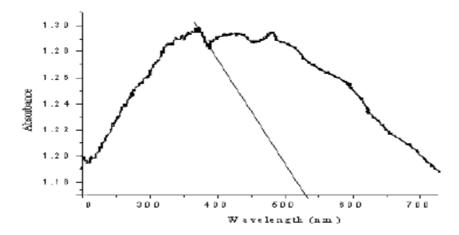


Figure.2. Uv- Visible absorbance of N-TiO₂/WO₃

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 (%) = $[A_0-A_t/A_o] \times 100$ (3.3) Where, A_o is the initial absorbance of the solution, A_t is the absorbance of the solution at time t in minutes

3.2.1 EFFECT OF OPERATING PARAMETERS

The amount of catalyst loading and pH value are among the major factors which influences the efficiency of degradation of PR [47]. For this reason the experiments were carried out to find optimum pH value and catalyst loading of the reaction mixture for the degradation of PR.

3.2.1.1 EFFECT OF CATALYST LOADING

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 [18]. 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 is given in the following Table1a with its respective figure3a

Table 1a.Percentage adsorption of PR under dark for different amount of N-doped TiO₂/WO₃

| Amount of catalyst (gram) | % adsorption of PR ± |
|---------------------------|----------------------|
| 0.15 | 2.14 |
| 0.25 | 3.87 |
| 0.35 | 4.65 |
| 0.45 | 6.32 |
| 0.55 | 5.20 |
| 0.65 | 3.01 |

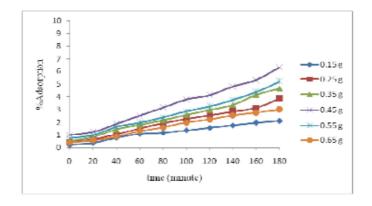


Figure 3 Percentage adsorption of PR under dark for different amount of N-doped TiO2/WO3

The results obtained for photocatalytic degradation of adsorbed PR under visible and UV irradiations are given in the following Table1b with their respective Figures3b and 3c

Table 2b. Percentage degradation of PR under Vis and UV irradiations for different amount of N-doped TiO2/WO3

| A C(gram) | % degradation of PR ± | |
|-----------|-----------------------|-------|
| | Vis | Uv |
| 0.15 | 61.75 | 48.01 |
| 0.25 | 78.88 | 57.21 |
| 0.35 | 85.33 | 66.05 |
| 0.45 | 93.87 | 75.74 |
| 0.55 | 89.23 | 70.21 |
| 0.65 | 71.89 | 51.89 |

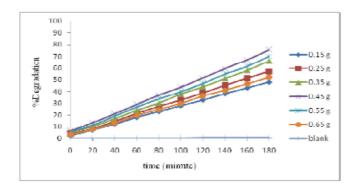


Figure 4. Percentage degradation of PR under UV irradiations for different amount of N-doped TiO₂/WO₃

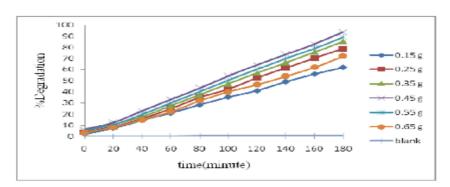


Fig3c. Percentage degradation of PR under visible irradiation for different amount of N-doped TiO2/WO3

The as-synthesized photocatalyst was highly active under visible irradiation than under UV irradiations. This may be due to the fact that the absorption edge of the modified TiO_2 particle shifts to visible light range [12].

The degradation efficiency of the as-synthesized catalyst increases with increasing the catalyst loading from 0.15 g - 0.45 g as shown in table1b above. But further increase up to 0.65 g was found to decrease the photocatalytic efficiency. Such patterned results have been reported from previous studies for different TiO2 based photocatalysts [13]. This observation can be explained by the photocatalyst optical properties as the main cause for the differences. Indeed, the total active surface area increased with increasing catalyst dosage, because of the penetration of UV and visible light into the suspension, which in turn increases the number of hydroxyl and superoxide radicals [27]

As can be seen from the above Tables1b the efficiency of degradation of the catalyst for the adsorbed PR increases from 48.01 to 75.74% under UV and from 61.75 to 93.87% under visible as the amount of the catalyst increase from 0.15 to 0.45 gram. Similar patterns have been reported for $Fe^{3+}TiO_2$ [32]. But since the intervals are mostly independent, direct comparison cannot be made between similar catalysts as the type (geometry) and size of the photoreactor, working condition, intensity, and wave length and incident radiation flux are different [11]. Any further increase of the catalyst concentration beyond 0.45g was resulted in decrease in efficiency. This phenomenon can be explained by the light scattering

caused by the light proof catalysts, indeed with increasing catalyst loading the light penetration through the solution and hence the photoactivated volume of the suspension shrinks [14]. In such condition part of the catalyst surface probably becomes unavailable for photon absorption and dye adsorption, thus, this may bring little stimulation to the catalytic degradation. When the amount of TiO₂ increases above a saturation level this can lead to high turbidity state and as a consequence the light photon absorption coefficient will decrease radically [12].

Therefore, when the concentration of N-doped TiO2/WO3 catalyst increases above 0.45 g/250 ml the degradation efficiency seems to reach equilibrium value and decreases slightly. The photodegradation efficiency of PR for different concentration of the as-synthesized composite (N-doped TiO2/WO3) under UV, visible and dark reactions are shown in Figures 3a, 3b and 3c respectively. These figures shows that, under dark and both UV and visible light source, the degradation efficiency of the catalyst increase as the concentration increases from 0.15 g to 0.45g and then decreases on further increase in concentration.

3.2.1.2 EFFECT OF INITIAL PH

In order to determine whether the PR solution is resistant to degradation under basic or acidic media, an experiment was performed at neutral pH and the result was found to be 22.6%under visible and 18.87% under UV. Dark experiment was also done to know the degree of photodegradation of adsorption of PR over the studied photocatalyst under non-irradiation, but in different pH values keeping the other parameters constant. Figure 4a represents the results obtained during photodegradation of adsorption of PR over the studied photocatalyst under non irradiation (dark) at different pH values. The results are given in the following Table2a.

Table 3a. Percentage adsorption of PR dark for different values of pH

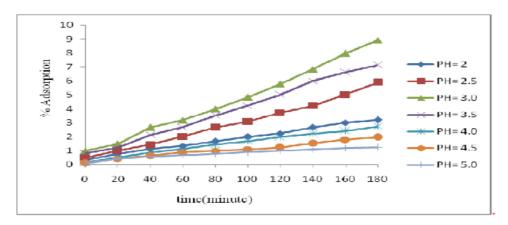


Figure 5. Percentage adsorption of PR under dark for different values of pH

The results for photocatalytic degradation of adsorbed PR under visible and UV irradiations are also given in the following Table2b with their corresponding Figures 4b and c

Table 4b. Percentage degradation of PR under Vis and UV irradiations for different values of pH

| pH value | % degradation of PR ± | |
|----------|-----------------------|-------|
| | Vis | Uv |
| 2 | 82.21 | 62.73 |
| 2.5 | 88.02 | 69.86 |
| 3 | 95.23 | 77.32 |
| 3.5 | 85 | 66 |
| 4 | 78.51 | 53.44 |
| 4.5 | 65.45 | 48.7 |

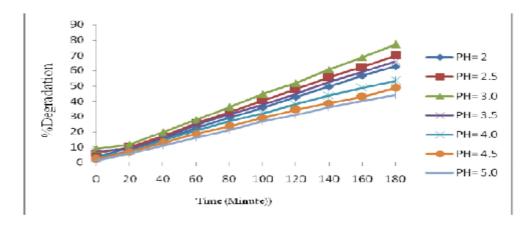


Figure 6. Percentage degradation of PR under UV irradiation for different values of pH

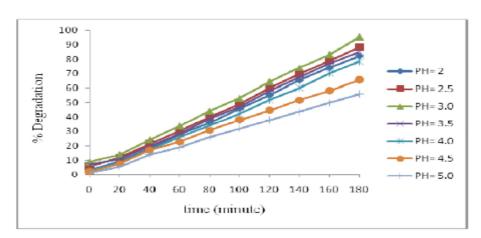


Figure 7Percentage degradation of PR under visible irradiation for different values of pH

Again the as-synthesized photocatalyst is highly active under visible irradiation than under UV irradiations. This may be due to the fact that the absorption edge of modified TiO2 shifts to visible light ranges [12]. The results shows that degradation efficiency is inversely proportional to pH i.e. degradation efficiency increases with decreasing the pH in each case but up to a certain value and such patterned results have been reported with previous studies for different TiO2 based catalysts [13]. The possible explanation for this result is that the amphoteric behavior of the semiconducting catalyst N-TiO2/WO3 and the change of surface charge properties of catalyst with change of pH value [4] around its Pzc according to the following reactions:

TiOH + H+ \leftrightarrow TiOH2 $^+$ where pH < pHpzc

 $TiOH + OH^{-} \longleftrightarrow TiO- +H_2O$ where pH >pHpzc

The point of zero charge of the catalyst was reported to be between 5 to 6.25 [54]

So when pH < 6.25 (acidic) the surfaces of the nano-sized N-TiO2/WO3 particles are positively charged, so strong adsorption of the anionic PR on to the N-TiO2/WO3 particles is observed as a result of the electrostatic attraction of the positively charged surface of the N-TiO2/WO3 catalyst with the anionic PR. In this experiment the highest degradation efficiency was observed at pH = 3. Similar results for N-doped TiO2 nano-particles were found, i.e. degradation efficiency increases as the pH decreased from 5.0 to 3 [38]. Further decrease in pH up to 2.0 affected the photocatalytic activity of the catalyst negatively. The reason given for the adverse effect of low pH on the photocatalyst performance is that the possible increase of H+ concentration may cause dissolution [3] and thereby reduces the crystal size of the prepared N-TiO2/WO3 nano-particles. Again at higher pH value, the hydroxyl radicals are so rapidly scavenged that they do not have the opportunity to react with N-TiO2/WO3 [42].

On the other hand, when the pH of the solution is greater than 6.25 the surfaces of nano-sized NTiO2/WO3 particles are negatively charged so the adsorption of PR molecules which are negatively charged is expected to be scarcely adsorbed. This may be due to columbic repulsion between the two negative surfaces and as a result the efficiency of degradation is lower [42]. But when pH = Pzc of the catalyst the interaction between the photocatalyst particles and PR is minimum due to the absence of any electrostatic force as a result the degradation is not efficient. Therefore the photocatalytic activity of anionic dyes such as PR mainly sulphonated dyes reached max in acidic condition followed by decrease in pH [42].

4 CONCLUSION

In this piece of work, a nano-crystalline modified anatase TiO₂ photocatalyst (N-TiO₂/WO3) initiated from commercial TiO₂ has been synthesized in order to have efficient TiO₂ based photocatalyst that works in visible light.

The effects of some selected operating parameters (effect of initial pH and effect catalyst loading) have been studied under visible, UV and dark. It was found that catalyst loading was directly proportional to the efficiency of degradation of the organic dye but up to a certain optimum value (0.45g/250ml) while pH was inversely related to the degradation efficiency for the prepared catalyst up to a fixed optimum pH value (pH = 3).

Therefore, optimizing the various operational parameters is of paramount importance from the design and the operational points of view as these could affect the degree of degradation efficiency of catalysts.

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REFERENCES

- [1] Anpo, M., 2004. Applications of titanium oxide photocatalysts and unique second-generation TiO2 photocatalysts able to operate under visible light irradiation for the reduction of environmental toxins on a global scale, *studies in surface science and catalysis*,130: 157–166,
- [2] Asahi, R., T. Morikawa, T. Ohwaki, K. Aoki, and Y. Taga, 2001. Visible-light photocatalysis in nitrogen-doped titanium oxides, *Science*, 293: 269–271.
- [3] Bahajady, M.A, N. Modrishahla and R. Hamzavi,2006.Kinetic study on photocatalytic degradation of C.I acid yellow 23 by Zno photocatalyst *.j.hazared. mater.B.* 133:226-232
- [4] Bahnemann, D.W., J. Cunningham, M.A. Fox, E. Pelizzetti, P. Pichat, N. Serpone, in: R.G. Zepp, G.R. Heltz, and D.G. Crosby 1994. Aquatic Surface Photochemistry, *Lewis Publishers*, *Boca Raton*, 261.
- [5] Baran, W., A. Makowski, and W. Wardas, 2008. The effect of UV radiation absorption of cationic and anionic dye solutions on their photocatalytic degradation in the presence of TiO₂, Dyes Pigm. 76: 226–230.

- [6] Beata Wawrzyniak, AntoniWaldemar Morawski, and Beata Tryba, 2006. Preparation of TiO2- Nitrogen-Doped Photocatalyst Active under Visible Light. *Inter. J. of Photoenergy*. 23:1-8.
- [7] Burda .C., Y. Lou, X. Chen, A. C. S. Samia, J. Stout, and J. L. Gole, 2003, Enhanced nitrogen dopingin TiO2 nanoparticles, *Nano Letters*, 3 (8): 1049–1051.
- [8] Cao, Y., H. Tan, T. Shi, T. Tang, and J. Li., 2008. Preparation of Ag-doped TiO2 nano particles of photocatalytic degradation of acetamiprid inn water. *J. Chem. Technol. Biotechnol.* 83,546-552
- [9] Carp.O, Huisman.C, and Reller, 2004. Photoinduced reactivity of titanium dioxide; progress in solid state chemistry. *J.hazardeous materials*. 32:171-177.
- [10] Chakrabarti, S. and B.K. Dutta, 2004, Photocatalytic degradation of model textile dyes in wastewater using ZnO as semiconductor catalyst, J. *Hazard. Mater.* B112, 269–278.
- [11] Chen D and A.K Ray., 1999. photocatalytic kinetics of phenol and its derivatives over uv and vivisible irradiated TiO2 *appl. Catal.B. Environ*. 23: 143-157.
- [12] Chen,J., D.,Wang, M Zhu, and C Gao,.,2007.Photocatalytic degradation of dimethoate using nanosized TiO2 powder. Desalination 207:87–94
- [13] Daneshvar, N., D., Salari, ,A., Niaei and A.R Khataee,.,2006. Photocatalytic degradation of the herbicide erioglaucine in the presence of nanosized titanium dioxide: Comparison and modeling of reaction kinetics. *Journal of Environmental Science and Health Part B*, 41:1273–1290
- [14] Epling G.A. and Lin C., 2002, Photo assisted bleaching of dyes utilizing TiO2 and visible light. Chemosphere 46:561-570)
- [15] Fox, M.A.and M.T.Dulay,1993, Heterogeneous photocatalysis. Chemical Reviews 93:341-357
- [16] Funda S., E.Sema, and A. Meltem., 2006, Photocatalytic performance of pure anatase nanocrystallite TiO2 synthesized under low temperature hydrothermal conditions, *Materials ResearchBulletin*,. 41 (12): 2276–2285.
- [17] Gaya, U.I. and A.H. Abdullah, 2008. Heterogeneous photocatalytic degradation of organic contaminants over titanium dioxide: a review of fundamentals, progress and problems, *J. Photochem. Photobiol. C: Photochem. Rev.* 9: 1–12.
- [18] Hay.J, W. Khan, and J.K.,Sugden, 1994. Photochemical decomposition of Phenol Red Phenol sulphonphtalein, *Dye and Pigments*, 24:305-312
- [19] Hayelom Hiluf,2011. synthesis and chracterization of N-doped TiO2/WO3 materials for photodegradation of phenol red in aqueous solution. M.Sc theis
- [20] Hoffmann,M., R., and S.T.Martin,1995. Environmental applications of semiconductor photocatalysis. *Journal Chemical Reviews* 95(1): 69-96
- [21] Hsien Yu-Hsiang, Chi-Fu Chang, Yu-Huang Chen, and Soofin Cheng, 2001. Photodegradation of aromatic pollutants in water over TiO2 supported on molecular sieves. *Applied Catalysis B: Environmental. 31: 241–249.*
- [22] Huang, M., C. Xu, Z. Wu, Y. Huang, J. Lin, and J. Wu, 2003. Photocatalytic dicolorization of organic dyes
- [23] Ihara T., M. Miyoshi, Y. Iriyama, O. Matsumoto, and S. Sugihara. 2003. Visible-light-active titanium oxide photo catalyst realized by an oxygen-deficient structure and by nitrogen doping, *Applied Catalysis B*, 42(4):403–409
- [24] Irie H.,Y.Watanabe, and K. Hashimoto, 2003.Nitrogen concentration dependence on photocatalytic activity of TiO2-xNx powders. *Journal of Physical Chemistry B*,. 107: 23, 5483–5486,
- [25] Keith L. H .and W. A. Telliard, 1979. Priority pollutants. I. A perspective view," *Environmental Science and Technology*, 13(4): 416–423,
- [26] Kisch H., E.A. Konstantinova, A.I. Kokorin, and K. Lips, 2003. C- and N-Doped TiO2: Visible Light Photocatalysis and EPR Investigation. *Institute of Chemical Physics*. 43: 126-128.
- [27] Konstantinou, I.K, and T.A. Albanis, 2004. TiO2-assisted photocatalytic degradation of azo dyes in aqueous solution: kinetic and mechanistic investigations—A *review, Appl. Catal.* B:Environ. 49:1–14.
- [28] Li D., H Haneda., S. Hishita., and Ohashi, 2005. Visible-light driven N-F-codoped TiO2 photocatalyst. Optical characterization, photocatalysis, and application to air purification. *Chemistry of materials*. 17:2596-2602
- [29] Lin, J., Yun-Yue, Tsung-Hung Chu, Shao-Sian Li, Chia-Hao Chuang, Chia-Hao Chang, Wei- Fang Su, Ching- Pin Chang, Ming-Wen Chu, and Chun-Wei Chen, 2007. Interfacial Nanostructuring on the Performance of Polymer/TiO₂ Nanorod Bulk Heterojunction Solar *Cells.Journal of the American chemical society.* 131:3644-364.
- [30] Liu, S.J., H. Yang, and J.-H. Choy, 2006. Microporous SiO2-TiO2 nanosols pillared montmorillonite for photocatalytic decomposition of methyl orange, *J. Photochem. Photobiol*. A: Chem. 179: 75–80.
- [31] Maria.D, H Alonso, S Frenso, M. FSuarez.and J Coronado., 2009. Development of alternative photocatalysis to TiO₂: Challenges and opportunities; *Energy Enviro.Sci.* 45:98-102
- [32] Nahar, M.S., K Hasegawa and S Kagaya, 2006. Photocatalytic degradation of phenol by visible light responsive iron-doped TiO2 and spontaneous sedimentation of the TiO2 particles. *Chemosphere* 65,1976-1983
- [33] Ni, M., M. K. H. Leung, D. Y. C. Leung, and K. Sumathy, 2007. A review and recent developments in photocatalytic water-splitting using TiO2 for hydrogen production. *Renew. Sustain. Ener. Rev.* 11: 401-425.

- [34] Obare S.O. and Meyer G.J., 2004. Nano-structured materials for environmental remediation of organic contaminants in water. *J. Environ. Sci. Health A.* 39: 2549–2582.
- [35] Ohno, T., T.Mitsui, and M.Matsumura, 2003. Photocatalytic activity of S-doped TiO2 photocatalyst under visible light. *Chemistry letters*. 32:363-369.
- [36] Radim and Beránek, 2007. Photoelectrochemistry with Surface-Modified TiO₂.J.hazardeous materials.32:56-59
- [37] Radwan A. Al-Rasheed 2005. Water treatment by heterogeneous photocatalysis an overview1Saline Water Desalination Research Institute Saline Water Conversion Corporation Al-Jubail 31951, Saudi Arabia Jeddah,
- [38] Sakthivel S., M.Janczarek, and H.Kisch, 2004. Visible light activity and photo electrochemical properties of nitrogen-doped TiO2. *Journal of physical chemistry*. 108:19384-19387
- [39] Sathish M., B.Viswanathan, R.P.Viswanath and C. S.Gopinath, 2005. A simple method to synthesize visible light active N-doped anatase TiO2 Photocatalyst. *Chem. Mater.* 17: 6349
- [40] Shaktivel,S., B.Neppolian, M.V Shankar, B Arabindo, M Palanicham ,and V Murugesan,2003. Solar photocatalytic degradation of azo dye: comparison of photocatalytic efficiency of ZnO and TiO2. *Solar Energy Materials Solar Cell* 77:65-82
- [41] Sun, J., L. Qiao, S. Sun and G. Wang, 2008. Photocatalytic degradation of Orange G on nitrogen-doped TiO2 catalysts under visible light and sunlight irradiation, J. Hazard. Mater. 155: 312–319
- [42] Tang W.Z, Z. Zhang, , H. An, M.O. Quintana and D.F. Torres. 1997. TiO2/uv photodegradation of azo dyes in aqueous solution. *Environmental technology*, 18. 1-12).
- [43] Topoglidis E., A. E. G. Cass, B. O'Regan and J. R. Durrant, 2001. Immobilisation and Bioelectrochemistry of Proteins on Nanoporous TiO2 and ZnO Films," *Journal of Electro analytical Chemistry*, 517: 20-27.
- [44] Tunesi,S.,and M. Anderson,1991. Influence of chemisorption on the photodecomposition of salicylic acid and related compounds using suspended titania ceramic membranes, *J. Phys. Chem.* 95: 3399–3405.
- [45] Valentin, Di, G. Pacchioni, and A. Selloni, 2004. "Origin of the different photoactivity of Ndoped anatase and rutile TiO2," *Physical Review B*, (I) 70, 8, 4
- [46] Wang, D. W. Bahnemann, and J. K. Dohrmann, 2000. A novel preparation of iron-doped TiO2 nanoparticles with enhanced photocatalytic activity, *Chemical Communications*, 16:1539–1540
- [47] Wang. Y 2000. Solar photocatalytiic degradation of eight commercial dyes in TiO2 suspension wat Res 34(3): 990-994
- [48] Xing, W. and H. H. Ngo 2008. Physico-Chemical Processes for Landfill
- [49] Yang H, K.Zhang, R.Shi, X.Li, X.Dong and Y.Yu ,2006. Sol–gel synthesis of TiO2 nanoparticles and photocatalytic degradation of methyl orange in aqueous TiO2 suspensions. *J. Alloys Compd.*413: 302–306.
- [50] Yu, H., X. Zheng, Z. Yin, F. Tao, B. Fang and K. Hou., 2007. Preparation of nitrogen-doped TiO2 nanoparticle catalyst and its catalytic activity under visible light, Chin. *J.Chem. Eng.* 15 (6) 802–807
- [51] Zaggout, F.R, 2006. Entrapment of phenol red pH indicator into a sol-gel matrix, Mater. Lett., 60: 1026-1030
- [52] Zhu,X., Yuan,C., Bao,Y., Yang,J. and Wu,Y.,2005. Photocatalytic degradation of pesticide pyridaben on TiO2 particles. Journal of Molecular Catalysis: Chemical 229:95-105