Effect of selected operating parameters on the photocatalytic efficiency of doped and undoped TiO2 for photodegradation of Methylene Blue in textile industry

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***Abstract* - Nowadays, photocatalytic mechanism of water purification using nanoparticles has gained wider acceptance. For this purpose, Crystal form of TiO_2 and N- TiO_2 was prepared from $TiCl_4$, Urea, NH_4OH by sol-gel method and simple solid phase reaction followed by calcinations at a temperature of 400 °C for 4h at each. The synthesized photocatalysts were characterized using XRD, FT-IR, SEM and Uv-Visible diffuse reflectance spectra. In the experiment, it was found that the absorption edge of N-TiO_2, were well efficient shift to visible light as compared to TiO_2. The PD efficiency of the catalysts for MB was increased from 24.52 to 46.0% and 57.05 to 96.02% under solar radiation as the amount of the catalyst increase from 0.15 to 0.45 gram for TiO_2 and N-TiO_2, respectively. In addition, the PD efficiency of the catalysts for removal of MB was increased from 35 to 52.04 and 57.00 to 97.00 under solar radiation as the calcination temperature of the catalyst increase from 300 to 500 at all. However, Additional increase in catalyst loading and calcination temperature was found to decrease the degradation efficiency.**

***Index Terms* - Degradation, nanoparticles, catalyst loading, calcination and methylene blue**

I. INTRODUCTION

The quality of water resources will directly affect the life. Environmental pollution, especially contamination of natural water by organic pollutants is one of the largest problems in modern society such as organic dyes, which are released from paper, dyeing process, pesticides, textile and other industrial process [1].

Dyes in waste-water are not readily degradable and are not easily removed from water by conventional chemical treatment systems. There are various industrial wastewater treatment techniques, specifically physical, chemical and biological treatment and activated carbon adsorption techniques [2]. Photocatalysis is among the fast developing and efficient technologies for purification of water, air and soil. With this approach, harmful organic compounds are broken down in the presence of catalyst and UV irradiation without producing secondary harmful pollutants.

Many attentions have been paid to the heterogeneous photocatalysis for pollution treatment over the last several decades. Such as transition metal oxides or sulphides semiconductors TiO_2, ZnO, WO_3, ZnS, Fe_2O_3, MgO and CdS are common [3]. Among the photocatalysts, TiO_2 considered as the most suitable one at present for photodegradation. Some properties of TiO_2 are, highly photo-active, remarkably stable and inexpensive. This made it as the most promising photocatalytic chemical which can be used in water purification [4]. However, due to the large band gap in TiO_2 and inefficient use of the photo generated electron hole pairs, the photocatalytic efficiency is not optimal. In order to have a practical application, the use of visible light source along with enhanced photodegradation rate is essential. This can be achieved via modification of semiconductors, addition of transition metals and other doping elements and use of coupled semiconductors [5]. In contrast, better visible optical response of TiO_2 could be achieved by using non-metal doping [6]. Then, the PD of MB using TiO_2 and N-TiO_2 nanoparticles with the effect of operating parameters has not been reported yet.

Therefore, the research project was aimed to enhance the photocatalytic efficiency of TiO_2 by doping it with Nitrogen and the impacts of catalyst loading and calcinations temperature with PD of MB under solar radiation.

Abbreviations

PD- photocatalytic degradation
MB- methylene blue
UV-ultraviolet

II. MATERIALS AND METHODS

2.1 EXPERIMENTAL SITE

The synthesis of photocatalysts, and photodegradation efficiency of the samples was carried out at Mekelle University department of chemistry laboratory.

2.2. EQUIPMENT AND APPARATUS

The equipment and apparatus used in this study were: X-ray diffraction (Bruker D8 Advance XRD, AXS GMBH, Karisruhe, West Germany X-ray diffractometer), UV/vis spectrophotometer (Gullen kamp model SP 62), FT-IR, SEM and apparatus including pH meter, beakers, fume hood, test tubes, furnace, oven, centrifuge, ice water bath, magnetic stirrer and analytical balance.

2.3. CHEMICALS AND REAGENTS

In this study the following chemicals were used: $TiCl_4$ (scientific park, N.Y, U.S.A., SD chemicals, 99.9%), $C_{16}H_{18}N_3SCl$ (MW 319.50 g/mol, BLULUX, 98%), (CH_3CH_2OH (MW. 58.03 $gmol^{-1}$, Park scientific, 99.8%), NH_2CONH_2 (MW 60.06 $gmol^{-1}$, extra pure BLULUX), and NH_4OH(MW 17.03 $gmol^{-1}$, Assay: 98%). All were analytical grade with no further purification.

2.4. EXPERIMENTAL METHODS

2.4.1. PREPARATION OF PHOTOCATALYSTS

2. 4. 1.1 PREPARATION OF TiO_2

3.5 ml of $TiCl_4$ was added to 50 ml deionized water and addition of 35 ml of ethanol with vigorous stirred for 30 minutes at room temperature. Drops of 25 % of ammonium hydroxide was added wisely into the solution. After stirring vigorously, the solution was made to settle for 12h. Then, the obtained precipitate was washed with deionized water. Then, the precipitate was dried at 200 °C for 4 h and finally amorphous TiO_2 was obtained. The amorphous TiO_2 was calcined at 400 ^oC for 4h [7].

2. 4. 1.2 PREPARATION OF N-DOPED TiO_2

25 g of TiO_2 and 75 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 400^oC for 4 h for solid phase reaction [8].

III. CHARACTERIZATION METHODS

The as-synthesized composite photocatalyst was characterized using SEM, 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 diffractometer. The sample was measured in the angular range (2Ө) of 10-80^0 at a scan rate of 0.020 min^{-1} using Cu Kα radiation (λ = 0.154056 nm) operating at 40 kV and 30 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.

3.1 PHOTOCATALYTIC DEGRADATION EXPERIMENT OF MB

PD of MB was carried out in 500 ml beaker. A known amount of the synthesized photocatalyst and 250 ml of MB (50ppm) solution was taken in a beaker. The suspension stirred in dark for 1h. Measured adsorption equilibrium before the solar radiation. Then 10 ml of the sample was withdrawn at 20minuts time interval over radiation time for 3h. The suspension was centrifuged and filtered to remove the catalyst particles before measuring absorbance. The absorbance of the clear solution was measured at different concentration of catalysts and different calcination temperature. To check whether the MB is easily degradable or not blank experiment (without addition of any catalyst) has also been done. PD experiment was conducted using the synthesized photocatalysts. Percentage degradation of MB was calculated using the following equation [9].

$$\%\text{Degradation methylene blue} = \frac{(C_o - C_t)}{} \times 100 \quad (1)$$

C_o is the initial concentration of pollutant; C_t is the concentration of MB at time t in minutes.

IV. RESULTS AND DISCUSSION

4.1.2. X-ray Diffraction (XRD) Analysis

The XRD patterns of the synthesized nanoparticle samples shows only anatase form of TiO_2 and the N-TiO_2. The average crystallite sizes of the as-synthesized 10.2 and 12.7nm for N-TiO_2 and TiO_2 powders. There was no any peaks resulted from nitrogen impurity in all cases (N-TiO_2) showing that nitrogen in the form of atom is uniformly distributed.

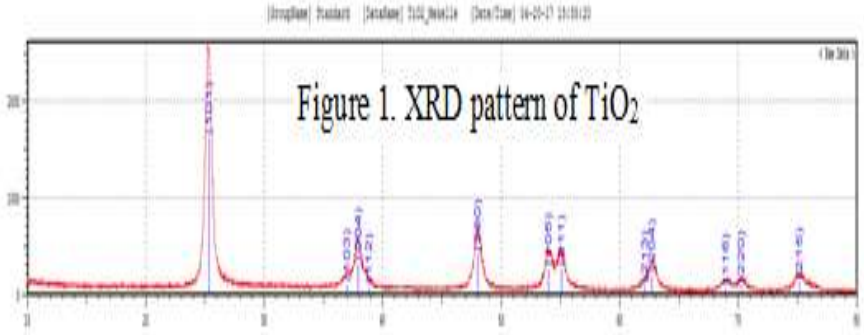
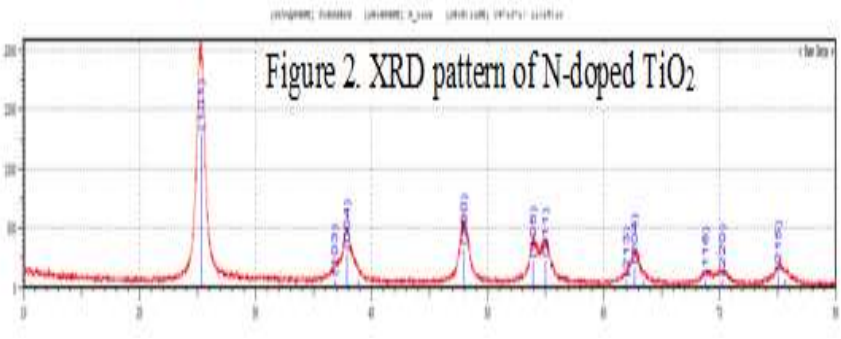
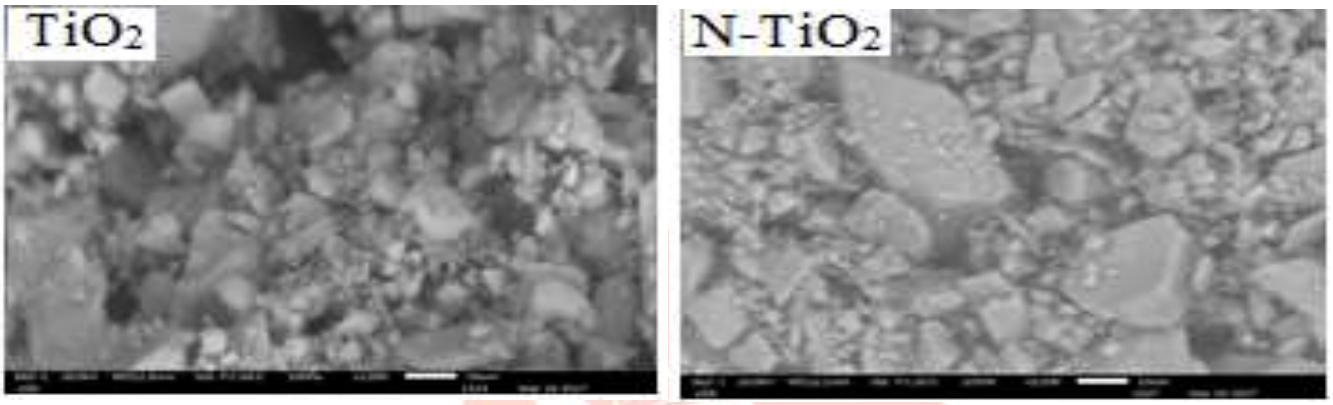


Figure 1. XRD pattern of TiO_2



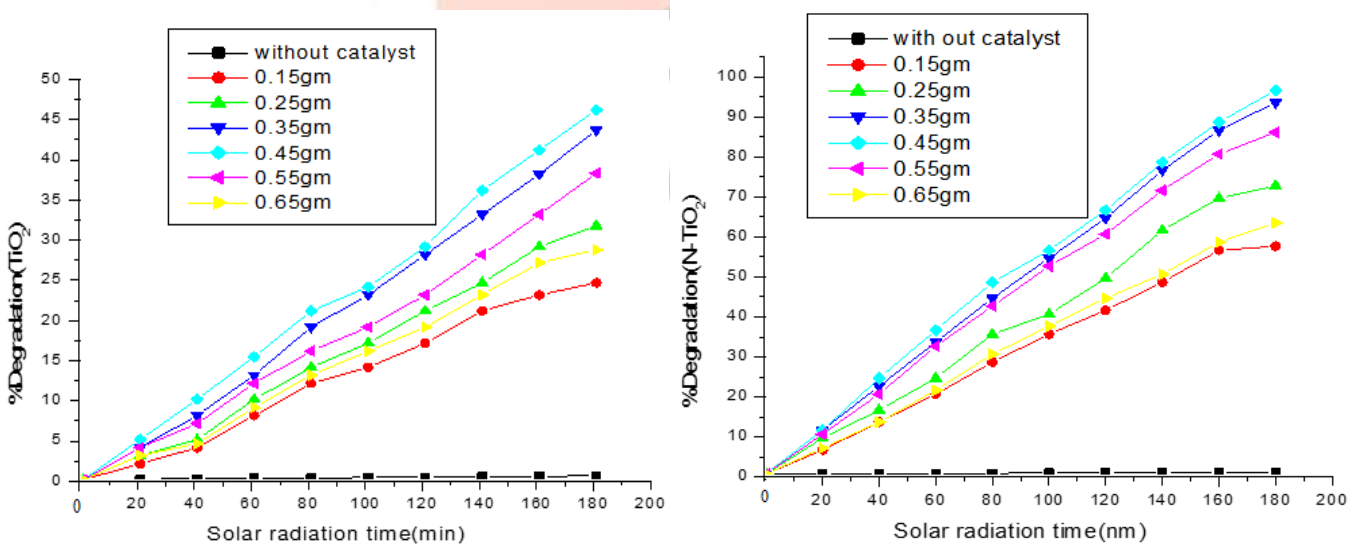
4.1.3. Scanning Electron Microscope (SEM)

Scanning electron microscope is a type of electron microscope that produces images on generated photons. The SEM images of N-TiO_2 sample show that the distribution of nitrogen on the surface of TiO_2 is uniform and the N-TiO_2 catalyst contains regular shaped crystal particles and the particle size was TiO_2 tetragonal. Thus, the crystallographic shape of N-TiO_2 is tetragonal.



4.2. Effect of catalyst loading

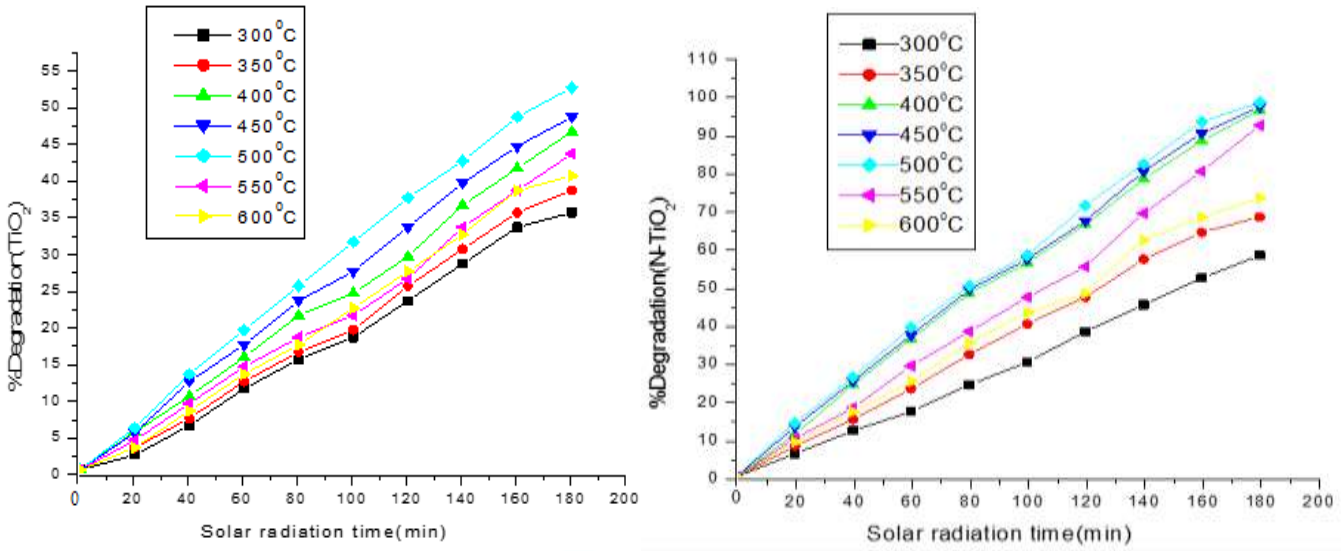
A series of experiments were conducted to study the effect of catalyst dosage on the degradation of MB and to get optimum catalyst loading by varying from 0.15 to 0.65gram. Nevertheless, insignificant changes were observed for the duration of 180 minutes under solar radiation and "blank" experiment without addition of any photocatalyst on to the solution of MB was done in order to determine whether the MB solution is resistant to degradation under solar radiation or not.



The effect of catalyst dosage TiO_2 and N-TiO_2 was observed and that the degradation efficiency increase with the increase in the amount of catalysts up to a certain level and then starts to decrease the efficiency with a further increase in the catalyst amount. Certainly, 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. Therefore, N- doped TiO_2 catalyst was more efficiently than the undoped TiO_2.

4.3. Effects of calcination temperature

The photocatalytic activity of the prepared nano-materials calcined at different temperatures. The concentration of $TiO_{2\ and}$ N-TiO_2 catalysts 0.45 g/250 ml at MB (50 ppt) was taken.



The photocatalytic activity of TiO_2, increased from 35.00 to 52.02 % with further increase calcination temperature from 300 to 500 ºC. But, further increase calcination temperature from 500 to 600 ºC the photocatalytic activity was decreased from 52 to 40 %. The removal efficiencies of MB by pure TiO_2 under solar radiation were low. At 500 ºC, it reached the optimal, because of complete crystallization of anatase at this temperature. The catalytic activity of the N- TiO_2 increased from 57 to 97 %, with increase

calcination temperature from 300 to 500 ºC. But, further increase calcination temperature from 500 up to 600 ºC the catalytic a ctivity of the catalyst was decreased to 73 %. The better efficiency was record at 500 ºC. High calcination temperature (above the optimal) produced low specific surface area, large particle size, and low crystallinity phase of the agglomerated doped-TiO_2. Subsequently, the less active site eventually lowers the photocatalytic activity of TiO_2. The energy of solar light is lower than the band gap energy of TiO_2, photoreactions and reactive oxidizing species could not be activated and produced [16].

V. CONCLUSION

In this pieces of work, the as-synthesized powder was characterized using XRD and SEM. The XRD diffraction was used to estimate particle size of the TiO_2 (12.7nm) and N-TiO_2 (10.2 nm). Uv-Visible absorption spectroscopy was used to estimate the band gap energy of TiO_2 and N-TiO_2, nanoparticle were 3.16eV and 2.50eV respectively. In the experiment, it was found that the absorption edge of N-TiO_2 decrease the band gap as compared to TiO_2. It was found that catalyst loading was directly proportional to the efficiency of degradation of the MB up to a certain optimum value for at (0.45 g/250 ml. However, catalytic activity of the catalysts decreased with further increase in concentration of dopant. while the catalytic activity was direct proportional with calcination temperature up to the optimal 500^0C. However, the catalytic activity of the (TiO_2 and N-TiO_2) decreased with further increase of calcination temperature above optimum, which has little photocatalytic activity.

VI. REFERENCE

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