Effect of Nitrogen Doping on Photocatalytic Activity of TiO$_2$

M.J. Pawar*, V.B. Nimbalkar, M.D. Gaonar, A.D. Khajone, R.K. Taywade

Laboratory of Materials Synthesis, Department of Chemistry, Smt. Narsamma ACS College, Kiran Nagar, Amravati – 444 606, Maharashtra, India.

**ABSTRACT**

Nitrogen doped TiO$_2$ nanoparticles (N-doped TiO$_2$) in different mol percentage (2-6 mol%) of nitrogen with anatase phase, have been prepared by using EDTA-glycol method. Samples were characterized by various physico-chemical techniques. Physico-chemical characterization revealed that crystallite size, surface hydroxylation, and tuning of optical band gap towards visible region of catalyst increases with increase in dopant concentration up to 4.0 mol% in TiO$_2$ host lattice. Thereafter, the samples were used to photocatalytic degradation of the organic dye methylene blue (MB) under sunlight irradiation directly. The progress of photodegradation reaction was monitored by UV-visible spectroscopy. During photocatalytic reaction, the effect of calcination temperature, amount of catalyst, initial concentration of dye and the effect of pH on the rate of degradation reaction was also studied. It is clearly shown that N doping in TiO$_2$ results in the enhancement of the degradation ability of MB in UV-visible light.

1. Introduction

Recently, significant progress has been achieved in the development of photocatalyst to remove organic/inorganic pollutants using solar energy [1]. Among all photocatalysts, TiO$_2$ appears as the most promising candidate for its high photocatalytic activities, environmental benign nature, high stability, and large abundance [2]. Modified TiO$_2$ photocatalysts are promising materials for various applications due to their tunable physico-chemical properties, environmentally friendly in nature, absorbing visible region of electromagnetic spectrum, capable of performing at room temperature, and effective at extremely low concentrations.

Unfortunately, the large band gap of pristine TiO$_2$ makes it only photoactive in UV light, restricting its effectiveness. To improve solar efficiency, various approaches, such as metal/non-metal doping, metal deposition, dye sensitization, defects introducing, semiconductor complex coupling, have been used to extend the photo-response of TiO$_2$: based photocatalyst into visible light region [3–6]. Particularly, non-metal doped TiO$_2$: exhibited stronger absorption in the visible light range with a red shift in the band gap transition [7]. Non-metal doped TiO$_2$ nanomaterials have revealed additional electronic states above the valence band edge of pure TiO$_2$. These additional electronic states are responsible for the red-shifted absorption of non-metal doped TiO$_2$: photocatalysts and which also lower its oxidation potentials [8]. The different non-metal dopants, such as nitrogen [9, 10], carbon, [11], phosphorus [12], sulfur [13], boron [14], iodine [15], fluorine [16], etc. have been doped into TiO$_2$: lattice and these doped materials provide appropriate impurity levels to tune the optical band gap in visible region with enhancement in photocatalytic efficiency.

Among the methods developed, nonmetal modifications of TiO$_2$: particularly through nitrogen doping, can achieve visible light-activated photocatalyst [6]. Nitrogen can be readily introduced into TiO$_2$: as it has a similar atomic size to oxygen, is highly stable, and has low ionization energy (4.5 eV). N-doping has been shown to reduce band gap of TiO$_2$: leading to visible-light photocatalysis. Progress has been made in our understanding of the electronic, optical, and structural composition of N-modified TiO$_2$: (N:TiO$_2$) [3, 6]. Despite these efforts, N:TiO$_2$: photocatalytic efficiency under visible light remains too low for practical applications [17–20]. It is well known that the visible-light photocatalytic activity of N:TiO$_2$: originates from the N 2p mid-gap energy states [3]. However, it was also suggested that this nitrogen-induced mid-gap energy states in the band gap can still act as recombination centers for the photo-generated electron-hole pair in this kind of mono-doping system [21]. So, electron-hole recombination remains a major obstacle that blocks the effective use of N:TiO$_2$: photocatalysts [22]. The nitrogen doped TiO$_2$: nanocrystals have consumed great attention due to its enhanced photocatalytic activity. This paper reports the preparation of different weight percentages of nitrogen doped TiO$_2$: nanoparticles by EDTA-glycol method.

2. Experimental Methods

2.1 Synthesis of Undoped and N-doped TiO$_2$

TiO$_2$: based photocatalysts were synthesized by a modified sol-gel method. In a typical process, 10 mL of titanium iso-propoxide was dissolved in 40 mL of anhydrous ethanol to produce solution. Meanwhile, 15 mL of nitric acid solution (1:5, volume ratio between nitric acid and deionized water) and a certain amount of 1, 3-diaminopropane (DAP) were added to another 10 mL of anhydrous ethylene glycol (EG) in turn to form DAP-EG-nitric acid-water solution. Next, this solution was slowly added dropwise to the solution of titanium iso-propoxide and ethanol under vigorous stirring to carry out a hydrolysis. Then, the obtained yellowish transparent sol was aged for 12 h after continuously stirring for 2 h. Subsequently, the resulting yellowish transparent sol was dried for 20 h in an oven at 75 °C, and then calcined for 4 h at a certain temperature with a heating rate of 5 °C/min. Finally, the TiO$_2$: based photocatalysts were successfully obtained. Through changing the weight content of ammonium chloride and calcination temperature, a series of nitrogen-doped TiO$_2$: nanoparticles were synthesized. They were denoted as N$_x$:TiO$_2$: where “$x$” represent the molar percentage of nitrogen ($x = 0, 2, 4$ and $6$). The synthesized samples were calcined at predetermined temperatures viz., 400, 450, 500 and 550 °C for 4 h.

2.2 Photocatalytic Decolorization of Methylene Blue (MB)

The photocatalytic reactivity of N-doped TiO$_2$: was evaluated by the decolorization of MB under visible light irradiation ($\sim$ 400 nm). A LED lamp of 15 W was used as a light source for testing. Different amount of the N-doped TiO$_2$: powder was added into 200 mL of 10 mg/L MB solution. Before open LED light, the suspension was put in the reactor and stirred until dye adsorption was completed. After that, the LED light was turned on. The concentration of MB dye solution was evaluated at given time intervals of every 30 min by using UV-vis spectrophotometry at wavelength of 664 nm ($A_{664}$).

---

*Corresponding Author: mjpa1809@gmail.com (M.J. Pawar)
2.3 Characterization

The identity of crystalline phase of the samples was identified by the X-ray diffraction (XRD) patterns, which were obtained by a diffractometer (type DX 2500) employing Cu Kα (1.54056 Å) radiation at a scan rate (2θ) of 0.05° s⁻¹, an accelerating voltage of 40 kV and applied current of 25 mA. UV-visible reflectance spectra for the samples were collected on a UV-visible spectrometer (UV-2550 UV/vis Spectrometer, Shimadzu). Photoluminescence (PL) emission spectra of the prepared samples were determined using Cary Eclipse fluorescence spectrophotometer at room temperature. The chemical structure was investigated by AVATAR 330 Fourier transform infrared spectrometer (FTIR) in which the IR spectrum was recorded by diluting the mixed powder in KBr and in the wavelength between 400 and 4000 cm⁻¹. N₂ adsorption-desorption isotherms, which were obtained on a ASAP 2020 apparatus, of the samples to analyze the Brunauer–Emmett–Teller (BET) surface area using multipoint BET method.

3. Results and Discussion

3.1 Crystalline Structure

Fig. 1 shows the XRD patterns of N-doped TiO₂ prepared by different temperatures. The patterns were recorded in 2θ range of 20°-80°. The lattice planes indexed in all diffraction patterns are associated to the pure tetragonal anatase phase of host TiO₂ material which has Ti⁴⁺ (octahedral) and O²⁻ (trigonal planer) coordination geometry. It is also observable that the anatase crystalline phase of TiO₂ remained unchanged with the incorporation of N in the TiO₂ lattice. The results show that all N-doped TiO₂ samples exhibit similar diffraction peaks appeared at 25.56°, 37.76°, 48.04°, 54.06°, 55.24°, 62.76°, 69.04°, 70.32° and 75.30°. These peaks represent to (101), (004), (200), (105), (211), (204), (116), (220), (215) and (303) planes, respectively, which is anatase structure of TiO₂; as followed Joint Committee on Powder Diffraction Standard (ICPDS no. 84-1286). The XRD peaks at 2θ = 25.56° (101) and 2θ = 48.04° (200) are often taken as the characteristic peaks of anatase crystal phase. The average crystallite size (d) can be determined from the broadening of the strong peak (101) by Scherrer formula Eq.(1) [23]:

\[
d = \frac{k \lambda}{\beta \cos \theta}
\]

where, \(\lambda\) is the wavelength of the X-ray radiation (in our test, \(\lambda = 0.15406 \text{ nm}\)), \(k\) is usually taken as 0.89, and \(\beta\) is the line width at half-maximum height of the main intensity peak after subtraction of the equipment broadening. The N-doped TiO₂ samples show reduced intensity with increased full-width at half-maximum of the Bragg peak. This might be because of the small nanoparticles size due to which all the dopants might have entered the lattice of octahedral position. However, some dopants might be remained onto the surfaces or grain boundaries. As a result, the periodicity of the lattice gets disturbed and affects the crystal growth which reduces the crystallite size.

The crystalline size of N-doped TiO₂ which was calculated using Scherrer equation is in the range of 11 to 25 nm. All peaks of N-doped TiO₂ are slightly broader than the peaks of pure TiO₂ due to incorporating N atom into the anatase TiO₂ structure. It was found that the average crystallite sizes of N-doped TiO₂ were smaller than that of undoped TiO₂ (Table 1). This indicated that N doping into TiO₂ anatase structure had significant effect on crystallites size [24]. However, these results can be concluded that the synthesized temperatures had no effect on crystallites size.

Table 1 Crystallite size and N-doped TiO₂ samples calcined at different temperatures

| Concentration of Nitrogen (mol%) | Crystallite Size (nm) |
|---------------------------------|----------------------|
| 400 °C                          | 18.9                 |
| 500 °C                          | 17.1                 |
| 550 °C                          | 17.5                 |

3.2 Porosity

The specific surface area, total pore volume and average pore diameter of N-doped TiO₂ prepared by different temperatures were analyzed by BET technique. The specific surface area and total pore volume of the N-doped TiO₂ samples were significantly increased when compared with the pure TiO₂. This is caused by the incorporation of nitrogen in anatase TiO₂ structure. Nitrogen atoms could interfere the growth of anatase TiO₂ crystals leading to the decrease of crystallite size. The N₂-TiO₂-450 and N₂-TiO₂-500 had larger specific surface area than the N₂-TiO₂-450 and N₂-TiO₂-500. Fig 2 presents the N₂ adsorption-desorption isotherms of N-doped TiO₂ samples calcined at 450 °C which are identified as type IV isotherms according to the IUPAC classification [16]. It was indicated that N-doped TiO₂ was classified as a mesoporous material (diameter in the range of 2-50 nm) with uniform pore size. This result is agreement with the calculated crystallite sizes as discussed previously. High surface area generally enhances the light harvesting ability of the photocatalyst [25, 26].

Fig. 1 XRD patterns of pure TiO₂ and N₂-TiO₂ catalysts calcined at different temperatures

https://doi.org/10.30799/jnst.312.20060401

Fig. 2 N₂ adsorption-desorption study of N-doped TiO₂ calcined at 450 °C

Fig. 3 (a) UV-vis spectra and (b) Band gap analysis of 2 mol% N-doped TiO₂ calcined at different temperature

Cite this Article as: M.J. Pawar, Y.B. Nimbalkar, M.D. Gaonar, A.D. Khajone, R.K. Taywade, Effect of nitrogen doping on photocatalytic activity of TiO₂, J. Nanosci. Tech. 6(4) (2020) 918–923.
3.3 UV-Visible Spectroscopy

Fig. 3(a)-{b} shows the diffuse reflectance spectra of Degussa P-25, amorphous, and various N-TiO$_2$ nanoparticle samples calcined at 400, 450, 500 and 550 °C, which possess various N doping molar ratios. The peaks of each sample showed absorptions between 300 and 400 nm in Fig. 3(a) and the enlarged peaks in Fig. 3(b), which exhibited a calculated band gap of 3.4, 3.0, 2.92, 2.97 and 2.97 eV, respectively. The band gap values exhibited a tendency to red shift toward lower wavelengths with an increase in nitrogen doping content that strongly affected the absorption region. Thus, it could be anticipated that nitrogen sources from nitric acid reacted with Ti ions resulting in the interstitial doping and modifying the energy state of the TiO$_2$ nanoparticle band gap, which could be reduced toward the visible region.

3.4 Photoluminescence Analysis

To evaluate the radiative recombination of excited electrons and holes, as synthesized N$_x$TiO$_2$–450 sample calcined at 450 °C were analyzed via PL spectra under an excitation wavelength of 290 nm and compared to an undoped as synthesized TiO$_2$ powder and results are presented in Fig. 5. Excited peaks in the spectra were observed at 391, 423, 441, and 454 nm indicating different emission sources. The peak at 391 nm could be attributed to the conduction to valence band energy state transition, peaks at 423 and 454 nm were signals from free excitations at the band edge and the excitation peak at 441 nm was due to localized self-trapped excitons [27, 28]. In addition to the PL analysis, the intensity virtually decreased for the 450 °C calcined sample, showing that the lifetimes of excited electrons and holes with regard to the N-doped TiO$_2$ nanoparticles were greatly enhanced and contributed to decomposition reactions with organics until the electrons and holes recombined.

3.5 FTIR Spectra

FTIR spectra of as-synthesized pure and N$_x$TiO$_2$–450 calcined at 550 °C nanoparticles are presented in Fig. 6. Clearly, both of the samples exhibited similar vibrations in the IR region. The intensive and broad band at low wavenumber range between 400 and 800 cm$^{-1}$ were ascribed to the stretching vibrations of Ti–O and Ti–O–Ti bonds [29]. Two peaks located at 3420 and 1620 cm$^{-1}$ were assigned to the stretching vibration of hydroxyl group on the surface and O–H bending of dissociated or molecularly adsorbed water molecules, respectively [30, 31].

Noticeably, compared with that in undoped TiO$_2$, the intensity of the two absorption bands in the as-synthesized N$_x$TiO$_2$–450 was stronger. This indicated that the N$_x$TiO$_2$–450 sample had more surface-adsorbed water and hydroxyl groups, which played an important role in the photocatalytic reaction. On the one hand, the hydroxyl groups can capture the photo-induced holes (h$^+$) when irradiated with light and then form hydroxyl radicals (OH) with high oxidation capability. On the other hand, the surface hydroxyl groups can also act as absorption centers for O$_2$ molecules and finally form hydroxyl radicals to enhance the photocatalytic activity.

3.6 Evaluation of Photocatalytic Activity

3.6.1 Effect of Nitrogen Doping

Depending on the method of the preparation and the end usage of the TiO$_2$ or doped TiO$_2$ photocatalysts, calcination temperatures have prominent influence on the activity of the prepared photocatalysts. Yu et al. [34] prepared nitrogen-doped TiO$_2$ nanoparticle catalyst and analyzed its catalytic activity under visible light. The N-doped TiO$_2$ samples were subjected to various calcination temperatures ranging from 300 to 700 °C. The results of their investigations revealed that the photocatalytic activity of the prepared photocatalysts increased with increase in temperature from 300 to 500 °C. At 500 °C it reached the maximum, because of complete crystallization of anatase at this temperature.

Photocatalytic activities of as-synthesized N$_x$-doped TiO$_2$ samples calcined at the temperatures ranging from 400-550 °C, were investigated by photodegradation of MB dye under visible-light irradiation. The photodegradation of MB in aqueous solution under visible light for 90 min the corresponding results are shown in Fig. 7. As expected, N-doped TiO$_2$ exhibited the higher visible-light photocatalytic activity due to the effect of N doping into the TiO$_2$ lattice. It was found in Fig. 7 that N$_x$TiO$_2$ had obviously the highest photocatalytic activity, suggesting that there was an optimum value for the N-doping.

![Fig. 5 PL spectra of as synthesized undoped TiO$_2$ and N$_x$TiO$_2$–450 samples calcined at 450 °C](https://doi.org/10.30799/jnst.312.20060401)

![Fig. 6 FTIR spectra of (a) undoped TiO$_2$: and (b) N$_x$TiO$_2$–450 samples](https://doi.org/10.30799/jnst.312.20060401)

![Fig. 7 Absorption of MB under visible light by using as synthesized undoped TiO$_2$: and N$_x$-doped TiO$_2$: calcined at different temperatures](https://doi.org/10.30799/jnst.312.20060401)

Cite this Article as: M.J. Pawar, Y.B. Nimbalkar, M.D. Gaonar, A.D. Khajone, R.K. Taywade, Effect of nitrogen doping on photocatalytic activity of TiO$_2$, J. Nanosci. Tech. 6(4) (2020) 918–923.
in any reactor system, the initial rates were found to be directly proportional to catalyst concentration, indicating the heterogeneous regime. They further observed that there is a limit of catalyst concentration that must be used for the photodegradation of a particular pollutant in wastewater, above which the rate of photocatalysis will even decrease. This is in agreement with recent reports [34-36]. Konstantinou and Albanis [32] also reported an enhanced degradation rates for optimum catalyst loading up to 0.4–0.5 g/L. In the present work, the photocatalytic activity of N-doped TiO₂ samples calcined at 450 °C was tested for 10 mg/L concentration of MB dye with the catalyst dose ranging from 0.2–0.8 g/L. The results are presented in Fig. 8. It was observed that, photocatalytic degradation efficiency increased with catalyst dosage from 0.2–0.4 g/L. The photocatalytic degradation efficiency has been decreased when catalyst dosage is over 0.4 g/L.

3.6.4 Effect of Oxygen Purging

In order to determine the influence of bubbling oxygen on the photocatalytic efficiency, MB photodegradation was performed by bubbling oxygen through an aqueous suspension containing 10 mg of dye and 0.4 g of catalyst per liter of solution under UV-visible light over N₄-TiO₂-450 catalyst (dosage: 0.4 g/L) and results are illustrated in Fig. 10 where the rate of MB degradation in oxygen bubbling solution is much larger than that in static oxygen and nitrogen bubbling solution. This implies that oxygen plays a critical but vital role in the TiO₂-based photocatalysis, enhancing the degradation efficiency even under lower concentration (oxygen in air i.e. static oxygen).

This result appears quite logical since during the chemical oxidation process, the emitted radiation can directly lead to the transformation of the target pollutant. For example, an organic dye, MB is first photo-excited (I), subsequently it may react with oxygen dissolved in water (II) and then leads to the formation of sub-products (III) [39].

\[
\begin{align*}
MB & \rightarrow MB^* \\
MB^* + O_2 & \rightarrow MB^{**} + O_2^* \\
MB^{**} & \rightarrow \text{Product}
\end{align*}
\]

3.6.5 Effect of Initial Dye Concentration

The photocatalytic activity of N₄-TiO₂-450 catalyst (dosage: 0.4 g/L) calcined at 450 °C was studied for varying concentration of MB dye ranging from 5–20 mg/L and the results are presented in Fig. 9.

It shows that the removal of MB decreases as the initial concentration of MB is increased from 5 to 20 mg/L. An initial dye concentration 10 mg/L is an optimum concentration for the highest degradation with catalyst dosage 0.4 g/L. The lower degradation efficiency at higher initial concentration can be attributed to the fact that the higher MB concentrations could absorb more photons, which reduces the available photons to activate the TiO₂ and this result in reduced degradation efficiency.

3.6.6 Effect of pH

Several authors have studied the effect of pH on the degradation of pollutants by catalyzed oxidation and have shown that pH is a parameter that affects the efficiency of the photodegradation process. The pH controls the reactions during the degradation of dyes or organic compounds and beside this generation of hydroxyl radicals also depends on the pH of the solution [40, 41]. Initially, the effect of pH on the photocatalytic degradation of MB dye in the range of pH 1–10 in presence of N₄-TiO₂-450 was studied under conditions (Catalyst dosage: 0.4 g/L, Dye Concentration: 10 mg/L) and results are presented in Fig. 11.
Initial dye concentration: 10 mg/L, Irradiation time: 90 min) as shown in Fig. 11. The percentage of dye removal showed an increase with a decrease in pH value and reached their maximum value in the acidic pH. At low pH value, the surfaces of the catalysts were highly protonated and became positively charged so that the dye cations were electrostatically attracted more towards the catalyst surface as more oxidizing holes increases and thus degradation of MB dye was enhanced. At acidic pH, the positive holes are considered as the major oxidation species, whereas hydroxyl radicals are considered as the predominant species at neutral or alkaline.

3.6.6 Reusability of Photocatalyst

Reusability of the catalyst is one of the most projected attractions of any heterogeneous catalyzed reaction, but only limited experiments are there on the reusability studies of powder photocatalysts [42, 43]. This may be due to the difficulties in separation of the catalyst powder after pollutant degradation and may also be due to the low reusability of the catalyst. Present catalysts are easily separable from the solution and also well dispersible under stirring. It is simple to detach the catalyst from the cleaned solution either by filtration or by centrifugation. There was no permanent adsorption of dye over the catalyst, and the cleaning merely arises from photodegradation. Regeneration of the best catalyst, 2 mol% N-doped TiO$_2$ (calcined at 450 °C), was done after each reaction, by centrifugation, washing with water, and further treatment at the temperature of the catalyst, that is, at 150 °C, for 1 h. The photocatalytic activity of the N$_2$-TiO$_2$-450 remains intact even up to ten consecutive experiments under the selected reaction conditions (Fig. 12).

4. Conclusion

In summary, a series of N-doped TiO$_2$ nanoparticles were successfully synthesized by EDTA-glycol method. The photocatalytic reactivity of TiO$_2$ was successfully enhanced by N-doped via EDTA-glycol method. The synthesized temperature at 450 °C was recommended as the optimal condition to prepare N-doped TiO$_2$. N-dopant could reduce the band gap energy, decrease crystallite size and increase the surface area of TiO$_2$. The enhanced photocatalytic activity of degradation of MB under UV-visible light irradiation was mainly attributed to the single phase composition, more surface hydroxyl groups, intense absorption in visible-light region and narrow band gap energy.

References

[1] Z.W. Chen, H. Jiang, W.L. Jin, C.K. Shi, Enhanced photocatalytic performance over Bi$_x$Ti$_{1-x}$O$_2$ nanosheets with controllable size and exposed (001) facets for Rhodamine B degradation, Appl. Cat. B: Environ. 180 (2016) 698–706.
[2] Y.C. Zhang, M. Yang, G. Zhang, D. Li, D. Lv, B.F. Wang, D. Pan, Y. Song, Doping Mo into TiO$_2$ nanomaterials: Improved light harvesting and photocatalytic efficiency, Appl. Cat. B: Environ. 195 (2016) 254–260.
[3] R. Asahi, T. Morikawa, K. Hashimoto, Highly dispersed nitrogen-doped anatase TiO$_2$ nanoparticles for photocatalytic mineralization studies, Mater. Chem. Phys. 173 (2016) 62–71.
[4] H. Irie, Y. Watanabe and K. Hashimoto, Carbon-doped anatase TiO$_2$ powders as a visible-light sensitive photocatalyst, Chem. Lett. 32 (2003) 772–773.
[5] S. Qi, J. Zhou, Z. Li, M. Jiang, J. Chen, J. Yan, Visible-light-active nitrogen-doped anatase TiO$_2$ nanocrystals for environmental applications, Appl. Cat. B: Environ. 125 (2013) 331–349.

Fig. 12 Reusability data over 0.4 g/L N$_2$-TiO$_2$-450 in the photodegradation of 200 mL of 10 mg/L MB, for 90 min

Removal Rate of MB (%) vs. Number of Runs

| Removal Rate of MB (%) | Number of Runs |
|------------------------|---------------|
| 0                      | 1             |
| 25                     | 2             |
| 50                     | 3             |
| 75                     | 4             |
| 100                    | 5             |

4. Conclusion

In summary, a series of N-doped TiO$_2$ nanoparticles were successfully synthesized by EDTA-glycol method. The photocatalytic reactivity of TiO$_2$ was successfully enhanced by N-doped via EDTA-glycol method. The synthesized temperature at 450 °C was recommended as the optimal condition to prepare N-doped TiO$_2$. N-dopant could reduce the band gap energy, decrease crystallite size and increase the surface area of TiO$_2$. The enhanced photocatalytic activity of degradation of MB under UV-visible light irradiation was mainly attributed to the single phase composition, more surface hydroxyl groups, intense absorption in visible-light region and narrow band gap energy.

References

[1] Z.W. Chen, H. Jiang, W.L. Jin, C.K. Shi, Enhanced photocatalytic performance over Bi$_x$Ti$_{1-x}$O$_2$ nanosheets with controllable size and exposed (001) facets for Rhodamine B degradation, Appl. Cat. B: Environ. 180 (2016) 698–706.
[2] Y.C. Zhang, M. Yang, G. Zhang, D. Li, D. Lv, B.F. Wang, D. Pan, Y. Song, Doping Mo into TiO$_2$ nanomaterials: Improved light harvesting and photocatalytic efficiency, Appl. Cat. B: Environ. 195 (2016) 254–260.
[3] R. Asahi, T. Morikawa, K. Hashimoto, Highly dispersed nitrogen-doped anatase TiO$_2$ nanoparticles for photocatalytic mineralization studies, Mater. Chem. Phys. 173 (2016) 62–71.
[4] H. Irie, Y. Watanabe and K. Hashimoto, Carbon-doped anatase TiO$_2$ powders as a visible-light sensitive photocatalyst, Chem. Lett. 32 (2003) 772–773.
[5] S. Qi, J. Zhou, Z. Li, M. Jiang, J. Chen, J. Yan, Visible-light-active nitrogen-doped anatase TiO$_2$ nanocrystals for environmental applications, Appl. Cat. B: Environ. 125 (2013) 331–349.

Fig. 12 Reusability data over 0.4 g/L N$_2$-TiO$_2$-450 in the photodegradation of 200 mL of 10 mg/L MB, for 90 min

Removal Rate of MB (%) vs. Number of Runs

| Removal Rate of MB (%) | Number of Runs |
|------------------------|---------------|
| 0                      | 1             |
| 25                     | 2             |
| 50                     | 3             |
| 75                     | 4             |
| 100                    | 5             |
Cite this Article as: M.J. Pawar, V.B. Nimbalkar, M.D. Gaonar, A.D. Khajone, R.K. Taywade, Effect of nitrogen doping on photocatalytic activity of TiO$_2$, J. Nanosci. Tech. 6(4) (2020) 918–923.