NITROGEN-DOPED NANO TITANIA'S PHOTOCATALYTIC DEGRADATION OF MALATHION UNDER DIRECT SUN LIGHT

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ABSTRACT
By using the sol-gel technique, nitrogen-doped nano Titania with different weight percentages (0.25–1.00 wt%) of dopants were created. The produced catalysts were characterised using a variety of analytical methods, including scanning electron microscopy (SEM), UV-visible diffuse reflectance spectroscopy (UV-DRS), and X-ray diffraction spectroscopy (XRD) (SEM). The synthesised samples were in anatase phase with 2 at 25.3o, according to the XRD data. According to a spectrum examination of UV-Visible diffuse reflectance, the dopant in TiO2 induced a considerable absorption shift towards the visible range. The produced nano catalyst has an erratic form, as revealed by SEM pictures. In direct sunlight, the photocatalytic effectiveness of produced nanomaterials was evaluated on the non-biodegradable herbicide Malathion.
Key words: Titanium dioxide, Malathion, Nitrogen, sunlight, sol-gel method

1. Introduction
A new method for purifying water and the air is heterogeneous photocatalysis by semiconductors [1]. Titanium dioxide is widely regarded as one of the best heterogeneous photocatalysts because of its key distinguishing characteristics, including high photocatalytic efficiency, thermal stability, low cost, and other critical characteristics [2]. While TiO2 outperforms other photocatalysts in many real-world applications, its photocatalytic activity is constrained by two flaws. Titanium dioxide's low bandgap energy (3.2 eV) limits the amount of visible light it can absorb. Second, low quantum efficiency is caused by the high rate of electron-hole recombination [3]. Doping TiO2 has been shown to be advantageous in investigations on the modification of TiO2 to address its shortcomings. In addition to the importance of visible light responsive photocatalyst, it is fascinating to look for new photocatalyst with appropriate particle size, crystal phase and other properties to improve the photocatalytic activity. Hence in our research work we have selected Nitrogen dopant to be doped in TiO2 and study its photocatalytic activity in direct sunlight.
There are several techniques for the synthesis of TiO2 nanomaterials like precipitation [4], electro spinning [5] hydrothermal, chemical vapour deposition [6], solvothermal [7] and so on. Among all the methods available, sol-gel method is advantageous because powders of homogenous concentrations and high purity can be synthesized at very low temperatures under stoichiometry control [8]. Hence, sol-gel method has been followed for the synthesis of Nitrogen doped TiO2 (N-TiO2) photocatalysts.
Synthetic organophosphorus compounds are a group of highly toxic agricultural chemicals widely used for plant protection [9]. Malathion, an organophosphorous pesticide with broad range of target pests, has been widely used in agriculture. Due to chemical stability and high toxicity, Malathion resists biodegradation [10]. So, Malathion was selected in order to check the photocatalytic activity of as prepared photocatalysts in direct sun light.

2. Experimental
2.1. Synthesis of photocatalysts
A series of TiO2 samples were prepared by doping with Nitrogen in the range of 0.25-1.00 wt % along with undoped TiO2 by sol-gel method. For preparation of undoped TiO2 isopropyl alcohol is taken as solvent and water was added to Titanium tetrachloride (Titanium precursor) for hydrolysis and condensation reactions to take place in presence of acid. In case of doped catalyst preparation, calculated quantities of urea, precursor

for Nitrogen was dissolved in solvent along with water and the resultant solution was added drop by drop to the solution of $TiCl4$. After complete addition, the colloidal suspension was allowed to stir for 45 min and aged. Thus obtained gel was dried in an oven. Later, it was well grinded and calcined at 400°C in muffle furnace at the rate of 2°/ min. Then, cooled in a desiccator and ground to form homogenous powder.

2.2. Characterisation of photocatalysts

XRD spectra were recorded for 2θ from 20° to 80° with, RIGAKU diffractometer using monochromatized CuKα radiation (λ=1.541A°) model Ultima IV with a Germanium solid state detector. UV-Visible absorption spectra of the samples were obtained by using Shimadzu 3600, UV-Visible NIR spectrophotometer using $BaSO4$ as reference scatter. The morphology of the nanoparticles was recorded JSM-6610 LV model which is equipped with an energy dispersive X-ray (EDS) spectrophotometer and operated at 20kV.

2.3. Photocatalytic activity of catalyst

Malathion solution (5mg/L) with catalyst was stirred in dark for few minutes to establish adsorption-desorption equilibrium on the catalyst surface. The reaction mixture was exposed to direct sunlight in summer season. At certain regular time intervals, 5mL aliquots of samples were collected through 0.45µm Millipore syringe filter. The filtrate was analyzed on spectrophotometer from 200-800 nm. Malathion has a characteristic absorption band at 266 nm [10]. Another peak was also observed at 214nm. However, the rate of photodegradation is followed using the decay of these bands. To have a comprehensive comparison, the reaction environment is maintained same for all the activity tests. The percentage degradation of dye was calculated from the following equation:

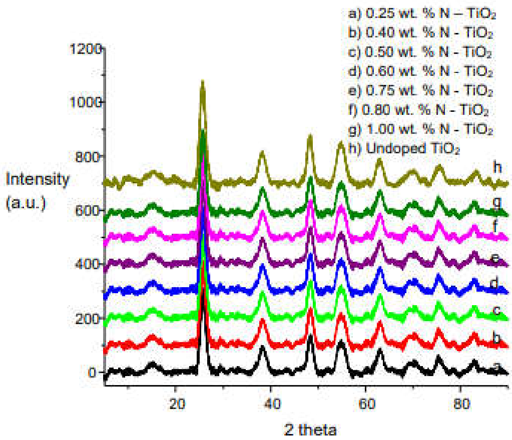
% of Degradation = Ao-At/ Ao × 100

Where *Ao* is initial absorbance of dye solution before degradation and *At* is absorbance of dye solution at time t.

3. Results & Discussions

3.1. X-Ray Diffraction & Transmission Electron Microscopic Analysis (XRD):

The XRD patterns of all the synthesized samples were represented in Fig. 1 and typical peaks were observed at 2θ=25.3°, 37.7°, 47.9°, 54.1°, which can be indexed to the (004) (200) (211) crystal facets of anatase $TiO2$ (JCPDS File no: 21-1272). From XRD patterns it is evident that all the synthesized samples are in anatase phase. The average crystallite sizes of the synthesized samples were calculated from Scherrer Equation and were found to be ranging from 11 to 12.1 nm.

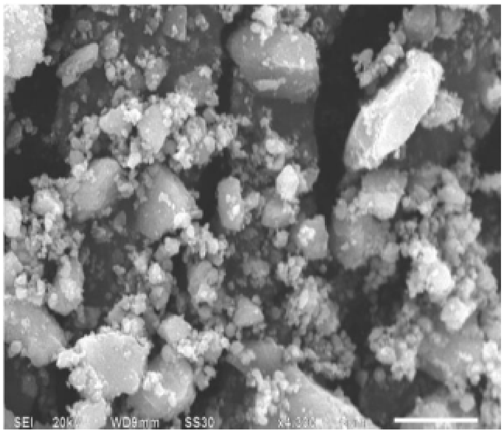


3.2. Ultra Violet-Visible Diffuse Reflectance Spectroscopic Studies:

From, UV-Visible DRS spectral data it was observed that the synthesized doped samples had a profound effect on its optical response in the visible wavelength range. Band gap for all the synthesized samples were calculated by using the formula Eg = (1240/λ), where Eg is band gap, λ is wavelength [11]. The band gap of synthesized undoped TiO2 was found to be 3.10 eV which is comparable with the literature value [12]. The doped samples showed band gap ranging from 2.70 - 3.10 eV. The band gap of doped samples was found to be reduced when compared with that of undoped sample. The narrowing of bandgap is may be due to formation of midgap band above valence band by N 2p states. Thus, the results demonstrated that all the synthesized doped samples had reduced bandgap and are active in visible region.

3.3. Scanning Electron Microscopic Studies:

The morphology of the samples was detected by using a Scanning Electron Microscope.

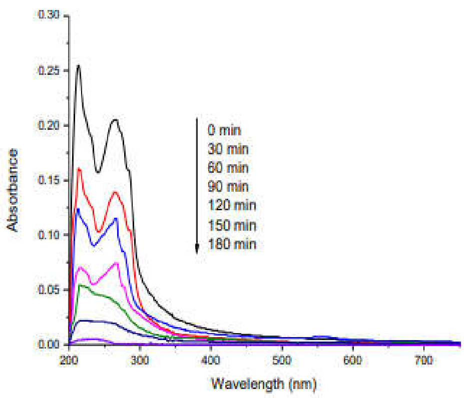


The morphology and particle size of the catalyst play very important role in its photocatalytic activity. SEM image of 0.75 wt.% of N- TiO2 is shown in Fig.2. The image showed irregular tiny clusters composed of large numbers of nanoparticles with lower aggregation and better distribution. From the SEM micrographs it can be inferred that aggregation is decreased greatly due to doping.

3.4. Photocatalytic Degradation

Photocatalytic degradation of Malathion was performed by following the procedure given in section 2.3. A blank test with no photocatalyst is also employed. There is no significant change in the concentration of pesticide.

Photocatalytic degradation of Malathion using different synthesized catalysts with various dopant concentrations were carried out with catalyst dosage of 1.0g/L. Among all the nano catalysts, 0.75 wt% N-TiO2 showed best photocatalytic activity.



The spectrum representing the degradation of Malathion using this sample was represented in Fig. 3. The absorbance gradually decreased as time passed and became almost zero after 180 min indicating complete degradation of Malathion under direct sunlight in summer season.

Conclusion

Successful nitrogen doping of the TiO2 matrix allowed for the study of its photocatalytic activity through the degradation of the organophosphorous insecticide Malathion in the presence of direct sunlight. The band-gap has been decreased and all of the generated samples were in the anatase phase. In addition to improving electron trapping and causing a response to visible light, nitrogen doping also prevented e-/h+ recombination throughout the photocatalytic process. Due to its high crystalline anatase phase, small particle size, substantial shift in band gap, and efficient separation of electrons and holes, 0.75 wt.% N-TiO2 outperformed all other synthetic catalysts in terms of photocatalytic activity under visible light. 100% degradation of Malathion with concentration of 5mg/L was achieved in 180 min. It can be concluded that doping TiO2 with Nitrogen is a promising route for enhanced photocatalytic degradation of pollutants in direct sunlight.

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