iJRASET
International Journal For Research in Applied Science and Engineering Technology

INTERNATIONAL JOURNAL FOR RESEARCH

IN APPLIED SCIENCE & ENGINEERING TECHNOLOGY

Volume: 9 **Issue:** V **Month of publication:** May 2021

DOI: https://doi.org/10.22214/ijraset.2021.34539

www.ijraset.com

Call: 08813907089 | E-mail ID: ijraset@gmail.com

International Journal for Research in Applied Science & Engineering Technology (IJRASET)
ISSN: 2321-9653; IC Value: 45.98; SJ Impact Factor: 7.429
Volume 9 Issue V May 2021- Available at www.ijraset.com

Photocatalytic Degradation of 4-NP by UV Rays

Rajeev Jha[1], Mrs. Mallika Jain[2]
[1, 2]*CSVT University, BIT, Durg, CG.*

Abstract: ***The photocatalytic degradation of 4-nitrophenol was investigated under UV rays in presence of Titanium Oxide and Boron doped Titanium Oxide as Photocatalyst. Complete degradation was achieved after irradiation under UV rays, being the reaction rate dependent on the initial pH. The effect of various parameters such as catalyst loading and initial concentration of 4-nitrophenol on degradation has been determined. The degradation was strongly enhanced in the presence of Titanium Oxide and Boron doped Titanium Oxide.***
Keywords: Anatase, Iso-propoxide, Nitro - Phenol, Doped, Adsorption-Desorption isotherm.

I. INTRODUCTION

Nitro-phenols are some of the most refractory pollutants, which can be present in industrial waste water. Among them, 4-nitrophenol (4-NP) is environmentally important for several reasons. Owing to high toxicity and carcinogenic character, 4-NP is characterized as environmentally hazardous material. This toxic pollutant is found to be present in the waste water in the production of pesticides, insecticides and herbicides and many synthetic dyes. The removal of this pollutant from wastewater is of great concern, because its complete biodegradation requires several days or weeks. Efficient treatment technologies are required to reduce 4- nitrophenol (4-NP) concentration in wastewater to acceptable levels. To overcome this problem a new oxidation technology called as Advanced Oxidation Processes (AOPs), which provides a complete mineralization of the organic and inorganic pollutants is used. Among several AOPs, the heterogeneous Photo-catalysis is one of the most promising technology in which semiconductor nanomaterial are used for purification of the wastewater. In the present study, an attempt has been made to investigate the advanced oxidative degradation of 4-nitrophenol using Titanium Oxide and Boron doped Titanium Oxide as photocatalyst under UV light.

II. EXPERIMENTAL

A. Materials and Methods

4-Nitrophenol (molecular formula C6H5O3N molecular weight 139.11) is extensively used as a disinfectant. 4-Nitrophenol is also called as p-nitro-phenol or 4-hydroxynitrobenzene is phenolic compound that has a nitro group at the opposite position of the hydroxyl group on the benzene ring. Table1. Properties of 4-Nitrophenol. The Structure of 4-Nitro phenol is shown in Fig. 1.
One of the best advantages of photochemical reaction is its use of near UV or solar light. The photocatalyst Titanium Oxide and Boron doped Titanium Oxide, was used for the study.

Table1. Properties of 4-Nitrophenol

Chemical formula	C6H5NO3
Appearance	Colorless or yellow pillars
Melting point	113 to 114 °C
Boiling point	279 °C
Solubility in water	10 g/L (15 °C) 11.6 g/L (20 °C) 16 g/L (25 °C)

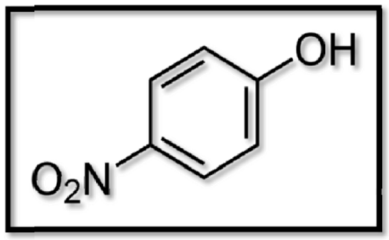


Fig.1. Structure of 4-Nitro phenol

B. Apparatus

The reactor was cylindrical, with a volume of 500 ml made from quartz glass. The quartz glass reactor was also equipped with a water jacket to control the temperature in between 20°C to 25°C. The photo-irradiation was performed with a 125 W mercury lamp as UV light source, emitting a wavelength of 354 nm.

C. Procedure

Preparation of PureTiO_2 and Boron doped TiO_2

Solvent - gel method was used to prepare TiO_2 using Titanium Iso-propoxide (TTIP) as a precursor known to be the main source of origin for Anatase type and was marked as sample TV1 in the instant experiment.

Boron doped TiO_2 catalyst was prepared through sol gel method using Titanium isopropoxide (TTIP) and Boric acid. . The so obtained Boron-doped TiO_2 sample was marked as sample BT1 in the instant experiment. Similarly two more samples of B- TiO_2 were prepared by adding 5% and 7% w/v solution of Boric acid, and are denoted as sample BT5 and BT7 respectively.

Initially, 4-NP stock solution of 2000 ppm was prepared by adding 2g of 4 - Nitro phenol in 1 litre water, from which a working stock solution of 200 ppm was prepared. Then, from stock solution of 200 ppm, standard solutions of different concentration, from 1-20 ppm were prepared.

III. RESULTS AND DISCUSSION

A. X-ray Diffraction Pattern

XRD patterns were recorded mainly to investigate the changes in phase structure of TiO2 and phase structure of Boron doped TiO_2. Figure 2 shows the XRD patterns of all the samples. The XRD pattern of sol-gel TiO_2 (TV1) showed diffraction peaks at approx. 25.460, 37.720, 48.310 and 54.680, which corresponds to (101), (004), (200) and (105) planes of Anatase TiO_2.

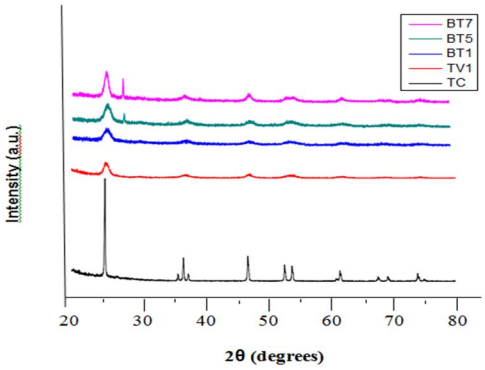


Fig.2. XRD pattern of commercial TiO_2 (TC), undoped TiO_2 (TV1) and Boron doped TiO_2 ($TiBO_3$) [BT1, BT5 & BT7].

B. BET Surface Area Analysis

The specific surface area, pore volume, and adsorption average pore width of un-doped and Boron doped TiO_2 were measured by BET method, summarized in Table 1 below. The results show that specific surface area and pore volume of Titania decreased with increasing content of Boron (TiBO3) doponent.

Table1. Specific Surface area, pore volume and Band gap result of samples

Samples	Surface area (m2/g)	Pore volume (cm3/g)	Band gap Ebg (eV)
TV1	235.4767	0.468387	3.06
BT1	179.1145	0.307402	3.05
BT5	129.5092	0.238238	3.03
BT7	63.3056	0.145009	3.02

The N_2 adsorption-desorption isotherm of un-doped and Boron doped TiO_2 is shown in Figure 3. This adsorption isotherm is a characteristic of meso-porous materials. (Pore size 2 to 50 nm). An adsorption isotherm is a graph that represents the variation in the amount of adsorbate (x) adsorbed on the surface of the adsorbent with the change in pressure at a constant temperature.

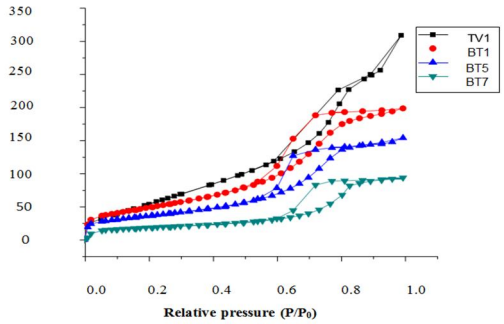
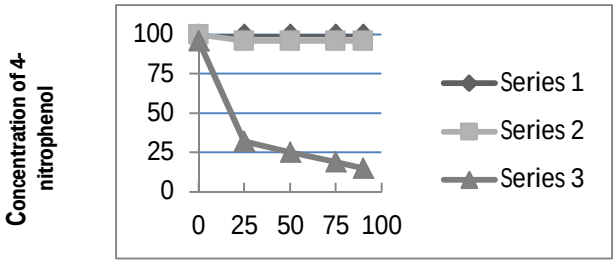


Fig.3. The N2 adsorption-desorption isotherm of un-doped and Boron doped TiO_2.

C. Photo-catalytic Degradation Studies

1) Photocatalytic Degradability of 4-nitrophenol: In the absence of the photocatalyst, the 4-nitrophenol solution on irradiation with the UV light has been found to be stable even after 90 min. In the presence of Titanium Oxide and in the absence of light there is a small decrease in 4- nitrophenol concentration initially and then found to be stable. The initial decrease is due to the adsorption of 4- nitrophenol by Titanium Oxide and the pollutant undergoes 96.6% degradation in 90 min on irradiation with Titanium Oxide in the presence of UV light of 354 nm. The photodegradation of 4-nitrophenol as a function of time is shown in Fig. 4.



Irradiation time (mins)

Fig. 4.

a) Series 1 - 4-Nitrophenol solution irradiated with solar light in the absence of TiO_2

b) Series 2 - 4-Nitrophenol solution treated with TiO_2 in dark

c) Series 3 - Degradation of 4-nitrophenol solution with UV light in the presence of TiO_2

2) Effect of Initial pH of the Solution: The most important parameter that influences the photocatalytic degradation is the solution pH. The efficiency of the catalyst is affected by the pH of the solution. The pH of the solution is adjusted before irradiation and it is not controlled during the course of reaction. The effect of varying the pH from 1 to 11 on the degradation of 4-nitrophenol is shown in Table 2. It is found that the degradation efficiency increases with an increase in pH from 1 to 11. Increase of pH of the 4-nitrophenol solution from 1 to 5 increases the degradation from 53.5% to 78.9% at the time of 60 min. Aslight increase in the degradation rate was observed for further rise in pH from 5 to 11. Many authors observed similar behavior in their studies (Sharma 2001; Sakthivel et al., 2003). At low pH, TiO_2 particle agglomeration reduces the pollutant adsorption as well as photon absorption. The increased efficiency in the alkaline pH range may be explained on the basis of increase in the formation of *OH radicals with an increase in pH. In acid and neutral solutions the formation of *OH radical can be given by the equation.

$H_2O + h^+ \rightarrow {}^*OH + H^+$ (1)

In alkaline solution the *OH radical is also formed from hydroxide ion.

$OH^- + h^+ \rightarrow {}^*OH$ (2)

Table 2 Effect of pH on the photocatalytic degradation of 4- nitrophenol using UV light.

pH	Percentage of degradation
1	53.5
3	64.2
5	78.9
7	86.7
9	90.2
11	95.5

4-Nitrophenol=2 · 10_4 mol/L; TiO_2= 75 mg/50 mL; irradiation time= 60 min.

3) Effect of Catalyst Dose: The effect of catalyst dose on maximum degradation (after 3 h) was investigated to optimize the amount of catalyst. The dose was varied from 0.1 to 1.5 g/L. The effect of change in dose in terms of degradation is presented in Figure 5.

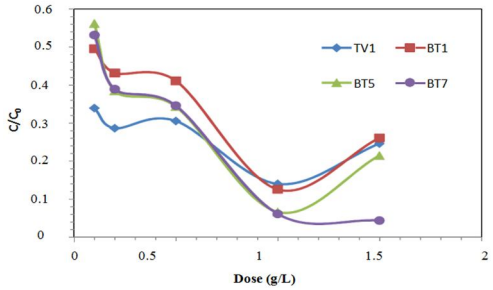


Fig. 5. Effect of catalyst dose on photo-catalytic degradation of 4-NP.

All the developed materials showed similar pattern of change in degradation along with dose. As the concentration of the catalyst was increased, the adsorption sites or active sites were also increased on the surface of the photo-catalyst. Due to which, the adsorption of 4-NP molecules on the catalyst surface was increased and thus, the increase in degradation occurred for 0.1 to 1.0 gm/L of dose. A further increase in dose did not improve the degradation which is possibly due to two reasons:

a) Accumulation of catalyst particles [40]

b) Increase in opacity of solution [41, 43].

These observations suggest that the 1.0 g/L dose of catalyst is optimum for present degradation study.

4) Effect of Boron Loading: Compared to pure TiO_2, the Boron TiO_2 catalysts exhibited a significant increase in 4-NP photo degradation efficiency as shown in Figure 6. where C_0 and C are the concentrations of 4-NP before and after irradiation, respectively. It can be observed that the presence of Boron species influences the photo-catalytic activity. All of the doped samples showed to be more photoactive than un-doped TiO_2 and BT7 catalyst having maximum Boron content showed the highest degradation of solution containing 5 mgL-1 of 4-NP.

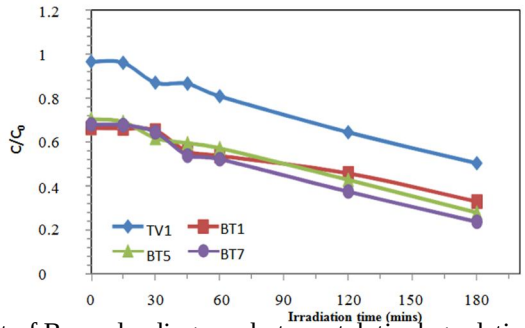


Fig.6. Effect of Boron loading on photo -catalytic degradation of 4 –NP

5) *Degradation Kinetics:* According to experimental results, the photo-catalytic degradation of 4-NP obeys the pseudo first-order reaction law as follows:

$$In\ C_0/C = kt$$

Where, C_0 represents the initial 4-NP concentration in mg/L, C represents final 4-NP concentration in mg/L, k is pseudo first order rate constant (min-1) and t is irradiation time in minutes. Values of k can be obtained from the regression equation of experimental data by plotting graph of Initial (C_0/C) versus time. Fig. 7. Shows the concentration change of 4-NP, Initial (C_0/C), as a function of irradiation time.

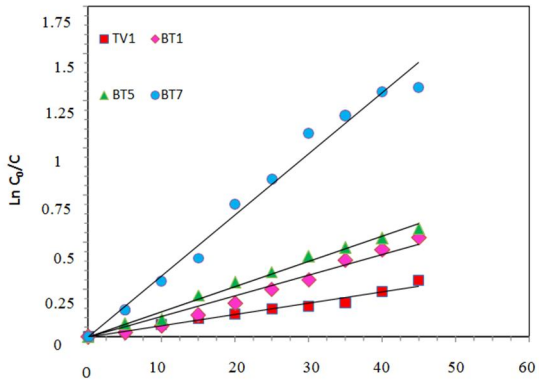
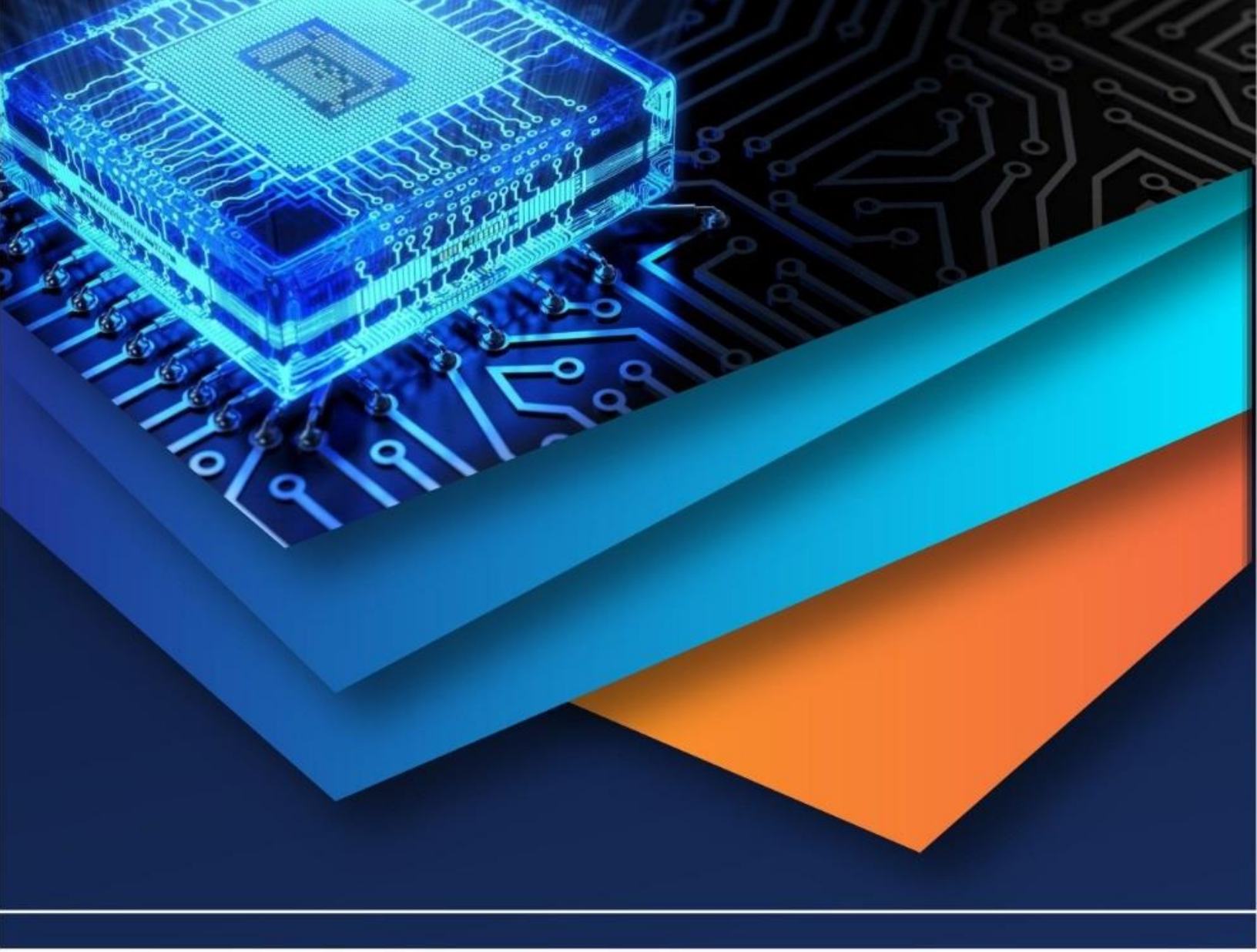


Fig.7. The concentration change of 4-NP, Initial (C_0/C), as a function of irradiation time.

When a small amount of Boron (BT1) is doped into TiO_2, the photo-catalytic activity of sample increases slightly as compared to un-doped TiO_2 (TV1). On further addition of Boron, the activity of BT5 sample also increases as compared to both doped and un-doped samples. The doped BT7 sample with highest Boron concentration showed highest photo-catalytic degradation of 4-NP.
The degradation experiments indicated that photo-catalytic activities of doped TiO_2 were higher than that of pure TiO_2. The activities increased as the Boron doping increased, with maximum degradation at 7% (w/v) concentration of boric acid. The kinetic modeling of photo-catalytic degradation data was also studied to compare the effect of boron doping on photo-catalytic activity.

REFERENCES

[1] Fujishima, K.Honda, Nature, 238 (1972) 37.
[2] Akihiko Kudo, Catalysis Surveys from Asia, 7 (2003) 31.
[3] Savas Sonmezoglu,Banu Erdogan,Seckin Akin,Iskender Askeroglous, The investigation of optical, structural and morphological properties of nano structured boron doped TiO2 thin films



10.22214/IJRASET

45.98

IMPACT FACTOR: 7.129

IMPACT FACTOR: 7.429

INTERNATIONAL JOURNAL FOR RESEARCH

IN APPLIED SCIENCE & ENGINEERING TECHNOLOGY