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# Enhancing Photocatalytic Activity of Nitrogen Doped TiO<sub>2</sub> for Degradation of 4-Chlorophenol under Solar Light Irradiation

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## ABSTRACT

The nitrogen doped TiO<sub>2</sub> as a heterogeneous photocatalyst via sol-gel method was successfully synthesized. The as-synthesized photocatalysts were characterized with X-ray diffraction (XRD), surface area measurements (BET and BJH), Fourier transform infrared spectroscopy (FT-IR), field emission scanning electron microscopy (FE-SEM), energy dispersive spectroscopy (EDS), and energy dispersive X-ray spectrum (EDX). The activities of as-prepared TiO<sub>2</sub> photocatalysts were examined to degrade 4-Chlorophenol aqueous solution under solar irradiation in a photoreactor; in addition, photocatalytic degradation mechanism and pathway were investigated. The results showed that 3 % wt N-doped TiO<sub>2</sub> nanoparticles (under conditions of solution pH of 4.0, catalyst loading of 2 g/L, initial 4-CP concentration of 10 mg/L, and irradiation time of 8 h) exhibited much higher photocatalytic degradation efficiency (91 %) as compared with that of 5 % wt N-doped (83 %), 1 % wt N-doped (71 %), and pure TiO<sub>2</sub> (35 %).

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## 1. Introduction

During the past two decades, shortage of freshwater resources has become a worldwide concern. According to a report been published by the UN Environmental Program, two third of the world's population will be living under water-scarce situations by the 2025 [1]. The problem gets complicated by the growing demands for freshwater supply with rapid population as well as agricultural and industrial development causing a degeneration of drinking water quality over the years. Over the past two to three decades,

increasing industrial activities has caused a growth in the release of hazardous organic contaminants into the environment [2]. Considering these complications, providing the efficient methods for industrial wastewater treatment seems to be very necessary [3]. In recent years, semiconductor photocatalysis has been exhibited to be an efficient method for eliminating contaminants in water and air [4]. Amongst the plentiful photocatalysts, titanium dioxide has been recognized as the most efficient catalyst for photocatalytic activities because of its thermal

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and chemical stability, non-photo corrosive, environmental friendliness, nontoxicity, and cost effectiveness [5]. Moreover, another important benefit of these photocatalysts is that the process often achieves complete mineralization of the organic pollutants to carbon dioxide and water, thereby avoiding the problem of unwanted by-products [6]. However, the main drawback is that bare  $\text{TiO}_2$  is activated under UV light irradiation below 387 nm ( $\sim 3\text{-}5\%$  solar spectrum) as a result of its wide band gap energy (3.2 eV for anatase phase and 3.0 eV for rutile phase) [7]. Significant attempts have been made to extend the light absorption of  $\text{TiO}_2$  further to the visible light region by modifying or using doping technique [8]. Doping  $\text{TiO}_2$  with nonmetal and/or metal atoms has attracted impressive attention due to its photoresponse in the visible light region. Different metals, such as Cd [9], Pt [10], Cu [11], Fe [12], and Co [13], have been used to tune the electronic structure and improve the photocatalytic activity of  $\text{TiO}_2$ . However, reported results showed that metal doping might cause thermal instability and increase of carriers trapping, which can reduce the photocatalytic efficiency. Recently, significant efforts have been made to modify  $\text{TiO}_2$  with nonmetals, such as S [14], C [15], I [16], N [17], P [18], and F [19], to efficiently extend the light absorption from the UV to the visible light region. Among the various types of non-metal doped, nitrogen doped  $\text{TiO}_2$  has been recognized as one of the best approaches to enhance the photocatalytic performance of  $\text{TiO}_2$  in solar light [20, 21].

In this work, we successfully prepared pure and N-doped  $\text{TiO}_2$  nanoparticles using the sol-gel method. The prepared samples from the points of view of morphological, structural, and textural properties were

characterized. The photocatalytic activities of the as-synthesized catalysts were evaluated to degrade 4-Chlorophenol (4-CP) under solar light, and photocatalytic degradation mechanism and pathway have been explored.

## 2. Experimental

### 2.1. Materials

Titanium (IV) isopropoxide (TTIP 99.9 %) from Sigma-Aldrich was purchased and utilized as the precursors of titanium. Chemicals including sodium hydroxide, 37 % of hydrochloric acid, glacial acetic acid and urea were purchased from Merck Company. 4-CP was purchased from Sigma-Aldrich. All materials were of analytical grade and used without further purifications.

### 2.2. Synthesis of N-doped $\text{TiO}_2$ photocatalysts

Sol-gel method was used to synthesize pure and N-doped  $\text{TiO}_2$  nanoparticles with titanium tetra isopropoxide (TTIP) as the titanium source and urea as a dopant source. To prepare N-doped  $\text{TiO}_2$ , 5.2 mL TTIP was taken in a beaker and 8 mL glacial acetic acid was added as a modifier. The mixture was stirred for 30 min; then, 28 mL distilled water that contains a desired amount of urea was added to the solution. The precipitate formed slowly dissolved on further addition of water; finally, transparent sol was obtained. After stirring the mixture for another half an hour, sol was allowed to form a gel on a steam bath. The obtained gels were dried in an electric oven set at 70 °C for 24 h. The color of powders changes to white after calcination at 400 °C for 3 h.

### 2.3. Characterization

The phase structure of the samples was analyzed by a Philips PW1730 X-ray diffractometer, with  $\text{Cu K}_\alpha$  radiation

( $\lambda=0.15406$  nm) at a scan rate of  $0.05^\circ$  in the range of  $2\theta=5^\circ-80^\circ$ , operated at 15 kV and 20 mA. Fourier transform infrared (FTIR) spectroscopic analysis of the prepared materials was recorded on a PerkinElmer spectrum II. N<sub>2</sub> adsorption-desorption isotherms were conducted on a Belsorp-mini II adsorption apparatus with all samples degassed at 120 °C prior to measurements. The BET surface area was investigated by a single point BET technique using the adsorption data at the relative pressure (P/P<sub>0</sub>) at 77 K. Average pore size and total pore volume of the catalysts were collected by a Barrett-Joyner-Halenda (BJH) model. The morphology of the materials was characterized by a TESCAN MIRA3 field emission scanning electron microscope (FE-SEM) instrument equipped with energy dispersive X-ray (EDX) and energy dispersive spectroscopy (EDS) operating at 15.0 kV.

#### 2.4. Photocatalytic evaluation

The activities of the TiO<sub>2</sub> photocatalysts were explored via the photocatalytic degradation of 4-CP solution under solar light. The experiments were carried out in a 240 mL photoreactor, equipped with magnetic stirring (MR 3001 K, Heidolph). Then, 0.2 g of catalyst was added to 100 mL aqueous solution containing 10 mg 4-CP. Before the solar irradiation, the mixture was maintained in the dark under stirring for 30 min to ensure the well performance of an adsorption-desorption equilibrium. The pH of solution was adjusted by adding 0.1 N HCl or NaOH and monitoring with a digital pH meter (Jenway 3510). After the photocatalytic reaction, the catalysts were separated by centrifugation (PIT320, Universal), and the resulting transparent solution was examined

using UV spectroscopy (UV2100, Unico). Finally, for calculation of the 4-CP degradation percentage amount, the following equation was used:

$$\% \text{ Degradation} = \left[ \frac{C_0 - C}{C_0} \right] \times 100 \quad (1)$$

where C<sub>0</sub> is the initial concentration of 4-CP and, C is the concentration of 4-CP at any time.

### 3. Results and discussion

#### 3.1. XRD

Fig. 1 shows the XRD patterns of pure TiO<sub>2</sub> and N-doped TiO<sub>2</sub> with different concentrations of nitrogen dopants. As shown in Fig. 1, diffraction peaks observed at  $2\theta$  values of  $25.27^\circ$ ,  $37.89^\circ$ ,  $48.03^\circ$ ,  $54.17^\circ$ ,  $55.42^\circ$ ,  $62.74^\circ$ ,  $68.75^\circ$ ,  $70.48^\circ$ , and  $75.14^\circ$  were indexed to (101), (004), (200), (105), (211), (204), (116), (220), and (215) crystal planes of anatase phase of TiO<sub>2</sub> (JCPDS card No. 21-1272). No characteristic peak related to nitrogen was observed which is attributed to low concentration of dopant, indicating that nitrogen doping has no effect on crystalline structure of TiO<sub>2</sub> anatase phase. The crystalline size of the as-prepared samples was calculated by Debye-Scherrer equation:

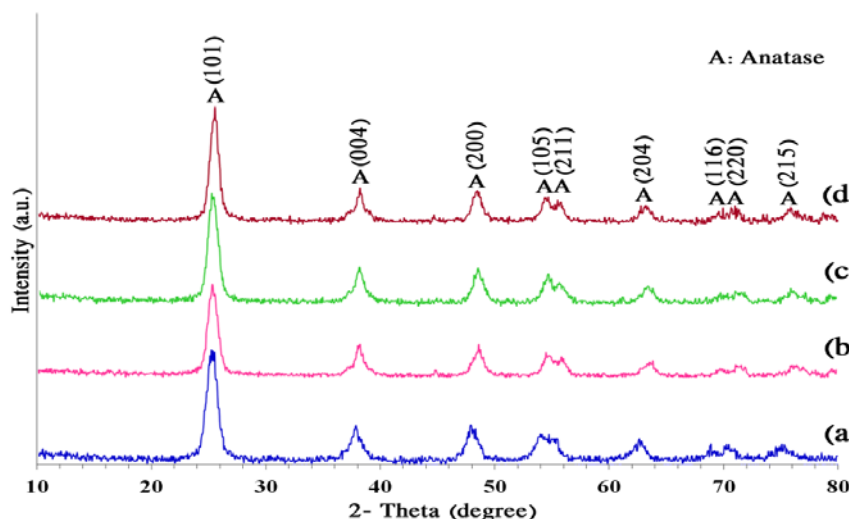
$$D = \frac{K\lambda}{\beta \cos \theta} \quad (2)$$

where D is the crystalline size,  $\lambda$  is the wavelength of X-ray radiation (0.1541 nm), K is the constant usually taken as 0.89, and  $\beta$  is the peak width at half-maximum height after subtraction of equipment broadening,  $2\theta=25.27^\circ$  for the anatase phase of TiO<sub>2</sub>.

The mean crystal sizes of pure TiO<sub>2</sub>, 1 %, 3 %, and 5 % wt N-doped were found to be 14, 18, 21, and 23 nm, respectively. As compared to pure TiO<sub>2</sub>, an increase in crystallite size for N-doped TiO<sub>2</sub> was

observed. This is attributed to the fact that the doping of nitrogen on  $\text{TiO}_2$  helped crystalline growth and caused an increase in size of prepared nanoparticles [22]. Moreover, in location of anatase peak (101) plane N-doped

samples, a small shift to higher diffraction angles was observed which is attributed to incorporation of  $\text{N}^{3-}$  in the  $\text{TiO}_2$  matrix and replacement by  $\text{O}^{2-}$  in unit cell [23].

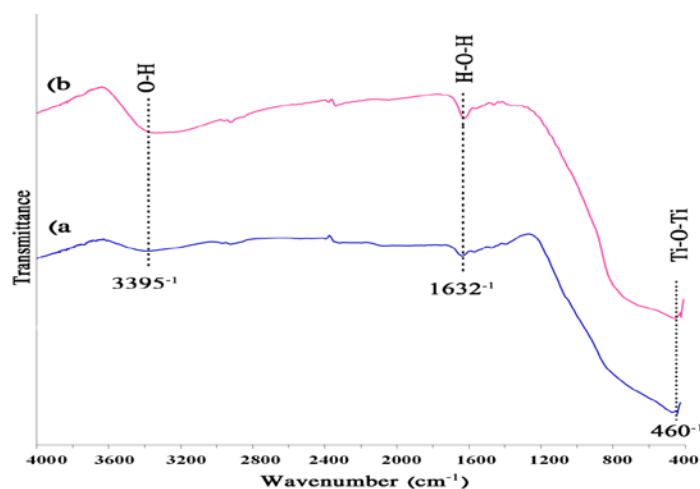


**Figure 1.** XRD patterns of a) bare, b) 1 % N-Doped, c) 3 % N-Doped, and d) 5 % N-Doped  $\text{TiO}_2$ .

### 3.2. FTIR

Fig. 2 depicts the FTIR spectra of the pure  $\text{TiO}_2$  and N-doped  $\text{TiO}_2$  in the range of  $400\text{--}4000\text{ cm}^{-1}$ . Obtained results obviously showed that, for both samples, there is a stretching vibration at  $460\text{ cm}^{-1}$ , which can be ascribed to the vibration of Ti-O-Ti bond [24]. As seen in Fig. 2, a broad peak located at  $3395\text{ cm}^{-1}$  appears for the O-H stretching

vibration of Ti-OH and  $\text{H}_2\text{O}$ , revealing the existence of hydroxyl groups in the matrix of pure and N-doped  $\text{TiO}_2$  [25]. Besides, the absorption band at  $1632\text{ cm}^{-1}$  is due to the presence of H-O-H bending vibration, which is probably due to the re-absorption of water from the atmosphere on  $\text{TiO}_2$  nanoparticles [26].



**Figure 2.** FTIR spectra of a) bare and b) 3 % N-Doped  $\text{TiO}_2$ .

### 3.3. N<sub>2</sub> adsorption

The surface area, total pore volume, and pore diameter of the specimens were evaluated using the N<sub>2</sub> adsorption method. According to the IUPAC nomenclature, the N<sub>2</sub> adsorption isotherms of bare TiO<sub>2</sub> and N-doped TiO<sub>2</sub> (Fig. 3) fit type IV, with a H<sub>2</sub> hysteresis loop, which reveals the mesoporous structure [27]. The type H<sub>2</sub> hysteresis loop indicates that pore structure is made up of interconnected networks of different sizes and shapes. The surface area values (S<sub>BET</sub>) of bare and N-doped TiO<sub>2</sub> are 109.42 and 101.23 m<sup>2</sup>g<sup>-1</sup>, respectively. As compared to bare TiO<sub>2</sub>, a

decrease in S<sub>BET</sub> N-doped TiO<sub>2</sub> was observed which is ascribed to an increase in crystal size of TiO<sub>2</sub> by nitrogen doping [23]. The relative Barrett-Joyner-Halenda (BJH) pore-size distributions of the catalysts are presented in the set of Fig. 3. The average pore size was collected from the maximum of pore-size distribution curves [22]. The pore-size distribution curve of the synthesized materials demonstrated the mesopores of ~4 nm. The total pore volumes of the bare and N-doped TiO<sub>2</sub> are 0.2312 and 0.2004 cm<sup>3</sup>g<sup>-1</sup>, respectively.

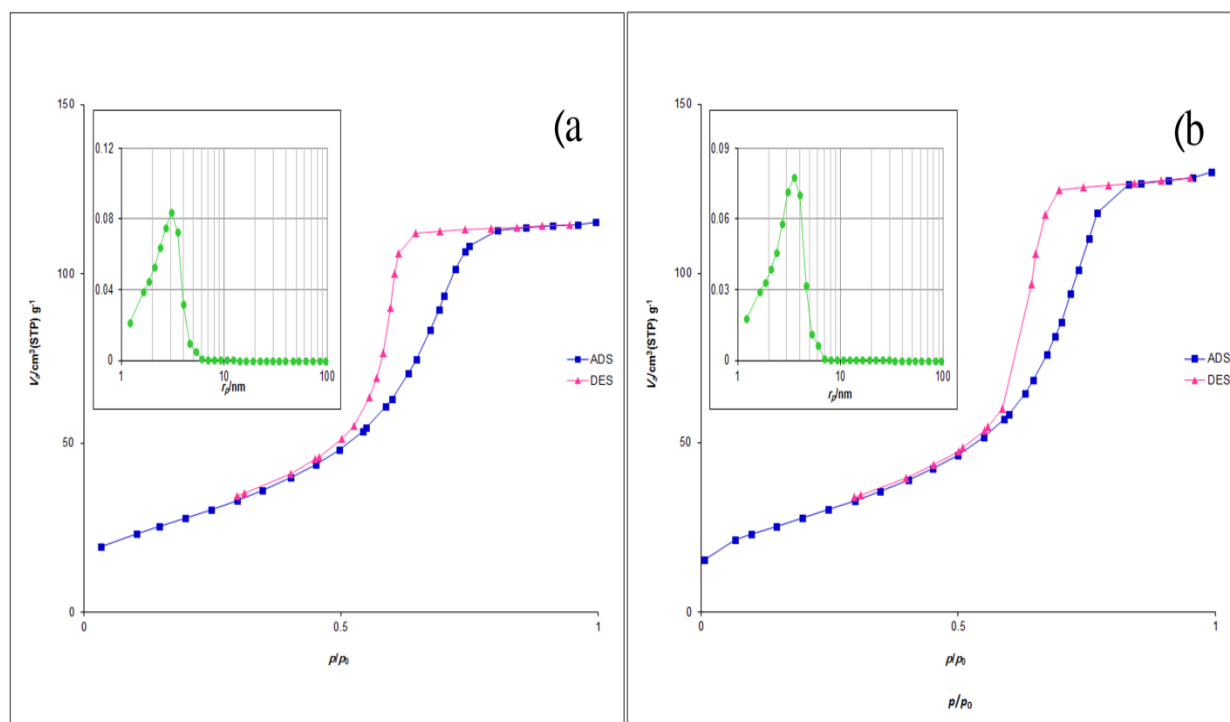


Figure 3. Adsorption-desorption spectra of the a) bare and b) 3 % N-Doped TiO<sub>2</sub>.

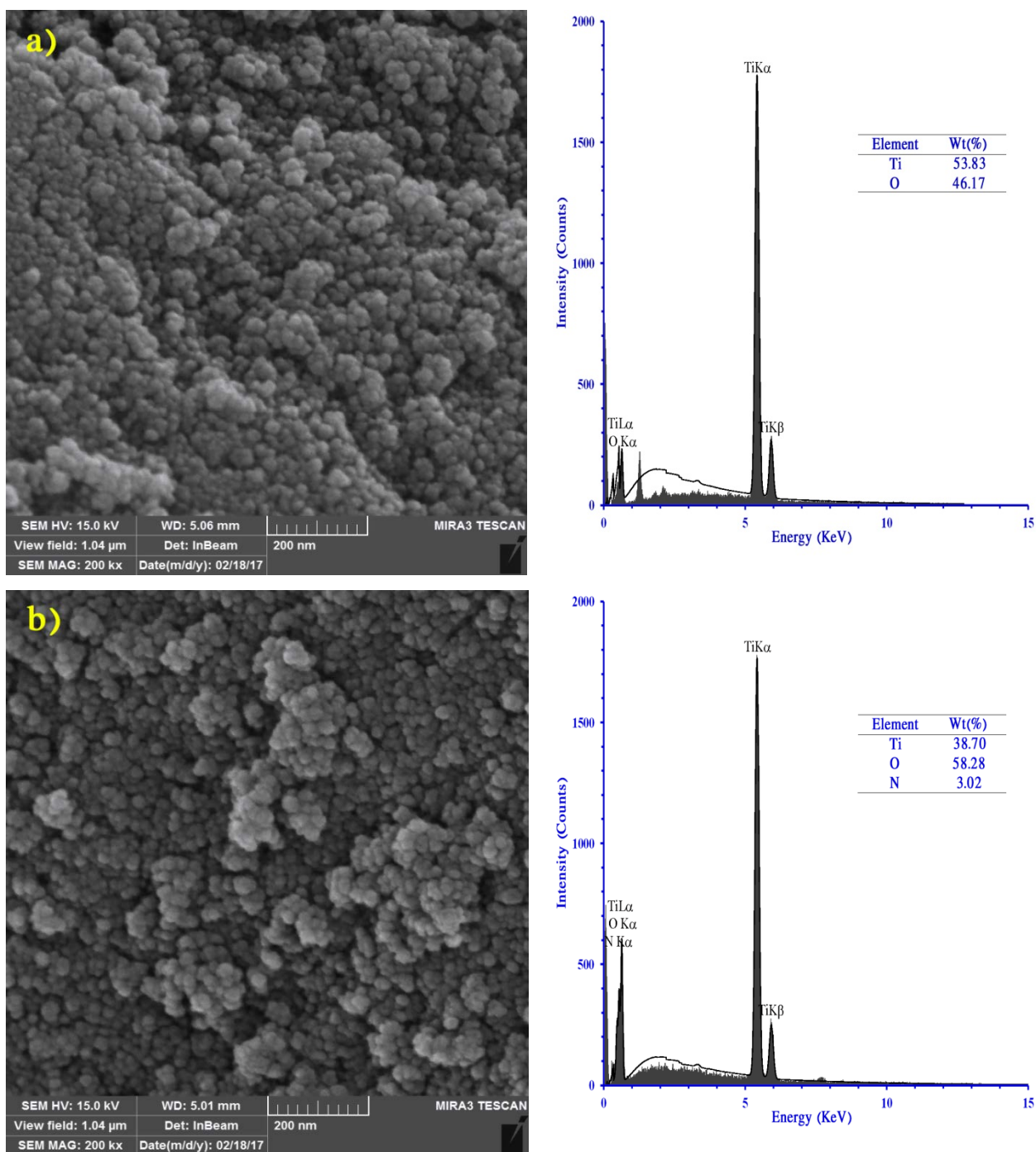
### 3.4. FE-SEM

To obtain information about the particles morphology, some selected powders were investigated by field emission scanning electron microscopy (FE-SEM). Fig. 4 gives FE-SEM images of pure and N-doped TiO<sub>2</sub>. Both bare and N-doped TiO<sub>2</sub> exhibit particle-like morphology with an irregular spherical shape and an average particle size of ~0.01

μm. Besides, slight agglomeration is detected in the samples that leads to the difference between calculated crystalline size by Scherer's equation and FE-SEM images [28]. The elemental compositions of the specimens were investigated by EDX and EDX spectra of bare and N-doped TiO<sub>2</sub>, exhibiting signals directly associated to the dopant. The spectrum demonstrates that the general

components are Ti and O with small levels of nitrogen. This finding corroborates the formation of N-doped TiO<sub>2</sub>. According to the obtained data from EDX analysis, N-doped TiO<sub>2</sub> is composed of 38.70 % titanium, 58.28 % oxygen, and 3.02 % Nitrogen. Except for Ti, O and N, no other peaks were

recognized in the spectrum, confirming the excellent purity of fabricated samples. Elemental mapping was performed by EDS to investigate the spatial distribution of elements in samples. As illustrated in Fig. 5, elements, including Ti, O, and N, were recognized and homogenously dispersed.



**Figure 4.** FE-SEM images of a) bare and b) 3 % N-Doped TiO<sub>2</sub>, along with corresponding EDX micrographs.



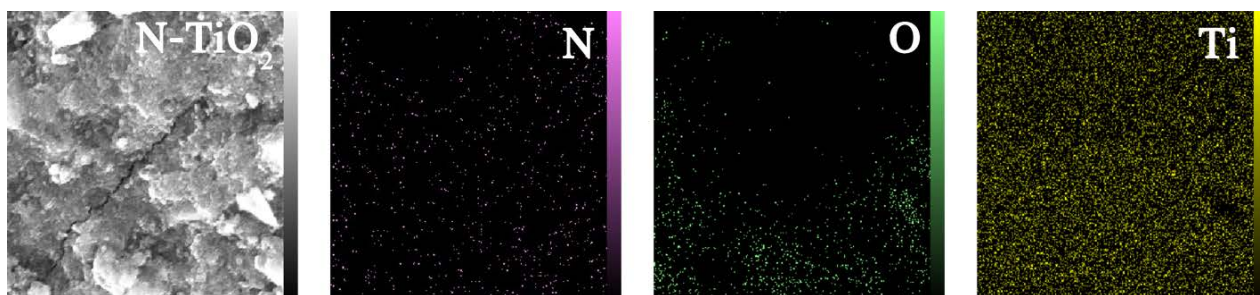


Figure 5. Elemental mapping of 3 % N-Doped TiO<sub>2</sub>.

### 3.5. Photocatalytic performance of synthesized samples

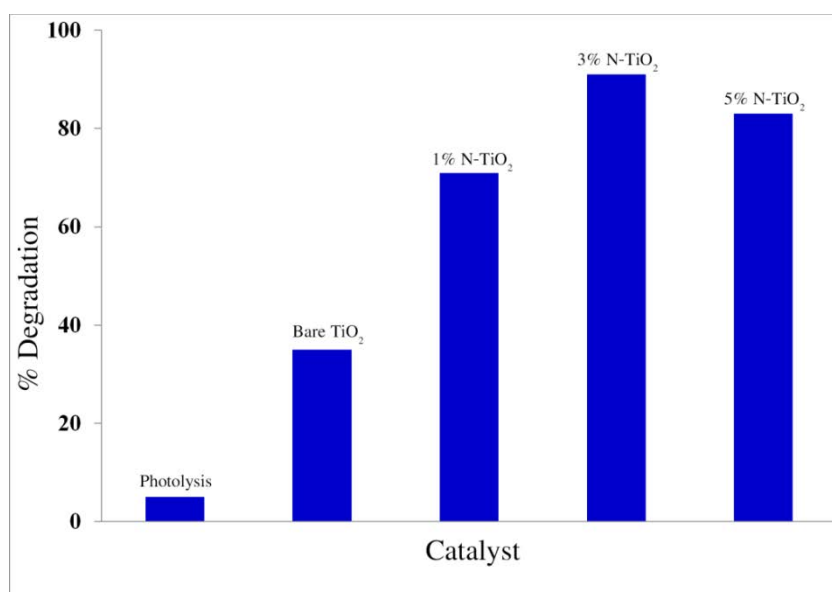
The photocatalytic performances of the prepared catalysts were tested for degradation of 4-CP under solar light illumination. The percentage of 4-CP degradation as a function of catalyst types is presented in Fig. 6. The catalysts including pure TiO<sub>2</sub>, 1 % wt, 3 % wt, and 5 % wt N-doped TiO<sub>2</sub> were examined, in which, for comparison purposes, 4-CP degradation in the absence of catalyst was tested. The obtained results show that, under solar irradiation after 8 h, very low degradation of 4-CP was detected [29] in the absence of catalyst, indicating that the photolysis of 4-CP could not undergo under solar irradiation. The percentage of 4-CP degradation on the pure TiO<sub>2</sub> under solar irradiation is low (36.2 %). After 8 h of illumination, no impressive removal was detected for the pure TiO<sub>2</sub>. By contrast, all nitrogen doped specimens showed higher activity compared to pure TiO<sub>2</sub>, indicating that doping enhanced the photocatalytic performance of TiO<sub>2</sub> under solar irradiations. This finding could be ascribed to the nitrogen excellently capturing the photo-induced electrons, leading to impedance of their recombination with holes and enhancement of the photocatalytic activity [30]. The rate of 4-CP degradation increased with increasing nitrogen amount up to 3 % wt N and, then, a decrease of the highest content of dopants.

This phenomenon may relate to the fact that by increasing dopants concentration, the number of N<sup>3-</sup> ions substituted by the O<sup>2-</sup> increased, leading to the increase of oxygen vacancy and Ti<sup>3+</sup>; thus, an improvement in photocatalytic activity is produced. However, a number of Ti<sup>3+</sup> and oxygen vacancy sites converted the recombination centers of photo-induced holes and electrons (h<sup>+</sup>/e<sup>-</sup>) when the dopants content increased, thus causing the reduction of photocatalytic performance [28].

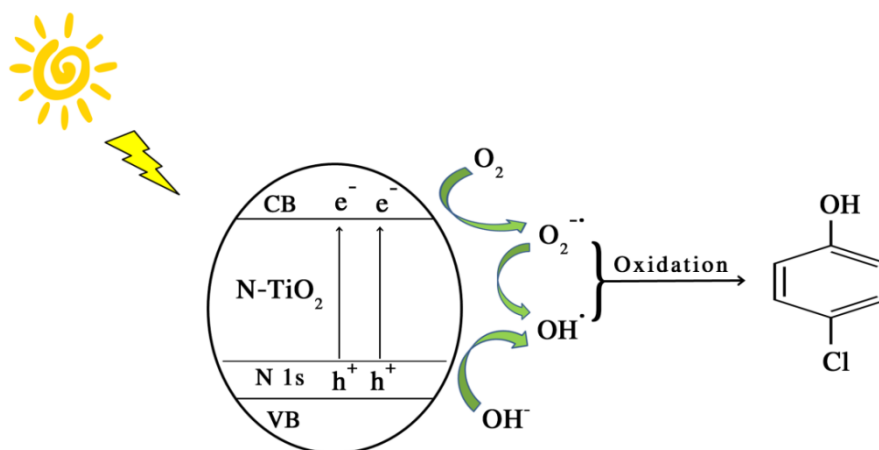
### 3.6. Photocatalytic degradation mechanism and pathway

The process of 4-CP photocatalytic degradation starts with absorption of an impressive number of photons by photocatalyst and photo-induced electrons and holes formed on the photocatalyst surface as illustrated in Scheme 1. As is known, the non-metal dopants do not shift the conduction band (CB) position of TiO<sub>2</sub>; thus, the electrons are promoted from the N-impurity level to the CB [31]; however, the positive holes are generated in the valence band (VB) [32]. On the one hand, the excited state electrons can be trapped by the dissolved O<sub>2</sub> adsorbed on the TiO<sub>2</sub> surface, thus forming the superoxide anion radicals (<sup>-</sup>O<sub>2</sub>). Then, superoxide anion radicals <sup>-</sup>O<sub>2</sub> react with adsorbed H<sub>2</sub>O to produce H<sub>2</sub>O<sub>2</sub> generating hydroxyl radicals (<sup>•</sup>OH) [33]. On the other hand, the photo-induced holes in VB can react

with  $\text{OH}^-$  to generate more  $\cdot\text{OH}$  radicals [34]. These series of reactions are listed as follows:



**Figure 6.** Photodegradation amount of 4-CP after 8 h solar light irradiation in the presence 2 g/L catalyst, pH of 4, and 4-CP concentration 10 mg/L.



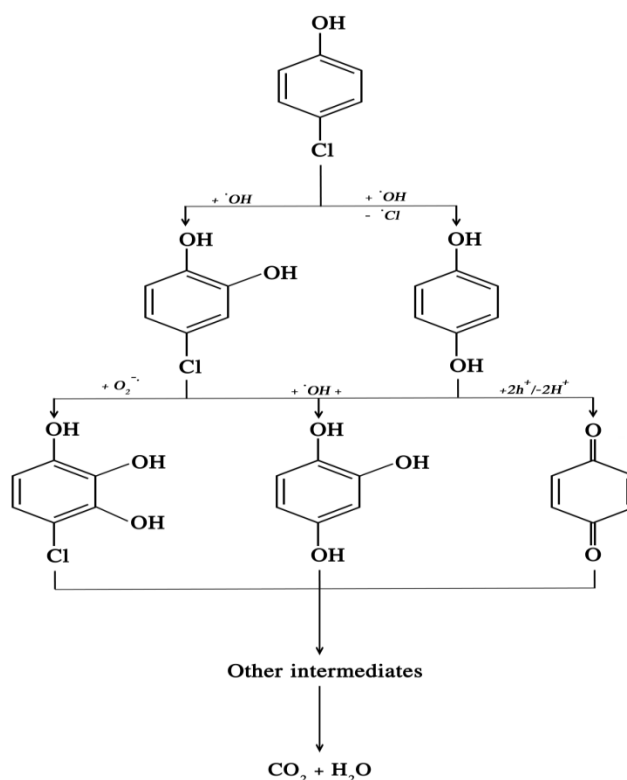
**Scheme 1.** The proposed mechanism for 4-CP degradation over N-doped  $\text{TiO}_2$  under solar light.

After generating  $\text{O}_2^{\cdot-}$  and  $\cdot\text{OH}$  as the most important oxidative radicals, these radicals attack 4-CP molecule. The proposed

degradation pathway of 4-CP by N-doped  $\text{TiO}_2$  photocatalyst is illustrated in Fig. 7. During the 4-CP oxidation, a number of

aromatic intermediates are formed whose five main intermediates include hydroquinone (HQ, C<sub>6</sub>H<sub>6</sub>O<sub>2</sub>), 4-Chlorocatechol (4-CC, C<sub>6</sub>H<sub>5</sub>ClO<sub>2</sub>), Benzoquinone (BQ, C<sub>6</sub>H<sub>4</sub>O<sub>2</sub>), Hydroxyhydroquinone (HHQ, C<sub>6</sub>H<sub>6</sub>O<sub>2</sub>), and 5-Chloro-1,2,4-benzenetriol (C<sub>6</sub>H<sub>5</sub>ClO<sub>3</sub>) [35-37]. In the first step, 4-CP is oxidized to 4-CC

and HQ; then, HQ is further oxidized into BQ and HHQ. Meanwhile, 4-CC is changed to HHQ and 5-Chloro-1,2,4-benzenetriol. Finally, after many steps of other intermediates oxidation, complete mineralization to CO<sub>2</sub>+H<sub>2</sub>O was achieved.



**Figure 7.** The proposed degradation pathway of 4-CP by N-doped TiO<sub>2</sub>.

#### 4. Conclusions

In the present study, pristine and N-doped TiO<sub>2</sub> were obtained by the simple sol-gel method. The physicochemical, morphological, and textural characteristics of the obtained TiO<sub>2</sub> samples were characterized by advanced analysis techniques. The photocatalytic activity of the samples was evaluated for degradation of 4-CP under solar irradiation. The photodegradation process was optimized using dopant concentration of 3 % wt nitrogen. Degradation efficiency of 91 % was attained at pH 4 after 8 h of solar irradiations. The results of the catalytic activity measurement demonstrated that 3 %

wt N-doped TiO<sub>2</sub> has higher photocatalytic degradation efficiency as compared with 5 % wt N-doped, 1 % wt N-doped, and bare TiO<sub>2</sub>. Therefore, it was concluded that doping of the nitrogen could significantly improve the photocatalytic activity of the as-prepared photocatalysts due to the efficient inhibition of the recombination of photo-generated electron-hole pairs. The band gap energy was reduced by the formation of additional energy level above the valence band by nitrogen doping. Both effects contribute synergistically to enhancing photocatalytic activity of the N-doped TiO<sub>2</sub>.

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