

## PHOTOCATALYTIC DEGRADATION OF 2,4-DICHLOROPHENOXYACETIC ACID ON N-DOPED TITANIUM DIOXIDE

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### Abstract

Photocatalytic degradation, especially heterogeneous catalytic oxidation is an emerging method for removing organic contaminants in water. TiO<sub>2</sub> catalyst with excellent mechanical and thermal properties has been paid much attention. However, TiO<sub>2</sub> catalyst suffers from reduced photonic efficiency. In this study TiO<sub>2</sub> catalyst has been prepared by sol-gel method and modified in presence of urea by thermal treatment at 450 °C for 1 hour with heating rate of 5 °C/min. This catalyst was used in photocatalytic degradation of 2,4-Dichlorophenoxyacetic acid (2,4-D). The influence of reaction parameters such as radiation source, pH, 2,4-D initial concentration and catalyst content was investigated. Under UVA radiation, with 2,4D solution of 60 ppm at pH 3 and catalyst content of 0.6 g/L, the conversion was of 63 %, but under VIS radiation only about 30 %.

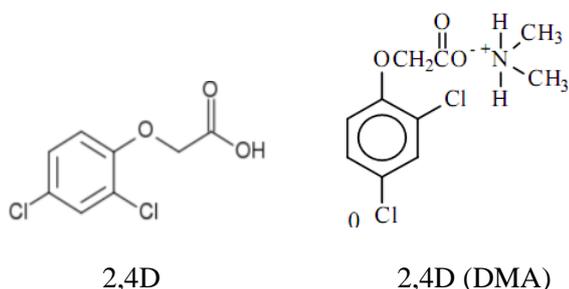
**Keywords.** TiO<sub>2</sub>, N-doped TiO<sub>2</sub>, 2,4-Dichlorophenoxyacetic acid, photocatalysis, UVA, VIS.

### 1. INTRODUCTION

During the last few decades the agrochemical industries have widely developed because of worldwide applications of pesticides and herbicides. These pesticides and herbicides are now abundantly found in water and food. The treatment of pollutants in water and air has nowadays attracted much interest, especially for chloroaromatic compounds such as 2,4-dichlorophenoxyacetic acid (2,4-D). This is a strongly acidic corrosive commercial herbicide containing an amount of free chlorophenol. In nature, chlorophenol could lastly exist and transform into dioxin (2,3,7,8-tetrachlorodibenzo-P-dioxin) which was listed as carcinogen (cancer-causing chemical). In addition to physical, biological methods for 2,4-D removal, many scientists have paid attention to photocatalytic degradation. Among the semiconductor photocatalysts (oxides, sulfides, etc.), TiO<sub>2</sub> has been most extensively investigated due to its high photocatalytic activity, chemical and biological stability, insolubility in water, acidic and basic media, non-toxicity and availability. Besides, TiO<sub>2</sub> photocatalysis is now being used in practical applications such as self-cleaning, sterilization, deodorizing and air-cleaning [1-4]. However, TiO<sub>2</sub> has rather large bandgap of 3.0-3.2 eV, and thus only a small fraction of the solar spectrum ( $\lambda < 380$

nm, corresponding to the UV region which takes only 3-5 % sunlight) is absorbed. It is thought that optimization of TiO<sub>2</sub> structure and properties are able to extend the absorption from the UV to visible light region and to enhance the photocatalytic efficiency. Doping metals or non-metals into TiO<sub>2</sub> structure has been investigated using various ways such as sol-gel, hydrothermal, hydrolysis methods...etc. N-doped TiO<sub>2</sub> materials have been synthesized by hydrolysis of TTIP in a water/amine mixture and the post treatment of the TiO<sub>2</sub> sol with amines or directly from a Ti-bipyridine complex or by ball milling of TiO<sub>2</sub> in a NH<sub>3</sub> water solution. N-doped TiO<sub>2</sub> nanomaterials were also obtained by heating TiO<sub>2</sub> under NH<sub>3</sub> flux at 500-600 °C or by calcination of the hydrolysis product of Ti(SO<sub>4</sub>)<sub>2</sub> with ammonia as precipitator or by decomposition of gas-phase TiCl<sub>4</sub> with an atmosphere microwave plasma torch or by sputtering /ion-implanting techniques with nitrogen or N<sub>2</sub> gas flux [5-8]. Asashi *et al.* found N 2p state hybrids with O 2p states in anatase TiO<sub>2</sub> doped with nitrogen because their energies are very close, and thus the band gap of N-TiO<sub>2</sub> is narrowed and able to absorb visible light [9]. In their work, Tran *et al.* observed that the N-doped TiO<sub>2</sub> refluxed in H<sub>2</sub>O<sub>2</sub> solution possessed higher surface area and higher photocatalytic activities than those refluxed in water [11]. The aim of this work was to study the efficiency of nitrogen-doped and

undoped TiO<sub>2</sub> as photocatalysts in the removal of 2,4-D in solution. The test on Cantosin 600DD solution -commercial 2,4D- was also fulfilled.



## 2. EXPERIMENTAL

### 2.1. Chemicals

The highly pure chemicals used as received such as Tetrabutyl orthotitanate (TBOT), Urea CO(NH<sub>2</sub>)<sub>2</sub>, Potassium hydroxide KOH, Sulfuric acid H<sub>2</sub>SO<sub>4</sub> were from Merck, TiO<sub>2</sub> -Anatase from Reade (England); TiO<sub>2</sub>-Rutile from Dupont, 2,4-Dichlorophenoxyacetic acid (2,4D) from China, 2,4D (DMA)-Cantosin 600DD solution from CPC factory (CanTho).

### 2.2. Procedure

Preparation and modification of TiO<sub>2</sub>: Anatase TiO<sub>2</sub> was prepared by sol-gel method from TBOT as precursor [1]. A quantity of TPBT was dropped into distilled water at ambient temperature with molar ratio TBOT:H<sub>2</sub>O = 1:30 at pH = 5. The solution was continuously mixed for 24h followed by washing and filtering then drying at 80 °C for 24 hours and heating at 400 °C for 1 hour. The obtained white powder TiO<sub>2</sub> (sample **K**) has been investigated by XRD, DRS, EDS, SEM and TEM images. The mixture of TiO<sub>2</sub> and urea with weight ratio of TiO<sub>2</sub>:urea = 1:0.5 and 1:1 (samples **KN1**, **KN2**, respectively) was heated with a temperature program of 5°C/min from ambient temperature to 450°C for one hour. The obtained yellow powder modified TiO<sub>2</sub> has been analysed with XRD, DRS, EDS, SEM and TEM images. For comparison the commercial anatase (sample **A**) and rutile (sample **R**) were similarly treated to become modified TiO<sub>2</sub> (samples **AN** and **RN**).

### 2.3. Characterisation of materials

The X-ray powder diffraction patterns of the samples were collected using D8 Advance - Bruker

with CuK<sub>α</sub> X-ray radiation with a 1.5406 Å wavelength. A beam voltage of 45 kV and a 40-mA beam current and a scanning rate of 1.5°/min were used. The nitrogen sorption measurements were performed using a Micromeritics system (Petrolab - Hanoi University of Technology). The adsorption and desorption experiments were done at 77 K after initial pretreatment of the samples by degassing at 200°C for 12 h. The specific surface areas of the samples were determined by BET method, using adsorption data in a relative pressure range of P/P<sub>0</sub> = 0.05-0.25. Pore size distribution was calculated by Barrett-Joyner-Halenda (BJH) method. Thermogravimetric analysis (TGA) was made with a Netzsch TG 209. Sample was heated to 800 °C in nitrogen atmosphere with a heating rate of 20°C/min. The morphology was studied by field emission scanning electron microscopy (FESEM) on a JEOL-JSM-6500F instrument with a Schottky emitter at an accelerating voltage of 2 kV and a beam current of about 1 μA. The surface morphology was performed on a Transmission Electron Microscope (TEM) (JEM-1400, JEOL, Japan), operating at an acceleration voltage of 200 kV; for these observations, the sample was prepared by dropping the CuO nanoparticles ethanol dispersion on carbon-coated Cu grids. DRS of the TiO<sub>2</sub> derivatives were made on V-550-C2951309 in the range of wavelength about 300-700 nm.

### 2.4. Investigation of photocatalytic activity of catalysts

The catalytic photodegradations of 2,4D were carried out in liquid phase. The UV photoirradiation was carried out using a portable lamp (18W; Reptisun, China) of 365 nm wavelength (650 lux) keeping the reactor at a horizontal position at a distance of 10 cm. In the adsorption step, a solution of 2,4-D (V = 500 mL, C = 90 ppm, pH = 3) was put into the reactor containing 0.25g of catalyst with strong agitation in the dark. The samples (5mL) were withdrawn after each 5 mins, centrifuged (5 mins, 2500 rpm) then the measurement of the absorbance was done. The adsorption equilibrium time was determined at constant absorbance equivalent to initial concentration of 2,4D solution. For photodegradation reaction, after obtaining the adsorption equilibrium, the UV (or VIS) irradiation of 26W power was started and the sampling was the same. The conversion of 2,4D (h%) was calculated by the equation:

$$h(\%) = \frac{C_{2,4-D}^o - C_{2,4-D}}{C_{2,4-D}^o} \times 100$$

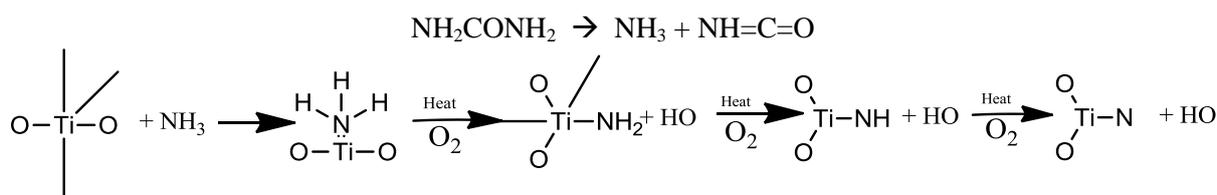
in which,

$C_{2,4-D}^o$  (ppm): initial concentration (after adsorption) of 2,4-D solution.

$C_{2,4-D}$  (ppm): concentration of 2,4-D solution at time t.

### 3. RESULTS AND DISCUSSION

Formation of N-TiO<sub>2</sub>: Tetrabutyl orthotitanate



Characterisation of products: XRD patterns:

The characteristic peaks of anatase at  $2\theta = 25.3^\circ; 37.8^\circ; 48.1^\circ; 55.1^\circ$  and rutile at  $27.5^\circ; 36.4^\circ; 41.7^\circ; 55.1^\circ$  shown in figure 1 indicated that solgel method with TOBT as precursor gave anatase rather than rutile TiO<sub>2</sub>.

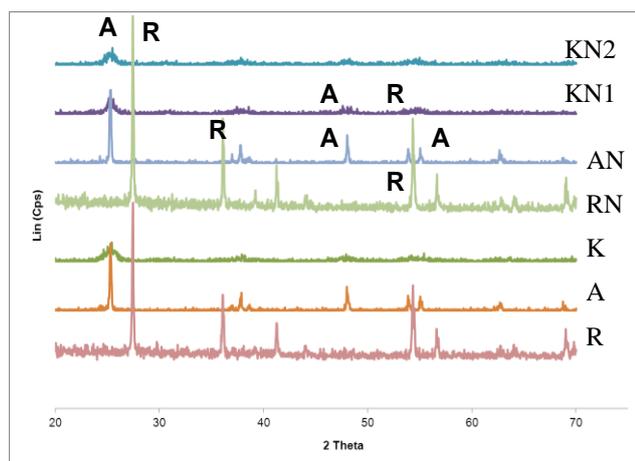


Fig. 1: XRD of various TiO<sub>2</sub> samples

Table 1: Results from EDS analysis

| Samples         | Mass content (%) |       |       |
|-----------------|------------------|-------|-------|
|                 | N                | O     | Ti    |
| AN              | 1.38             | 43.70 | 54.92 |
| KN <sub>1</sub> | 1.52             | 42.34 | 56.14 |
| KN <sub>2</sub> | 1.68             | 42.11 | 56.21 |
| RN              | 0.25             | 44.83 | 55.42 |

Energy Diffractive Spectroscopy (EDS) gave information about atomic contents in samples (table 1). The urea quantity added in KN<sub>2</sub> was double greater than that of KN<sub>1</sub> but there was no

hydrolysed in water to form  $[\text{Ti}(\text{OH})_n\text{X}_m]^{z-}$  ions. As the alkoxide reacted with water the metallic ions enhanced their coordination by using d orbitals to receive free electrons of oxygen atoms of OH ligands. The bonding between TiO<sub>6</sub><sup>2-</sup> octahedrals from dehydration of  $[\text{Ti}(\text{OH})_n\text{X}_m]^{z-}$ . Anatase phase TiO<sub>6</sub><sup>2-</sup> has side-by-side structure while rutile has angle-by-angle one [7]. When heating TiO<sub>2</sub> in solid nitrogen containing medium, the urea thermal decomposition formed powder modified TiO<sub>2</sub>:

considerable change in nitrogen content in both samples. From Diffuse Reflectance Spectra (DRS) of all the samples we could determine their bandgap energy values. It can be seen that the nitrogen modification for TiO<sub>2</sub> (3.16 eV) has been moving absorption wavelength towards VIS region (from 392 to 408 nm) thus KN<sub>1</sub>, KN<sub>2</sub> had smaller bandgaps (3.05 eV and 3.04 eV, respectively). This concerned a structure change or the formation of surface defect in the nitrogen modification of TiO<sub>2</sub>. The bandgap energy values calculated from DRS results were listed in table 2. Asashi et al. [9] has found N 2p state hybrids with O 2p states in anatase TiO<sub>2</sub> doped with nitrogen because their energies are very close, and thus the band gap of N-TiO<sub>2</sub> is narrowed and able to absorb visible light.

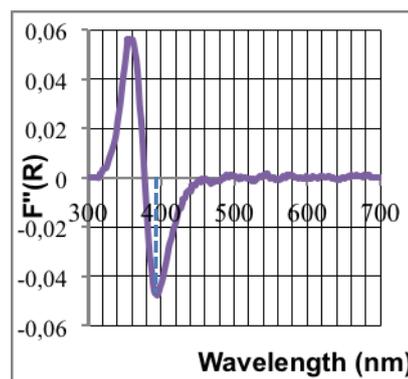


Fig. 2: Result from EDS analysis

Photocatalytic activity. The preliminary tests showed that the direct decomposition of 2,4D under UV or VIS light without catalyst happened very slowly (< 0.5 % of conversion after 8 h). It is noted that without irradiation the equilibrium adsorption of 2,4D on catalysts was obtained after about 20

mins where its initial concentration of solutions were determined.

Table 2: Results from DRS analysis

| Sample          | $\lambda$ (nm) | $E_g$ (eV) | S (m <sup>2</sup> /g) |
|-----------------|----------------|------------|-----------------------|
| K               | 392            | 3.16       | 129                   |
| KN <sub>1</sub> | 406            | 3.05       | 100                   |
| KN <sub>2</sub> | 408            | 3.04       | 100                   |
| A               | 392            | 3.16       |                       |
| AN              | 408            | 3.05       |                       |
| R               | 418            | 2.98       |                       |
| RN              | 416            | 2.97       |                       |

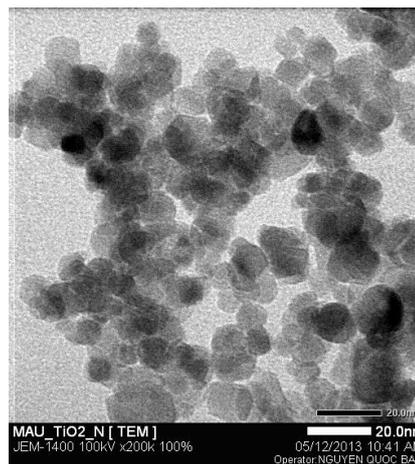


Fig. 3: SEM image of KN<sub>1</sub>

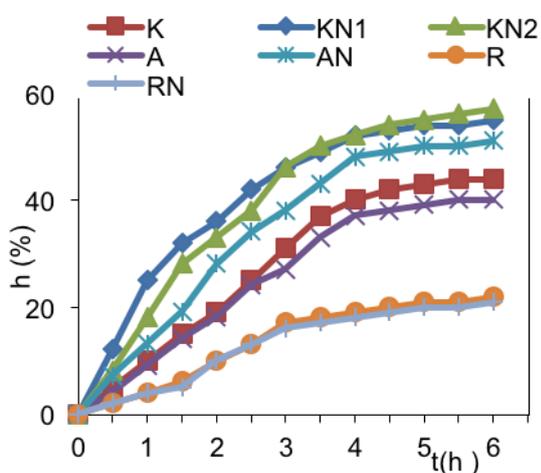


Fig. 4: Conversion of 2,4D under UVA irradiation on various catalysts

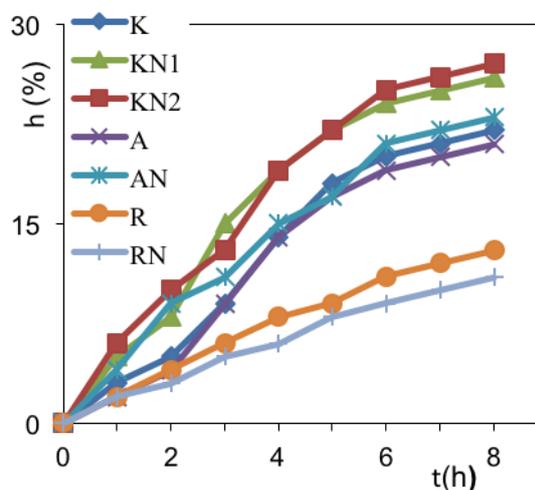


Fig. 5: Conversion of 2,4D under VIS irradiation on various catalysts

To investigate the photocatalytic activity of N-doped TiO<sub>2</sub> (AN, RN, KN<sub>1</sub>, KN<sub>2</sub>) and undoped TiO<sub>2</sub> (A, R, K) the degradation of 2,4D (Fig. 4, 5) was carried out using UVA and VIS light. As can be seen, the N-doped TiO<sub>2</sub> appeared to be somewhat more efficient (~ 60%) than the starting anatase TiO<sub>2</sub> powder (~ 40%), which was more pronounced after a prolonged time of irradiation. Such behavior was expectable since, as already mentioned, the absorption edge of the doped catalysts is shifted to the visible range and higher absorption. Additionally, in spite of the fact that N-doped TiO<sub>2</sub> showed slightly increased value  $E_g$  in comparison with TiO<sub>2</sub> (in the frames of the evaluation error), the higher photocatalytic activity of the former in the visible range can be also assigned to its higher absorption in this region.

The aim of the modification of TiO<sub>2</sub> catalysts was to reduce their bandgaps or to shift the maximum absorption wavelength to the visible

region. Table 2 showed a little change in  $\lambda$  or the absorption bands of KN<sub>1</sub> and KN<sub>2</sub> were nearer the VIS region than the others and followed the order in catalytic activity: R < RN < A < K < AN < KN<sub>1</sub> < KN<sub>2</sub>. However the difference in activity between KN<sub>1</sub> and KN<sub>2</sub> was rather slight, we have chosen KN<sub>1</sub> for following experiments.

The influence of pH was indicated in figure 6. In general, in acidic medium the photocatalytic degradation of 2,4D on KN<sub>1</sub> at pH = 3 is better than pH = 7 or pH = 10. It could be thought that in acidic medium the TiO<sub>2</sub> surface had positive charge while 2,4D as weak acid in hydrolysis gave negative charge. This could enhance the adsorption of 2,4D on TiO<sub>2</sub> surface then effective decomposition. In practice commercial 2,4D was normally used in the dimethylamine form named Cantosin-600DD and the influence of pH on its degradation was similar. In this case 2,4-D was an electron donor while Cantosin a proton donor. This proton adsorbed

photolysed electrons on catalyst surface available for redox reaction. Furthermore, the 2,4-D decomposition varied on changing  $\text{KN}_1$  catalyst content in order:  $0.7 \text{ g/L} < 0.4 \text{ g/L} < 0.5 \text{ g/L} < 0.6$

$\text{g/L}$ . This indicated the role of catalytic sites on surface in increasing catalyst content but an amount  $\text{KN}_1$  in excess could reduce light absorption.

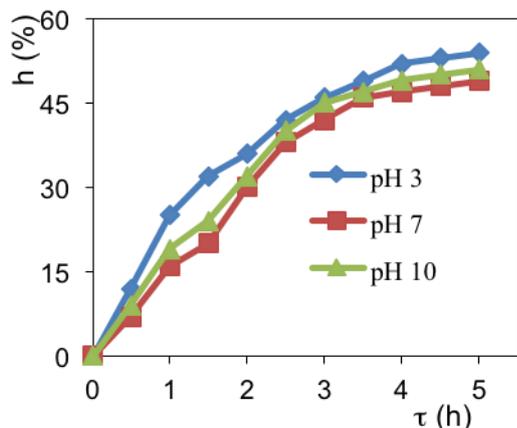


Fig. 6: Conversion of 2,4D at different pH under UVA irradiation on  $\text{KN}_1$

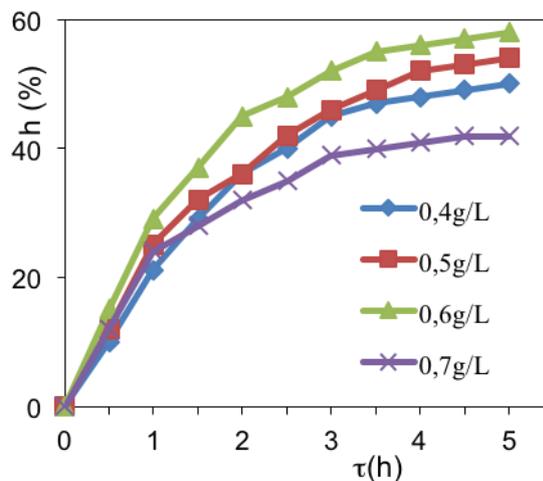


Fig. 7: Conversion of 2,4D in Cantosin at various content of  $\text{KN}_1$  under UVA irradiation

#### 4. CONCLUSION

$\text{TiO}_2$  catalyst prepared by sol-gel method has been modified in presence of urea by thermal treatment at  $450^\circ\text{C}$  for 1 hour with heating rate of  $5^\circ\text{C}/\text{min}$ . The catalyst has characteristic peaks at  $2\theta = 25.3^\circ$ ;  $37.8^\circ$ ;  $48.1^\circ$ ;  $55.1^\circ$  of anatase form with BET surface of about  $120 \text{ m}^2/\text{g}$ . On doping  $\text{TiO}_2$  by nitrogen, it can be observed an absorbance wavelength shift from 392 to 408 nm leading to reduced bandgap and enhanced efficiency in photocatalytic degradation of 2,4-Dichlorophenoxyacetic acid (2,4-D). Under UVA radiation, the conversion of 2,4D solution of 60ppm at pH 3 and catalyst content of  $0.6 \text{ g/L}$  was of 63 % but under VIS radiation only about 30 %.

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