CHEMICAL ENGINEERING TRANSACTIONS
VOL. 43, 2015
A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.aidic.it/cet
Chief Editors: Sauro Pierucci, Jiří J. Klemeš
Copyright © 2015, AIDIC Servizi S.r.l.,
**ISBN** 978-88-95608-34-1; **ISSN** 2283-9216
DOI: 10.3303/CET1543121

# A Novel Approach for the Production of Nitrogen Doped $TiO_2$ Nanoparticles

Yana Ruzmanova, Marco Stoller*, Marco Bravi, Angelo Chianese

Sapienza University of Rome, via Eudossiana 18, 00184, Rome
marco.stoller@uniroma1.it

In this study a visible light active nitrogen doped nanostructure titanium dioxide was synthesized by a simple mixing of Degussa P25 and Urea powder and further thermal treatment under the adequate conditions. Photocatalytic activity of produced nanoparticles was verified by providing of photocatalytic degradation of phenol aqueous solution. Mainly this work was focused on the investigation of the following effects: urea concentration, temperature treatment, catalyst loading and initial phenol concentration. Kinetics study was also carried out. The approach appears to be successful and may be applied for example during the photocatalytic treatment of wastewater streams without or with a limited aid of UV lamps.

## 1. Introduction

In recent years humanity has faced a number of critical environmental problems among which the shortage of drinking water in many parts of the world. According to the United Nations report (The United Nations World Water Development Report 4: Managing Water under Uncertainty and Risk, Vol. 1, 2012) “Around 700 million people in 43 countries suffer today from water scarcity and by 2025, 1.8 billion people will be living in countries or regions with absolute water scarcity, and two-thirds of the world's population could be living under water stressed conditions”. In search of an optimal solution of water pollution problem scientists have drawn attention to the heterogeneous photocatalysis because of its great potential to remove aqueous and air pollutants through complete mineralization. Among the known semiconductor photocatalysts titanium dioxide is the most widely used due to its high photocatalytic activity, chemical stability and low cost. Technologies for the synthesis of photocatalysts for industrial production already exist, by bottom-up approaches of core-shell-shell nanoparticles (Ruzmanova et al., 2013a), doped titania nanoparticles (Ruzmanova et al., 2013b) or undoped titania (Vaiano et al., 2014). As well, top-down approaches exists such as the commercial Degussa P25. In many wastewater treatment processes, such as those already adopted in the agricultural (Ochando et al., 2014), textile (Stoller et al., 2011) and tannery industries, photocatalysis may be used successfully to aid the purification by means of biotechnology (Cicci et al., 2013), NF (Stoller et al., 2014) or RO (Ochando and Stoller, 2014) membrane processes. Nevertheless there are a number of technological problems concerned with the industrial-scale using of $TiO_2$. For example, $TiO_2$ (anatase) has a relatively wide band gap 3.2 eV, therefore it can be excited only by UV light which is quite expensive and requires the use of special protective measures. This leads to high operating costs, which affects sensibly the total treatment costs.
In this study a visible light active nitrogen doped nanostructure titanium dioxide was synthesized and photocatalytic activity of produced nanoparticles was verified by providing of photocatalytic test in liquid phase. Phenol aqueous solution was adopted as a pollutant model. Commercial photocatalyst Degussa P25 was used as a base of doped nanoparticles. Urea was used as a precursor of nitrogen. The doping process suggested by Nawawi (Nawawi and Nawi, 2014) was adopted in this work.

Please cite this article as: Ruzmanova Y., Stoller M., Bravi M., Chianese A., 2015, A novel approach for the production of nitrogen doped tio2 nanoparticles, Chemical Engineering Transactions, 43, 721-726 DOI: 10.3303/CET1543121

## 2. Experimental procedure

### 2.1 Materials

The chemicals used in this work are reported in Table 1.

*Table 1: Chemicals used in the N-$TiO_2$ preparation procedure and photocatalitic degradation of phenol*

| Chemical | Formula | Purity |
|---|---|---|
| Degussa P25 | $TiO_2$ | Anatase – 70%<br>Rutile – 30 % |
| Urea | $NH_2CONH_2$ | |
| Hydrochloric acid | HCl | 38% |
| Phenol | $C_6H_6$ | 87% |

### 2.2 Photocatalyst synthesis

3 g of commercial $TiO_2$ Degussa P25 was mixed with 0.5, 1, 1.5, 2 g of urea powder by mechanical mixing. In order to achieve homogeneity stirring lasts for 20 min. After this period of time, every sample was divided in four equal parts, which were calcinated under at atmospheric pressure for 2 h at 300, 350, 400 and 450 °C, respectively. After the thermal treatment the samples were cooled down to ambient temperature and treated by ultrasound in a 0.1 N HCl solution to eliminate possible impurities. Finally, the samples were washed with distilled water and centrifuged. The so obtained yellow coloured precipitate was dried at 85 °C.

### 2.3 Phenol degradation mechanism

The main reaction site for the elimination of phenol is the bulk liquid, where the attack of hydroxyl radicals on the ring carbons results in various oxidation intermediates. Among them the most numerous are hydroquinone, catechol, and p-benzoquinone. The secondary products like chloro-hydroquinone, 4-chlorocatechol and resorcinol are eventually converted to acetylene, maleic acid, carbon monoxide and carbon dioxide (Ahmet, 2010). Figure 1 shows the degradation mechanism of phenol.

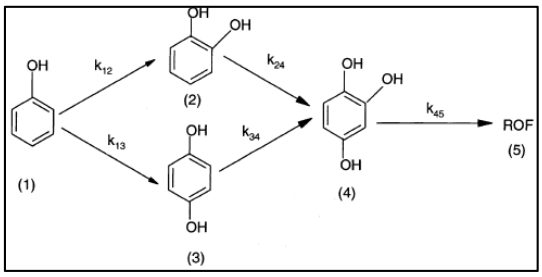


*Figure 1: Mechanism for the degradation of phenol (Sivalingam, 2004)*

## 3. Results and discussion

### 3.1 Effect of urea concentration

In order to study the effect of dopant precursor concentration N-$TiO_2$ nanoparticles with different amount of urea were prepared. The result is shown in Figure 2. It was found that 1 g of urea was the optimal concentration to use. Both increasing and decreasing the dopant precursor amount a reduction of the photocatalytic activity of the catalyst was observed.

### 3.2 Effect of temperature treatment

In order to determine an optimal temperature for N-$TiO_2$ nanoparticles, thermal treatment samples with various amount of urea were calcined at 300, 350, 400, 450 °C. Figure 3 shows the result of photocatalytic degradation of 12 ppm phenol aqueous solution assisted by N-$TiO_2$ calcined at different temperatures. Photocatalyst calcined at 350 °C shows much higher activity if compared to the other samples. The worst result were achieved by the N-$TiO_2$ calcined at 300 °C. This may be justified by the low calcination temperature (300°C) that appears to not be sufficient for a correct anatase crystalline structure formation.

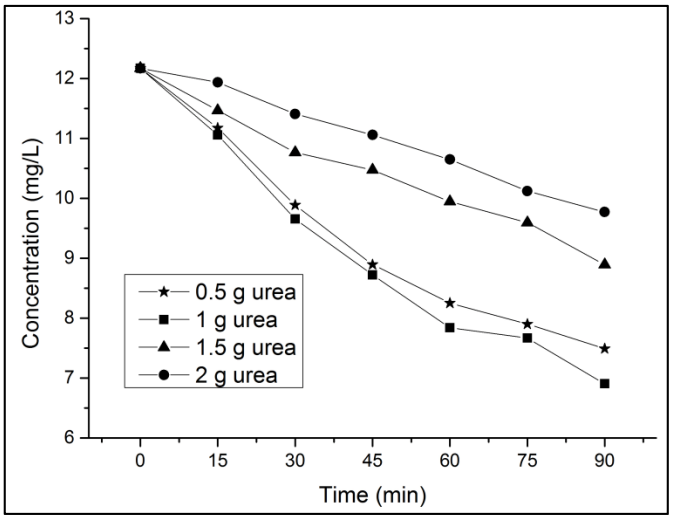


*Figure 2: Effect of urea concentration`(catalyst – N-$TiO_2$ [calcination at 350 °C], phenol initial concentration – 12 ppm, phenol volume – 200 mL, pH of solution – 6.8, irradiation – 140 W visible light lamp, irradiation time – 90 min)*

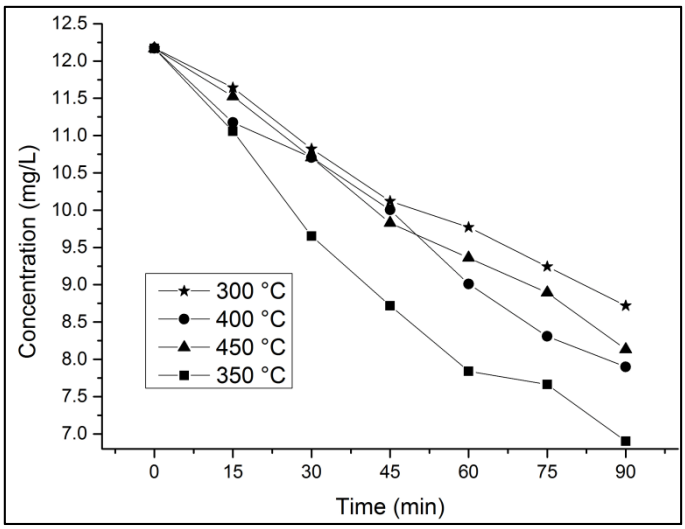


*Figure 3: Effect of N-$TiO_2$ thermal treatment in the photocatalytic degradation of phenol (catalyst – N-$TiO_2$ (1g of urea), phenol initial concentration – 12 ppm, phenol volume – 200 mL, pH of solution – 6.8, irradiation – 140 W visible light lamp, irradiation time – 90 min)*

### 3.3 Effect of initial catalyst loading

Chapter 2 Efficiency of the photocatalytic degradation process strongly depends on the loading of the catalyst. This parameter can be considered as one of the key factors influencing the reaction kinetics. In this work, an optimal catalyst loading of 1 g/L was determined experimentally. For this purpose, the photocatalytic tests with 0.5, 1 and 1.5 g/L of N-$TiO_2$ were reported. Figure 4 visibly shows that 0.5 g/L are not a sufficient loading for the maximum efficiency of 12 ppm phenol degradation. Increasing of the catalyst loading to 1 g/L significantly increases the reaction rate. But a further enhancement of N-$TiO_2$ leads to the decreasing of phenol degradation efficiency. This can be justified by the contrasting effects of catalyst addition: promotion, enhanced catalytical activity, and demotion, limited light penetration (Zulfacar, 2011). Nanoparticles create the effect of shielding hiding each other from the light flux and thus decreasing the effective light irradiation that reaches $TiO_2$ active sites.

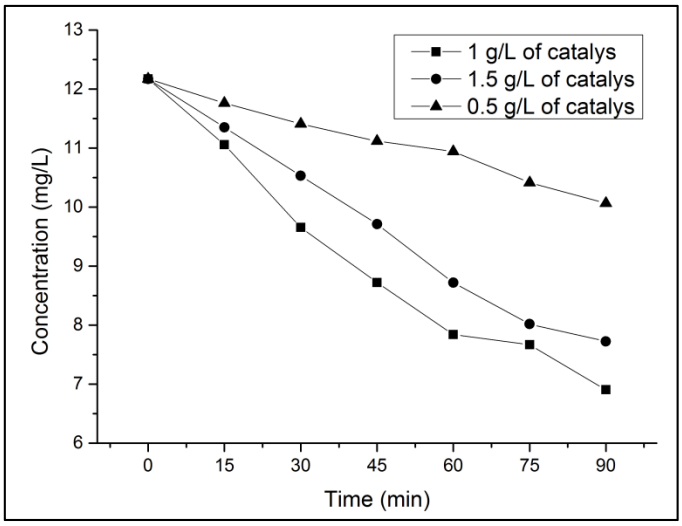


*Figure 4: Effect of N-$TiO_2$ loading in the photocatalytic degradation of phenol (catalyst – N-$TiO_2$ (1g of urea, calcination 350 °C), phenol initial concentration – 10 ppm, phenol volume – 200 mL, pH of solution – 6.8, irradiation – 140 W visible light lamp, irradiation time – 90 min)*

### 3.4 Effect of initial phenol concentration

Photocatalytic degradation of 12, 50, and 100 ppm phenol aqueous solutions were assisted by 1g/L of N-$TiO_2$ nanoparticles. The result is reported in Figure 5. The increasing of pollutant concentration in this case decreases the efficiency of photocatalytic process. Excessively high concentration of organic compounds leads to the saturation of the surface of titanium dioxide and decreases the absorption of photons by the photo catalyst particles, which naturally reduces its activity or deactivates it (Chong, 2010).

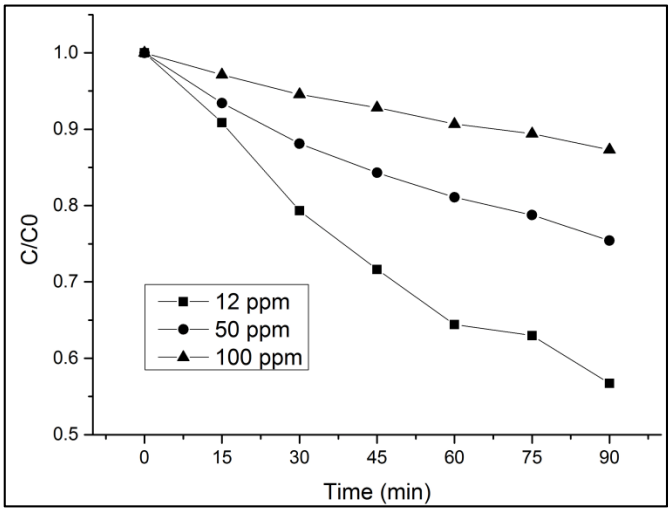


*Figure 5: Effect of initial pollutant concentration in the photocatalytic degradation of phenol (catalyst – N-$TiO_2$ (1g of urea, calcination 350 °C), catalyst loading – 1 g/L, phenol volume – 200 mL, pH of solution – 6.8, irradiation – 140 W visible light lamp, irradiation time – 90 min)*

Phenol photocatalytic degradation can be considered as a pseudo-first order chemical reaction. All the kinetic parameters are summarized in Table 2.

*Table 2: Kinetic parameters of phenol photocatalytic degradation assisted by N-$TiO_2$ nanoparticles (in bold the parameters that have been changed in the search for the optimal value)*

| $TiO_2$, g | Urea, g | Thermal treatment, °C | Phenol concentration, ppm | Catalyst loading, g/L | k, $min^{-1}$ | $R^2$ |
|---|---|---|---|---|---|---|
| 3 | 2 | 350 | 12 | 1 | 0.0024 | 0.986 |
| 3 | 1.5 | 350 | 12 | 1 | 0.0034 | 0.987 |
| 3 | 0.5 | 350 | 12 | 1 | 0.0059 | 0.967 |
| 3 | 1 | 350 | 12 | 1 | 0.0066 | 0.976 |
| 3 | 1 | 300 | 12 | 1 | 0.0037 | 0.995 |
| 3 | 1 | 400 | 12 | 1 | 0.0049 | 0.991 |
| 3 | 1 | 450 | 12 | 1 | 0.0044 | 0.994 |
| 3 | 1 | 350 | 100 | 1 | 0.0016 | 0.985 |
| 3 | 1 | 350 | 50 | 1 | 0.0033 | 0.966 |
| 3 | 1 | 350 | 12 | 1 | 0.0066 | 0.976 |
| 3 | 1 | 350 | 12 | 0.5 | 0.002 | 0.988 |
| 3 | 1 | 350 | 12 | 1 | 0.0066 | 0.976 |
| 3 | 1 | 350 | 12 | 1.5 | 0.0053 | 0.991 |

Figure 6 shows a comparison between photolysis of phenol and photocatalysis assisted by N-$TiO_2$ nanoparticles.

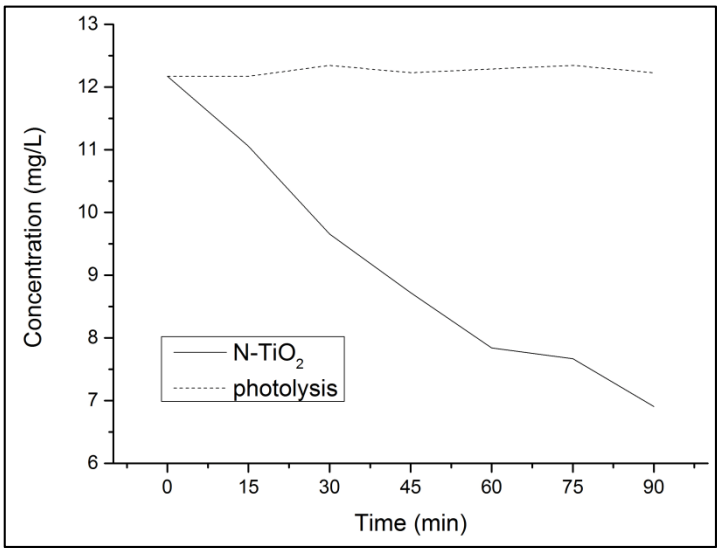


*Figure 6: Comparison between photolysis of phenol and photocatalysis assisted by N-$TiO_2$ nanoparticles (catalyst – N-$TiO_2$ (0.3 g of urea for 1 g of $TiO_2$, calcination 350 °C), catalyst loading – 1 g/L, phenol volume – 200 ml, pH of solution – 6.8, irradiation – 140 W visible light lamp, irradiation time – 90 min)*

## 4. Conclusions

Chapter 4 In this study nitrogen doped titanium dioxide nanoparticles were synthesized by mechanical mixing of Degussa P25 and urea powder followed by thermal treatment. The effect of urea concentration, temperature of calcination, phenol initial concentration and catalyst loading were studied. The results showed that increasing of initial pollutant concentration affect negatively on the photocatalysis efficiency. Excess amount of catalyst decreases the light penetration which leads to the worse catalytic activity of nanoparticles. Thermal treatment plays a key role in the formation of $TiO_2$ crystalline structure that why it's important to determine an optimal calcination temperature. In this study the sufficient temperature was determined as 350 °C. Finally, the concentration of dopant precursor can strongly effect on the reaction rate. Degradation of phenol was considered as a pseudo-first order reaction. The maximum efficiency 41 % of photocatalytic degradation of 12 ppm phenol aqueous solution in 90 min was achieve under the optimal conditions: urea concentration 0.3g for 1g of $TiO_2$ calcinated at 350 °C for 2h, catalyst loading 1g/L.
Chapter 5 The use of doped titania nanocatalyst may be of importance to reduce the operating costs of wastewater treatment processes.

### References

Ahmed S., Rasul M. G., Martens W. N., Brown R., Hashib M. A., 2010, Heterogeneous photocatalytic degradation of phenols in wastewater: A review on current status and developments, Desalination 261, 3–18

Chong M. N., Jin B., Chow C. W. K., Saint C., 2010, Recent developments in photocatalytic water treatment technology: A Review, Water Research 44, 2997-3027

Cicci, A., Stoller, M., Bravi, M., Microalgal biomass production by using ultra- and nanofiltration membrane fractions of olive mill wastewater, 2013, Water Research 47, 4710-4718.

Nawawi W.I., Nawi M.A., 2014, Carbon coated nitrogen doped P25 for the photocatalytic removal of organic pollutants under solar and low energy visible light irradiations, Journal of Molecular Catalysis A: Chemical 383– 384, 83– 93

Ochando-Pulido, J.M., Stoller, M., Di Palma, L., Martinez-Ferez, A., Threshold performance of a spiral-wound reverse osmosis membrane in the treatment of olive mill effluents from two-phase and three-phase extraction processes, 2014, Chemical Engineering and Processing: Process Intensification 83, 64-70.

Ochando-Pulido, J.M., Stoller, M., Boundary flux optimization of a nanofiltration membrane module used for the treatment of olive mill wastewater from a two-phase extraction process, 2014, Separation and Purification Technology 130, 124-131.

Ruzmanova, Y., Ustundas, M., Stoller, M., Chianese, A., Photocatalytic treatment of olive mill wastewater by n-doped titanium dioxide nanoparticles under visible light, 2013a, Chemical Engineering Transactions 32, 2233-2238.

Ruzmanova, Y., Stoller, M., Chianese, A., Photocatalytic treatment of olive mill wastewater by magnetic core titanium dioxide nanoparticles, 2013b, Chemical Engineering Transactions 32, 2269-2274.

Zulfacar M., Nairul N. A. H., Akmal H. M. R., Abdul Rahman M., 2011, Photocatalytic degradation of phenol in a fluidized bed reactor utilizing immobilized $TiO_2$ photocatalyst: characterization and process studies, Journal of applied science 11(13), 2320 - 2326

Sivalingam G., Priya M. H., Madras G., 2004, Kinetics of the photodegradation of substituted phenols by solution combustion synthesized TiO2, Applied Catalysis B: Environmental 51, 67–76

Stoller, M., Pulido, J.M.O., Di Palma, L., On the relationship between suspended solids of different size, the observed boundary flux and rejection values for membranes treating a civil wastewater stream, 2014, Membranes 4, 414-423.

Stoller, M., Movassaghi, K., Chianese, A., Photocatalytic degradation of orange II in aqueous solutions by immobilized nanostructured titanium dioxide, 2011, Chemical Engineering Transactions 24, 2292-2342.

UNESCO (United Nations Educational, Scientific and Cultural Organization), 2012 The United Nations World Water Development Report 4: Managing Water under Uncertainty and Risk <unesdoc.unesco.org> accessed 10.10. 2014

Vaiano, V., Sacco, O., Stoller, M., Chianese, A., Ciambelli, P., Sannino, D., Influence of the photoreactor configuration and of different light sources in the photocatalytic treatment of highly polluted wastewater, 2014, Journal of Chemical Reactor Engineering 12.