The decolourisation of Methyl Orange and textile effluent under UV using commercial and synthesized nano-TiO$_2$

N N Nyangiwe$^1$, B Baatjie$^2$, C Greyling$^3$, M Khenfouch$^3$, M Maaza$^{4,5}$

$^1$Natural Resources and the Environment, Source directed scientific measures group, CSIR, P O BOX 395, Pretoria, 0001
$^2$Technology Station in Clothing and Textiles, Cape Peninsula University of Technology, Bellville
$^3$Africa Graphene Center, Physics department, Eureka Building, College of Science, Engineering and Technology, University of South Africa, Florida, Roodepoort 1710.Gauteng
$^4$UNISA Africa Chair in Nanosciences-Nanotechnology, College of Graduate Studies, University of South Africa, Muckleneuk ridge, PO Box 392, Pretoria, South Africa
$^5$NanoAfNet, Nanolaboratories, iThemba LABS-National Research Foundation of South Africa, Old Faure Road, P O Box 722, Somerset West 7129, Western Cape Province, South Africa

Corresponding authors: khenfouch@yahoo.fr/nyangiwenangamso9@gmail.com

Abstract. The efficiency of the nanophotocatalysts was determined in a laboratory prepared solutions of model dye compound methyl orange (MO), which is a dyestuff typically applied on textiles. The reduction in the concentration of the dye over time was measured by using UV-VIS spectrophotometry. The decolourisation of MO solutions was characterized at the onset and after exposure to 9W germicidal UV lamps at various time intervals, viz. 30, 60, 120, 180, 300 and 420 minutes. The color transformation from dark-orange, (MO) to a transparent clear solution or a slightly colored solution is an indication of the decomposition of the organic dye contaminants into lower molecular weight organics and innocuous CO$_2$ and water. The results show that the commercial nano-TiO$_2$ is more efficient in decolourising the model dye and the textile effluents.

1. Introduction

In recent years, the photocatalytic decolourisation of dyes has attracted increasing attention due to prominent application prospects in the areas of treatment of pollutants in water [1,2,3]. Nanoparticles of titanium dioxide, nano-TiO$_2$ were evaluated for their ability to decompose organic contaminants [4]. The nano-TiO$_2$ investigated includes a comparison of commercial, round Evonik P25® and particles synthesized via a hydrothermal method. Nanophotocatalysis using nanostructured semiconductors constitute one of the emerging technologies due to their high catalytic efficiency [5]. Photo catalysis has great potential for waste-water treatment. A universal range of semiconductors have been studied for their photocatalytic capacity and TiO$_2$ have been revealed to be the most active [6]. TiO$_2$ was selected as the photocatalyst for this work due to its high efficiency, low toxity and insolubility in water. Its operation at ambient temperature, low cost and it is ideal trace level pollutant removing ability [7] have also been considered. Because of its excellent photocatalytic activity, TiO$_2$ is an exclusive choice in many photo catalysis applications.

The photocatalytic decolourization of a dye is understood to take place according to the following mechanism in figure 1.
As shown in figure 1, when the photocatalyst titanium dioxide (TiO$_2$) absorbs the ultraviolet (UV) radiation from daylight or other bright light source (fluorescent lamps), it produces pairs of electrons and holes. The electron of the valence band of the titanium dioxide becomes excited when illuminated by light. The excess energy of this excited electron promotes the electron to the conduction band of titanium dioxide, therefore creating the negative-electron (e$^-$) and the positive-hole (h$^+$) pair. This stage is denoted as the semiconductor's 'photo-excitation' state.

The color transformation from dark-orange, (MO) to a transparent clear solution or a slightly colored solution is an indication of the decomposition of the organic dye contaminants into lower molecular weight organics and innocuous carbon dioxide and water. A number of methods were proposed to prepare nanostructure TiO$_2$ including microwave irradiation, chemical vapor deposition, spray pyrolysis, electrochemical deposition and sol–gel method. Photocatalytic oxidation process with metal oxides has a potential to break down the organic pollutants. Among the metal oxides, TiO$_2$ ranks among the most attractive and capable candidates for decolourisation of waste water from many industries.

Titanium dioxide (TiO$_2$) displays its exclusive photocatalytic activity at an excellent choice of a photocatalysis application. Previously researchers have compared the photocatalytic activities of various TiO$_2$ powders using twelve types of commercial anatase TiO$_2$ and three types of rutile TiO$_2$, and concluded that the activity of the auto oxidation is much higher for anatase than that of rutile.

Despite the many known advantages of using TiO$_2$, it suffers from the shortcoming of having a large band gap (~3.2 eV) which restricts its use to the ultraviolet region. Suitable radiation wavelengths are not very abundant in the solar radiation spectrum that reaches the Earth, which limits the use of TiO$_2$ in solar energy utilization. Observed a correlation between the photocatalytic activity in the UV photodecolourisation of phenol solutions and the particle size and that prismatic rutile particle with length around 5 nm and breadth of 60 to 100 nm showed the highest activity. This is interesting as anatase is usually more reactive than rutile. The results were based on tests conducted on phenol solutions. None of these studies were scaled up to real industrial textile effluents, which will require ability to scale up the production of these novel shaped nanoparticles.

Your brightly colored clothes might have a dark story to tell. Hidden in the bright oranges (figure 2) of textile wastewater are some pretty harmful pollutants. Difficult to degrade, these compounds end up in waterways and may well outlast your outfit. Can we clean up and re-use water effluent from the textile industry?
In this paper we attempt to tell a lighter side of the tale using special nano-based catalysts. Water polluted by textile dyes is a complex issue; impacting animal and plant life in waterways, and holds safety implications for human and agricultural purposes. For dry countries like South Africa under threat of climate change, these are important questions. The answer could lie in the use of light with a little help from nanosized titanium dioxide or rather, nano-TiO$_2$. Nano-TiO$_2$ acts as a photocatalyst with the ability to destroy organic contaminants from water[23]. Scientists know this process as photocatalytic treatment, harnessing the power of light. The photocatalytic properties of titanium dioxide have been known for decades and recently nanosized titanium dioxide has entered the market place. In this paper we are exploring these processes, and their application in treatment of dyes such as methyl orange etc.

The textile industry is one of the most chemically concentrated industries on earth and the top polluter of clean water (It takes about 2000 liters of water to produce enough fabric to cover one sofa). The clothing and textile industry is South Africa’s sixth largest employer in the manufacturing sector and the 11th largest exporter of manufactured goods. The textile industry is not only amongst the largest industrial liquid waste generators, it is also chemically intensive. As a result, very large volumes of effluent containing a wide range of dyes, auxiliaries, salts, acids, alkalis and occasionally even heavy metals, are often generated [24]. The effluent from the dyeing is categorised by strong colour, high pH, high Biological Oxygen Demands (BOD), Total Suspended Solids (TSS), Chemical Oxygen Demands (COD), the presence of heavy metals like Cu, Hg, Cd, Zn, elevated temperatures and low or no biodegradability. Most dyes incorporated in the colour table are Azo dyes and available commercially, most of which are difficult to decolorize due to their complex aromatic molecular structure and synthetic origin [25].

The main aim of this paper is to compare the decolourisation of model dyes and textile effluent using both commercial and laboratory synthesized nano-TiO$_2$ under UV. In this study we investigated commercially available round shaped nano-TiO$_2$ and similar such particles synthesized via a hydrothermal method. The hydrothermal method of production produces rod and ribbon-shaped particles. The effect of these nanophotocatalysts was determined in laboratory-prepared solutions of model dye compounds. The sol-gel synthesis, although has high yield, suffers from a long ageing time.

2. Experimental details

2.1. Materials
Titanium dioxide (P25®, size 21 nm) as photocatalyst was supplied by Evonik. Methyl Orange (MO) as representative model dye compound was purchased from KIMIX, South Africa. Synthesized nano-TiO$_2$ was synthesized by a sol gel technique using titanium isoproproxide as the titanium precursor, and 50 ml of HCl acid as the peptizing agent to control hydrolysis and favor rutile crystal structure growth. The pH of the dyes solution was adjusted with 1 M HCl. The titanium ion concentration was set at 0.5 M and the peptizing agent concentrations at 4 M and the synthesis was conducted over 24 hours. After the preparation of clear sol was aging by adding water drop-wise. Consequently, and after the aging, the complete solution including the gel is transferred to the hydrothermal reactor. It was hydrothermally treated at 220 °C for one hour.

2.2. Photo catalytic activity experiment
MO solution was prepared at 50 mg/l concentration amount of 0.04 g MO was added to 800 ml of deionized water in a one liter beaker separately. Then 2.4 grams of P25® TiO$_2$ was added and the solution was placed on a magnetic stirrer plate. The solution was sonicated for 30 minutes. Before starting running the experiment, a control sample of a 10 ml to aliquot was removed. A 9 W UV lamp
was placed inside the solution to provide energy to the nano-TiO$_2$. The solution was irradiated for 30, 60, 120, 180, 300, and 420 minutes. After the solutions were exposed to UV light, the samples were centrifuged for 15 minutes in order to separate nano-TiO$_2$ from the rest of the solution before measuring the absorbance by a UV-Vis spectrophotometer.

2.3. Characterization
UV-Vis spectrophotometry (Perkin Elmer, Lambda 35) was used to measure the absorbance and % color changes of the dyes were calculated from the absorbance data. The structural properties of the prepared and commercial nano-TiO$_2$ were analysed using X-Ray diffractometer. The particle shape and morphology were observed using High-Resolution Transmission Electron Microscopy (HRTEM). The surface area has been performed to indicate the sample surface area and porosity. Figure 3 below shows methyl orange calibration using UV-Vis spectrometer.

3. Results and discussion
Titanium dioxide is considered for this treatment because of its availability, low cost and effectiveness as a catalyst, speeding up the removal of color from the textile wastewater. The proof is clear to see in images showing the decolourisation of methyl orange. UV irradiation of nano-TiO$_2$ excites electrons from a filled valence band to an empty conduction band, giving rise to electron-hole pairs. These generate free radicals which attack covalent bonds in the dyes. While nano-TiO$_2$ photo catalysis represents a striking method for breaking down these complex organic compounds to simpler compounds, scope remains for studies that can improve the efficiency of dye pollution. Measures such as these may yet lead to long-term solutions for treating textile industry wastewater.

3.1. UV-Vis analysis
Initially the control experiments were carried out under the following conditions: photolysis of dye solution with UV-light in the absence of TiO$_2$, dye solution with nano-TiO$_2$ in dark and the dye solution under irradiation of UV-light with TiO$_2$. After 30 min of magnetic stirring in the presence of photocatalyst without UV irradiation, more than 50%, 40% and 90% decrease in concentration of MO; the results of the measurements are shown in the Figure 4 - 5. This is due to the adsorption of dye molecule on the surface of nano-TiO$_2$. Figure 4 shows solutions of methyl orange (MO) after treatment with nano-TiO$_2$ under UV light at various time including: 0 min to 420 min, after centrifuging. The spectrum shows with a peak at approximately 462 nm, the decolourisation of MO at a different photodecolourisation times. As the color of the dyes becoming less concentrated the absorption peak intensity decreases with increasing decolourisation time which means that there are many molecules interacting with light. After exposing the MO solution for 420 min to UV irradiation, the reduction of
MO is up to 98% and the absorption peak is completely removed, the solutions has been decolorized. Figure 5, shows the decolourisation of MO suspension at a several decolourisation times. The color transformation from dark-orange to colorless MO demonstrates that the MO has been degraded by the TiO$_2$ nanoparticles under UV irradiation. Figure 6 shows MO treated by synthesized nano-TiO$_2$ is too longer to decolorize, only about 70% color removed after 420 min. The color transformation from dark-orange (MO) to a transparent clear solution or a slightly colored solution is an indication of the decomposition of the organic dye contaminants into lower molecular weight organics and innocuous CO$_2$ and water. Figure 7 shows the actual effluent from a textile company, the effluent took longer to decolorize because the high concentration dyestuffs preventing the transmission of UV light from the source through the solution. The effluent may contain other elements that could be interacting and or blocking light.

![Figure 4](image-url)  
**Figure 4.** Showing absorption spectra of MO degraded by nano-TiO$_2$ under UV irradiation.

![Figure 5](image-url)  
**Figure 5.** Showing plot of concentration versus decolourisation times.
3.2. XRD analysis

Figure 8 below shows the characteristic peaks of the commercial nano-TiO$_2$ and synthesized nano-TiO$_2$. XRD spectrum of commercial nano-TiO$_2$ detected 10 characteristic peaks, since the commercial nano-TiO$_2$ is P25, it consists of anatase and rutile. So the 10 characteristic peaks detected correspond to both anatase and rutile. The peaks at 25.4° and 48.4° are the characteristic reflection for anatase and rutile [26,27]. The intensity of XRD peaks of the sample reflects that the formed nanoparticles are crystalline and broad diffraction peaks indicate very small size crystallite. Powder X-ray diffraction (XRD) was used for crystal phase identification and the estimation of the anatase–rutile ratio and the crystallite size of each phase present. In the case of synthesized nano-TiO$_2$ referred as NPs in the diffractogram below,
six peaks were detected even though the peaks were not prominent like the ones for commercial nano-
TiO$_2$ referred as power in the diffractogram. The synthesized nano-TiO$_2$ a prominent peak around 52. 4°
which correspond to rutile.

![Graph showing X-ray diffractograms of TiO$_2$ powder and synthesized nano-TiO$_2$.]

**Figure 8.** X-ray diffractograms of nano-TiO$_2$ powder in black line and synthesized nano-TiO$_2$ in red line.

3.3. **HRTEM analysis**

The morphology and particle size of commercial nano-TiO$_2$ and synthesized nano-TiO$_2$ were further
investigated by HRTEM analysis. These images do not represent a novelty as TEM images of the popular
P25 photocatalyst are frequently reported in the literature [28,29,30] It can be estimated that the particle
size of synthesized nano-TiO$_2$ in figure 9 (a) and commercial nano-TiO$_2$ in figure 9 (b) nanoscale with
the grain size from 20-30 nm range. From Figure 9 (a) and (b), HRTEM confirmed that both commercial
nano-TiO$_2$ and synthesized nano-TiO$_2$ produced rod and ribbon-shaped particles.

![HRTEM images of synthesized and commercial nano-TiO$_2$.]

**Figure 9.** HRTEM photograph of the A (a) synthesized nano-TiO$_2$ (b) commercial nano-TiO$_2$.

3.4. **BET Surface Areas and Porosity Measurements**
The surface area has been performed to indicate the sample surface area and porosity of P25 TiO₂ and synthesized TiO₂. Surface area of the photocatalyst is a crucial factor in photocatalytic activity as it resolves the quantity of available catalytic sites. Specific surface area (SSA) measurements were carried out using BET analysis both P25 TiO₂ and synthesized TiO₂ as shown in Table 1 and Table 2. For the comparison, the surface area of P25 TiO₂ and synthesized TiO₂ was also acquired under the same experimental condition. It can be seen that the P25 TiO₂ has higher values of surface area than synthesized TiO₂. It was initially observed that P25 TiO₂ have a SSA of 85.90 m² g⁻¹, then the surface area increased to 102.26 m² g⁻¹. In the case of synthesized TiO₂, the SSA increased from 60.96 m² g⁻¹ to 69.45 m² g⁻¹. The corresponding Barrett–Joyner–Halenda (BJH) pore-size distribution and pore volume of P25 TiO₂ and synthesized TiO₂ are presented in Table 1 and Table 2 respectively. BJH adsorption pore size distribution with a mean values for P25 TiO₂ and synthesized TiO₂ are 23.64 nm and 31.17 nm. BET total surface area 375.42 m² g⁻¹ and a total pore volume of 0.74 cm³ g⁻¹ for P25 TiO₂, the obtained BET total surface area and total pore volume for synthesized TiO₂ were 257.2 m² g⁻¹ and 0.6 cm³ g⁻¹. Due to the large density of crystalline TiO₂, this obtained BET surface area is very high for P25 TiO₂ and synthesized TiO₂ with high crystallinity [31-32]. As a result, the comparative high surface area and the assimilated porous structure will be valuable for the successive adsorption and photocatalytic reactions.

| Catalyst   | BET SSA (m² g⁻¹) | Pore Volume (cm³ g⁻¹) | BJH Average Pore Size (nm) |
|------------|------------------|-----------------------|-----------------------------|
| P25 TiO₂   | 85.90            | 0.22                  | 9.91                        |
|            | 89.62            | 0.04                  | 9.32                        |
|            | 97.64            | 0.24                  | 8.39                        |
|            | 102.26           | 0.24                  | 66.95                       |

Table 1. Physical properties of the supported P25 TiO₂ photocatalysts.

| Catalyst     | BET SSA (m² g⁻¹) | Pore Volume (cm³ g⁻¹) | BJH Average Pore Size (nm) |
|--------------|------------------|-----------------------|-----------------------------|
| Synthesized TiO₂ | 60.96            | 0.16                  | 10.28                       |
|              | 63.12            | 0.06                  | 10.30                       |
|              | 63.67            | 0.19                  | 9.04                        |
|              | 69.45            | 0.19                  | 95.06                       |

Table 2. Physical properties of the supported synthesized TiO₂ photocatalysts.

4. Conclusion

From this paper the authors managed to decolorize MO and the actual textile effluent using nano-TiO₂ under UV irradiation. Although nano-TiO₂ photo catalysis is an attractive approach, there are some factors that restrain the performance of photo decolourisation such as catalyst activity -i.e. slow decolourisation rate of organics. In addition to a prompt removal of the colors, nanoparticles of titanium dioxide TiO₂-based photo catalysis were simultaneously able to fully oxidize the dyes, with a complete mineralization of carbon into CO₂. The resulting water is not only colorless but also detoxified when submitted to such a treatment. Photo catalysis appears as a valuable treatment for purification and reuse of colored aqueous effluents.
Acknowledgements

The author’s would like to thank the Department of Science and Technology together with the National Research Foundation for funding this project, South Africa. We would like also to thank Mr Jules Lind and Prof Veruscha Fester from Cape Peninsula University of Technology, Chemical Engineering department, South Africa, for preparing TiO$_2$ nanoparticles and the CSIR for providing some of the resources for this project. Special thanks to Prof Janice Limson for valuable comments.

References

[1] Han F, Kambala V S R, Srinivasan M, Rajarathnam D and Naidu R 2009 Appl. Catal. A: General 359 25
[2] Vinu R, Akki S U and Madras G 2010 J. Hazard. Mater. 176 765
[3] Gaya U I and Abdullah A H 2008 J. Photochem. Photobiol. C: Photochem. Reviews 9 1
[4] Nagaveni K, Sivalingam G, Hegde M.S and Madras G 2004 Appl. Catal. B : Environ. 48 83
[5] Khataee A R, Vatanpour V and Ghadim A R A 2009 J. Hazard. Mater. 161 1225
[6] Nickheslat A, Amin M M, Izanloo H, Fatehizadeh A and Mousavi S M 2013 J. environ. public health 2013 9
[7] Joshi K M, Patil B N and Shrivastava V S 2011. Arch. Appl. Sci. Res. 3 596
[8] Joshi K M and Shrivastava V S 2011 Int. J. Environ. Sci. 2 8
[9] Bizani E, Fytianos K, Poularios I and Tsiridis V 2006 J. Hazard. Mater. 136 85
[10] Kawahara T, Miyazaki H, Karuppuchamy S, Matsui H, Ito M, Yoshihara M 2007 Vacuum. 81 680
[11] Matsui H, Karuppuchamy S, Yamaguchi J and Yoshihara M 2007 J. Photochem Photobiol A: Chem. 189 280
[12] Matsui H, Yamamoto S, Izawa Y, Karuppuchamy S and Yoshihara M 2007 Mater. chem. phys. 103 127
[13] Matsui H, Kira K, Karuppuchamy S and Yoshihara M 2009 Currt. Appl. Phys. 9 592
[14] Karuppuchamy S and Ito S 2008 Vacuum 82 547
[15] Neppolian B, Choi HC, Sakhthivel S, Arabindoo B and Murugesan V 2002 Chemosphere 46 1173
[16] Sökmen M and Özkan A 2002 J. Photochem. Photobiol. A: Chem. 147 77
[17] Muruganandham M and Swaminathan M 2004 Sol. Energy Mater. Sol. Cells 81 439
[18] Santhi K, Manikandan P, Rani C and Karuppuchamy S 2015 Appl Nanoscience 5 373
[19] Fujishima A, Hashimotoand K and Watanabe T 1999 Tokyo BKC 123
[20] Ray A K and Beenackers A A C M 1998 Catal. today 40 73
[21] Fox M A and Dulay M T 1993 Chemical reviews 93 341
[22] Testino A, Bellobono I R, Buscaglia V, Canevali C, D’Arienzo M, Polizzi S, Scotti R and Morazzoni F 2007 J. Am. Chem. Soc. 129 3564
[23] Nyangiwe N 2014 03, npep.co.za.
[24] Barclay S and Buckley C 2000 1
[25] Özer A, Akkaya G and Turabik M 2006 Dyes and pigments 71 83
[26] Ba-Abbad M M, Kadhum A A H, Mohamad A B, Takriff M S and Sopian K 2012 Int. J. Electrochem. Sci. 7 4871
[27] Thamaphat K, Limsumwan P and Ngotawornchai B 2008 J. Nat. Sci. 42 357
[28] Datye A K, Riegel G, Bolton J R, Huang M and Prairie M R 1995 J. Solid State Chem. 115 236
[29] Martra G, 2000 Appl. Cata. A: General 200 275
[30] Ohno T, Sarukawa K, Tokieda K and Matsumura M 2001 J. Cata 203 82
[31] Zhang Y, Ying Zhang, Zhao Z, Chen J, Cheng L, Chang J, Sheng W, Hu C and Shunsheng C 2015 Appl. Catal. B: Environ. 165 715
[32] Wang G, Zhu X and Yu J 2015 J. Power Sources 278 344