Preparation of Heat Treated Titanium Dioxide (TiO₂) Nanoparticles for Water Purification

A O Araoyinbo¹*, M M A B Abdullah¹,², A Rahmat², A I Azmi¹, P Vizureanu²,³ and W M F Wan Abd Rahim¹

¹Faculty of Engineering Technology, Universiti Malaysia Perlis, Perlis Malaysia
²Center of Excellence Geopolymer and Green Materials (CEGeoGTech), School of Materials Engineering, Universiti Malaysia Perlis (UniMAP), Perlis, Malaysia
³Gheorghe Asachi Technical University of Iasi, Faculty of Materials Science and Engineering, Blvd. D. Mangeron 41, 700050, Iasi, Romania

Email: alaba@unimap.edu.my

Abstract. Photocatalysis using the semiconductor titanium dioxide (TiO₂) has proven to be a successful technology for waste water purification. The photocatalytic treatment is an alternative method for the removal of soluble organic compounds in waste water. In this research, titanium dioxide nanoparticles were synthesized by sol-gel method using titanium tetraisopropoxide (TTIP) as a precursor. The sol was dried in the oven at 120°C after aging for 24 hours. The dried powder was then calcined at 400°C and 700°C with a heating rate of 10°C/min. The phase transformation of the heat treated titanium dioxide nanoparticles were characterized by X-Ray Diffraction (XRD) and the surface morphology by Scanning Electron Microscopy (SEM). The photocatalytic activity of the heat treated titanium dioxide nanoparticles in the degradation of methyl orange (MO) dye under ultraviolet (UV) light irradiation has been studied. At calcination temperature of 400°C, only anatase phase was observed, as the calcination temperature increases to 700°C, the rutile phase was present. The SEM images show the irregular shape of titanium dioxide particles and the agglomeration which tends to be more significant at calcined temperature of 700°C. Degradation of methyl orange by 5 mg heat treated titanium dioxide nanoparticles gives the highest percentage of degradation after irradiation by UV lamp for 4 hours.

1. Introduction

Clean water is a crucial source of continuous existence and disease free water is essential for human beings as well as for the socioeconomic development of communities and states. Presently many societies are facing rising demands of potable water as the availability of fresh water supplies are depleting due to the extended droughts, population growth, more stringent health based regulations, decline in water quality particularly of groundwater due to increasing groundwater and surface water pollution, unabated flooding and competing demands from a variety of competing users [1]. Poor sanitation, water scarcity, deterioration of water quality, emergence of waterborne diseases, and lack of cleanwater supply are all posing global challenges due to the rising demand by an increasing world population [2].

Dyes are a significant source of water contaminants released from the industrial effluents. The waste water released by the textile industries is rated as one of the most polluting effluent among the entire industrial sectors including pigment, leather, food and paper industries [3]. Photocatalysis by
semiconductor particles are a promising technology that has great potential to control aqueous organic contaminants and considered as a new oxidation technology for water purification treatment [4]. There are several potential photocatalysts used for degradation of various organic compounds and dyes but the most promising and widespread substance is the titanium dioxide (TiO2) nanoparticles.

Titanium dioxide nanoparticles are significantly more reactive than larger particles due to their larger surface area. Titanium dioxide nanoparticles have shown to be a relatively cheap and effective for removing organic compounds and pollutant gases due to its high chemical stability, high photocatalytic activity, non-toxicity and high ability to break molecular bonds leading to degradation [5].

Photocatalytic oxidation reactions have high potential to completely mineralized organic compounds to carbon dioxide (CO2), water vapor (H2O) and other inorganic substances by solar light or the photocatalytic system equipped with artificial ultraviolet (UV) light [6]. Photocatalysis using titanium dioxide photocatalyst is a rapidly expanding technology for water treatment from refractory and toxic organic pollutants such as dyes, pesticides and pharmaceuticals [7].

In this project, the heat treated titanium dioxide (TiO2) nanoparticles act as a water filtration medium and the methyl oranges (MO) act as a model pollutant compound. The titanium dioxide nanoparticles were synthesized via sol-gel method and calcined at 400°C and 700°C in the furnace. The properties of titanium dioxide nanoparticles were characterized by X-Ray Diffractometer (XRD), Scanning Electron Microscope (SEM), Energy Dispersive Spectroscopy (EDS) and UV-Vis Spectrophotometer. Degradation of methyl orange was investigated by photocatalysis process in the presence of titanium dioxide nanoparticles under UV light irradiation.

2. Materials and methods

2.1. Preparation of titanium dioxide nanoparticles

The materials that were used to synthesized titanium dioxide are titanium tetraisopropoxide (TTIP), ethanol (C2H5OH), deionized water (H2O) and hydrochloride acid (HCl). Titanium dioxide nanoparticles were synthesized via sol-gel method, 12 ml s of TTIP was dissolved into 100 ml s of ethanol in the beaker and stirrer for 30 minutes using a magnetic stirrer.

For hydrolysis reaction, 3 mls of deionized water and 1 ml of hydrochloride acid were added to the solution drop wise. The mixed solution was then stirred constantly for 2 hours to get a homogeneous solution. The pH value of the mixed solution was maintained in the acidity range of pH 3, after aging for 24 hours, the gel was dried and then heated at 400°C and 700°C.

2.2. Characterizations

The heat treated titanium dioxide (TiO2) nanoparticles prepared by sol-gel process were then characterized by X-ray diffraction (XRD), and Scanning Electron Microscopic (SEM). The phase transformation and the surface morphology of titanium dioxide nanoparticles were observed.

2.3. Photocatalytic degradation

The photocatalytic activity of the titanium dioxide (TiO2) nanoparticles was examined by the degradation of methyl orange (MO) under UV light illumination. Three different concentrations of dye solutions (10 mg/l, 20mg/l and 30mg/l) were prepared by dissolving 10 mg, 20 mg and 30 mg of methyl orange powder in 1 litre of deionized water separately in the beaker, the pH value of the solution was measured to be 7.

The synthesized titanium dioxide nanoparticles were mixed in the methyl orange solution of various concentrations to understand the co-relation of the initial concentration of methyl orange and photocatalytic activity. The suspensions containing 3 mg, 5 mg and 7 mg catalyst and 30 mls of methyl orange were stirred for 30 minutes in the dark to establish adsorption-desorption equilibrium to eliminate the error due to any initial adsorption effect and pre-produced electrons and holes from environmental light sources. A 25Watts ultraviolet (UV) germicidal lamp fixed at a distance of 27 cm above the surface of the solution was used as a UV light source. The stirred suspensions were then irradiated with UV light and 4 mls of the mixed solution was drawn out every hour for absorbance
analysis. The absorption spectra of methyl orange were measured using a UV–Visible spectrophotometer.

3. Results and discussion

3.1. Phase analysis

The XRD patterns of titanium dioxide nanoparticles were obtained and the phases present were identified by JCPDS database (Powder Diffraction Files, Joint Committee on Powder Diffraction Standards) shown in Figure 1.

The 120°C dried titanium dioxide exhibit an amorphous phase where no distinct peak is identified. The 400°C titanium dioxide exhibit anatase phase and the significant peaks were observed. This result confirmed that width of the anatase peak diffraction from XRD indicating the smaller crystalline size at 400°C.

Phase transformation occurred from anatase phase to thermodynamically more stable rutile phase when calcination temperature increases to 700°C.

![Figure 1. XRD patterns of titanium dioxide nanoparticles.](image)

The anatase and rutile peaks obtained with decrease intensity. Among the XRD peaks, the width of 25.4° is a useful peak since it has high intensity which in turn is used to determine the crystal size. The peak value corresponds to the tetragonal anatase phase.

3.2. Morphology analysis

The SEM images were analyzed under 10 kx magnification. The morphology of the titanium dioxide nanoparticle powders dried at 120°C is shown in Figure 2, most of the particles are spherical shaped and different in sizes.

The titanium dioxide nanoparticles heated at 400°C and shown in Figure 3 shows a more uniform particles at the surface, while an increase in the temperature to 700°C as shown in Figure 4 shows that the particle size increase and the agglomeration becomes more significant. These results explained the effect of the heat treatment on the particle size.

Higher surface area of titanium dioxide nanoparticles gives good performance. In the rutile form, the atoms occupy the least space.
Figure 2. Titanium dioxide nanoparticles dried at 120°C.

Figure 3. Titanium dioxide nanoparticles calcined at 400°C.

Figure 4. Titanium dioxide nanoparticles calcined at 700°C.

This makes the rutile form the most stable at higher temperatures. An important requirement for improving the titanium dioxide catalytic activity is to increase its specific surface area, which is certainly dependent on the crystal size. The smaller the catalyst, the larger will be its specific surface area. Calcination temperature is also important for removing the organic molecules from the final products and completing the crystallization. Very high calcination temperature will result in aggregation and phase transformation, and this affects the microstructures as well as the properties of titanium dioxide nanoparticles.

3.3. Photocatalytic Activity
Methyl orange (MO) is an organic dye that is commonly used as organic model compound in wastewater photocatalytic degradation studies. UV-Vis spectra of MO have two absorption band
maxima situated at 270 nm and 465 nm. The band at 465 nm was used for quantification. The photocatalytic activity of titanium dioxide nanoparticles were examined by the efficiency of degradation of methyl orange. Different concentrations of methyl orange (10, 20 and 30 mg/l) were used to evaluate the degradation percentage by using 400°C and 700°C heat treated titanium dioxide nanoparticles. The graph of absorbance versus wavelength was obtained from the UV-Vis Spectrophotometer. The peak of the graph was identified and the maximum absorbance value at the 463 nm wavelength at different time was observed. Figure 5 shows the absorbance spectra of 10 mg/l methyl orange degrade by 5 mg heat treated titanium dioxide nanoparticles. The absorbance value decreases as the time of irradiation increases.

![Graph of absorbance spectra](image)

**Figure 5.** Absorbance spectra of 10 mg/l MO with 5 mg heat treated TiO$_2$ (700°C).

The absorbance value at 463 nm wavelength of every hour after irradiation is tabulated in the Table 1. The percentage of degradation is calculated, it shows that as irradiation time increase, the percentage also increases. After 4 hours of irradiation, the percentage reach 49.28% and marked the highest among all the degradation group using different titanium dioxide nanoparticles and methyl orange concentrations.

| Amount of TiO$_2$ | Irradiation Time | Absorbance value at 463 nm | Percentage of Degradation(%) |
|-------------------|------------------|---------------------------|-----------------------------|
|                   | 0 hour           | 0.968                     | 0                           |
| 5 mg              | 1 hour           | 0.870                     | $\frac{0.968 - 0.870}{0.968} \times 100\% = 10.12$ |
|                   | 2 hour           | 0.746                     | $\frac{0.968 - 0.746}{0.968} \times 100\% = 22.93$ |
|                   | 3 hour           | 0.628                     | $\frac{0.968 - 0.628}{0.968} \times 100\% = 35.12$ |
|                   | 4 hour           | 0.491                     | $\frac{0.968 - 0.491}{0.968} \times 100\% = 49.28$ |

**Table 1.** The percentage of degradation of TiO$_2$ for 4 hours irradiation.
Figure 6 shows the removal rate of methyl orange after 4 hours UV light irradiation. Comparison is made based on the calcination temperature of titanium dioxide nanoparticles, the concentrations of methyl orange and the amount of loading catalyst. 10 mg/l of methyl orange gives the highest removal rate in between 20 mg/l and 30 mg/l concentrations. The removal rate of 10 mg/l methyl orange by 5 mg titanium dioxide nanoparticles mark the highest while the removal rate of 30 mg/l methyl orange by 5 mg titanium dioxide reached the lowest. Both groups of titanium dioxide nanoparticles were calcined at 700°C.

![Graph showing removal rate of MO versus calcination temperature of TiO₂.](image)

**Figure 6.** The removal rate of MO versus calcination temperature of TiO₂.

4. Conclusions
Titanium dioxide (TiO₂) nanoparticles were successfully synthesized via sol gel process. The XRD patterns of titanium dioxide nanoparticles has shown the phase transformation from anatase to rutile when calcination temperature increase from 400°C to 700°C. The crystallinity of titanium dioxide increase when calcination temperature increase and results in good photocatalysis reactions. The peaks of titanium dioxide nanoparticles were identified. The morphology of the titanium dioxide nanoparticles was examined using scanning electron microscopy (SEM). The morphology analysis from SEM confirms an agglomeration of particles from the sol gel method; the nanoparticle is spherical shape with different sizes. Degradation of methyl orange by heat treated titanium dioxide nanoparticles at 700°C give the optimum results among all the groups. This research indicates that the heat treated titanium dioxide nanoparticles are effective in degradation of methyl orange. The lowest concentrations of methyl orange give the greatest removal rate. Another observation made to prove the photocatalytic degradation process is the colour changes of aqueous methyl orange. When the time of UV light irradiation increases, the orange colour will became lighter. The findings of this research indicates that the heterogeneous photocatalysis in presence of ultraviolet light is a method which can be implemented and used for the complete degradation of azo dyes from waste water.

5. References
[1] Dalton J S, Janes P A, Jones N G, Nicholson J A, Hallman K R and Allen G C 2002 *Environmental Pollution* 120 415-422
[2] Kanakaraju D, Glass B D and Oelgemoller M 2014 Environmental Chemistry Letters 12(1) 27–47
[3] Tiwari D K, Behari J and Sen P 2008 World Applied Sciences Journal 3(3) 417-433
[4] Madjene F, Aoudjit L, Igoud S, Lebik H and Boutra B 2013 Transnational Journal of Science and Technology 3(10) 34-39
[5] Jallouli N, Elghniji K, Trabelsi H and Ksibi M 2017 Arabian Journal of Chemistry 10 S3640-S3645
[6] Tayade R J, Surolia P K, Kulkarni R G and Jasra R V 2007 Science and Technology of Advanced Materials 8(6) 455-462
[7] Natarajan T S, Thomas M, Natarajan K, Bajaj H C and Tayade R J 2011 Chemical Engineering Journal 169(1-3) 126-134
[8] Ioannou P, D Nica P, Paun V, Vizureanu P and Agop M 2008 Physica scripta 78 065101

Acknowledgements
I would like to express my gratitude to Universiti Malaysia Perlis (UniMAP) and Center of Excellence Geopolymer and Green Materials (CEGeoGTech) for giving me the opportunity to be involved in this project.