

## Studies on Photodegradation of Methylene Blue (MB) by Nano-sized Titanium Oxide

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**T**HE PHOTOCATALYTIC degradation of methylene blue was investigated by various types of titanium dioxide particles which include three different nano particle size (28, 65 and 200 nm) as a result of calcinations temperature. Titanium oxides were characterized by scanning electron microscopy (SEM) and X-ray diffraction. The degradation was monitored by measuring the change of dye concentration as a function of irradiation time under UV radiation. The anatase type in nano size, 28 nm and 65 nm has an expected high rate than rutile of titanium which its size equals 5 to 200 nm for photodegradation efficiency, while the commercial titanium grade has degradation rate less than the three calcinated nano sized types.

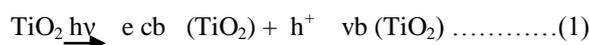
The effects of UV radiation time and the initial concentration of MB were investigated. The results indicate that the rate of degradation increases as UV radiation time increasing. The kinetics study indicate that the photodegradation of MB by TiO<sub>2</sub> behaves as first order reaction.

**Keywords:** Nano titanium dioxide, Photocatalyst, Photodegradation, Calcination and Methylene blue.

Photocatalysis, as a research area, has witnessed a huge change over the past two decades with significant advancements being in the synthesis of novel materials and nano-structures, and the design of efficient processes for the degradation of pollutants and the generation of energy<sup>(1-3)</sup>.

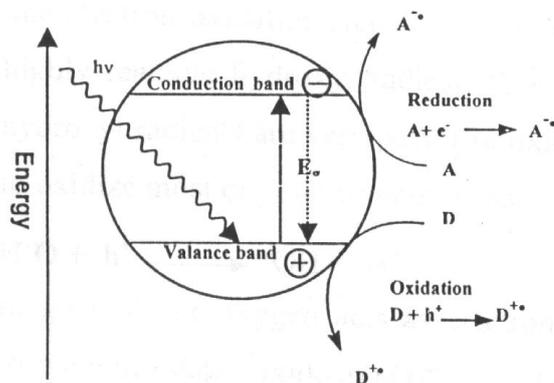
Photocatalysis refers to the acceleration of the rate of chemical reactions (oxidation/reduction) brought about by the activation of a catalyst, usually a semiconductor oxide, by ultraviolet (UV) or visible radiation. Also, applications of semiconducting catalysts for environmental air purification, water disinfection, hazardous water remediation, and water purification protection have attracted much attention in the last few years<sup>(4-10)</sup>.

Photocatalysis over a semiconductor oxide such as TiO<sub>2</sub> is initiated by the absorption of a photon with energy equal to, or greater than the band gap of the semiconductor (.3.2 eV for anatase), producing electron-hole (e-/h+) pairs, as written in Equation 1.



Among the semiconducting materials, one of the most used is titanium dioxide due to its commercial availability, low cost, chemical stability, photostability, and high efficiency in photocatalytic processes<sup>(11,14)</sup>.

The TiO<sub>2</sub> particles can act as either an electron donor or acceptor for molecules according to the medium. The valence band hole is strongly oxidizing, and the conduction band electron is strongly reducing. At the external surface, the excited electron and the hole can take part in redox reactions with adsorbed species such as water, hydroxide ion (OH<sup>-</sup>), organic compounds, or oxygen. The charges can react directly with adsorbed pollutants, but reactions with water are far more likely where water molecules are far more populous than contaminant molecules. Oxidation of water or OH<sup>-</sup> by the hole produces the hydroxyl radical (OH<sup>\*</sup>), an extremely powerful and indiscriminant oxidant as represented by Fig. 1.



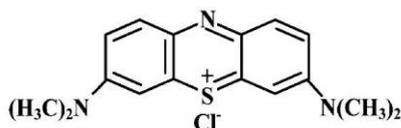
**Fig.1. Mechanism for the photo-activation of a semiconductor catalyst (TiO<sub>2</sub>).**

According to the importance of TiO<sub>2</sub> as a photo catalyst of degradation of dyes, this work aimed to study the effect of nano-prticle size on the rate of photodegradation process.

## Material and Methods

### Materials

Titanium dioxide (TiO<sub>2</sub>) commercial (Fluka), Titanium chloride (TiCl<sub>4</sub>), a ReagentPlus grade was supplied from SIGMA-ALDRICH and Methylene blue 3,7-Bis(dimethylamino)-phemazo-thionium chloride. M. F. C<sub>16</sub>H<sub>18</sub>N<sub>3</sub>SCl . 3H<sub>2</sub>O , M. wt. 373.5g was purchased from Fluka.



Methylene blue is non-coordinating reagent and it may be considered as redox reagent or cationic dye. It is dark green odourless crystal with bronze luster or crystalline powder and is easily soluble in water (4g/100ml), and chloroform, but is insoluble in ether.

#### *Preparation of TiO<sub>2</sub>*

One ml of TiCl<sub>4</sub> was added to the 30ml ice-cold distilled water with constant stirring. 10ml of 30% ammonia solution was added drop-wise with continuous stirring and maintaining the temperature around 5 to 10 °C for 5 hr. The precipitated titanyl hydroxide was repeatedly washed with distilled water to remove the chloride ions from the solution. The removal of Cl<sup>-</sup> ions was confirmed by using silver nitrate solution. The titanyl hydroxide was dried in oven at 100 °C for 4 hr. The dried powders were calcinated at different temperatures at 100 °C for 2 hr in presence of air. To study the effect of the calcinated temperatures on the TiO<sub>2</sub> activity, the dried powders were calcinated at different temperatures 450 °C, 500 °C and 700 °C for 4 hr<sup>(15)</sup>.

#### *Characterization of TiO<sub>2</sub>*

##### *X-ray diffraction (XRD) of TiO<sub>2</sub>*

X-ray diffraction (XRD) (X0 Pert MPD, Ni filtered Cu K<sub>α</sub> radiation, Phillips) was used for the identification of crystalline phase of TiO<sub>2</sub> particles.

##### *Morphology of TiO<sub>2</sub>*

The surface morphology of TiO<sub>2</sub> was characterized by scanning electron microscopy (SEM) (JEOL-JSM 5800LV, Japan).

#### *Photocatalytic study*

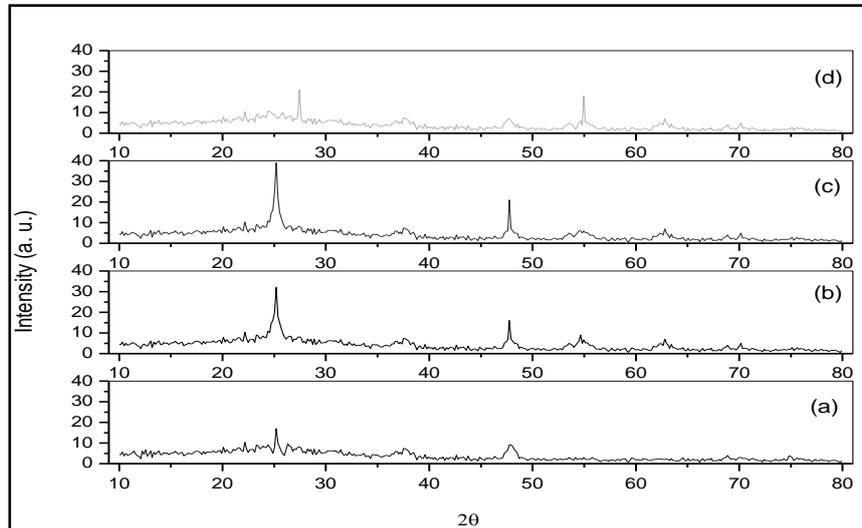
The experimental set up was employed for the photocatalytic studies by using photoreactor (180Watt). The concentration of MB dye solution was 2.5×10<sup>-5</sup>M. The concentration of MB dye after photodegradation was analysed by using a UV-V is spectrophotometer (schmadzo) by measuring the change in absorbance values at 610 nm.

The control experiment was carried out by irradiating an aqueous solution of MB dye by using the three calcinated TiO<sub>2</sub> prepared where no observable loss of dye was observed.

## **Result and Discussion**

#### *X-ray diffraction (XRD) of TiO<sub>2</sub>*

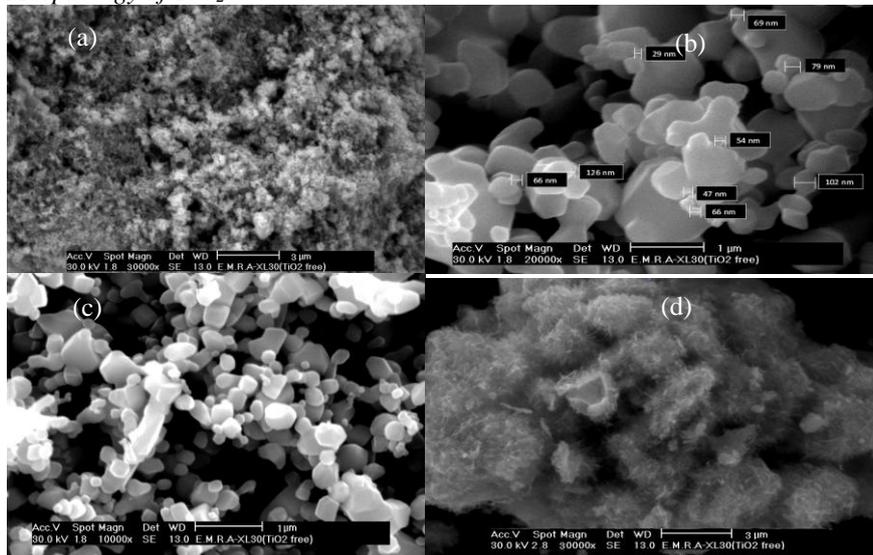
The X-ray diffraction patterns of both the commercial TiO<sub>2</sub> (a) and that treated (b, c, d) are shown in Fig. 2. Peaks at 2θ = 25.50° (101) and 48.0° were observed for all samples. These peaks characterized to anatase form of TiO<sub>2</sub>. It is observed that the sharpness of the first peak (at 2θ = 25.50° (101)) increases with calcination at 450 °C and 500 °C. On the other hand, the calcinated sample at 700 °C shows specific peaks at 2θ = 27.50° (110) and 54.5° which characterized to the formation of rutile phase. From the X-ray diffraction, the particle size of the calcinated samples equal to 65, 28 and 200 nm for the for the TiO<sub>2</sub> calcinated at 450 °C, 500 °C and 700 °C.



**Fig. 2.** XRD patterns of different titanium oxides prepared (a) commercial, (b) 65 nm, (c) 28 nm and (d) 200 nm, which its calcination temperatures are (b) 450 °C, (c) 500 °C and (d) 700 °C .

The high value of the particle size at 700°C may be due to the phase transformation from anatase to rutile and/or to the formation of some aggregate particle by heating as confirmed by X-ray pattern.

#### *Morphology of TiO<sub>2</sub>*

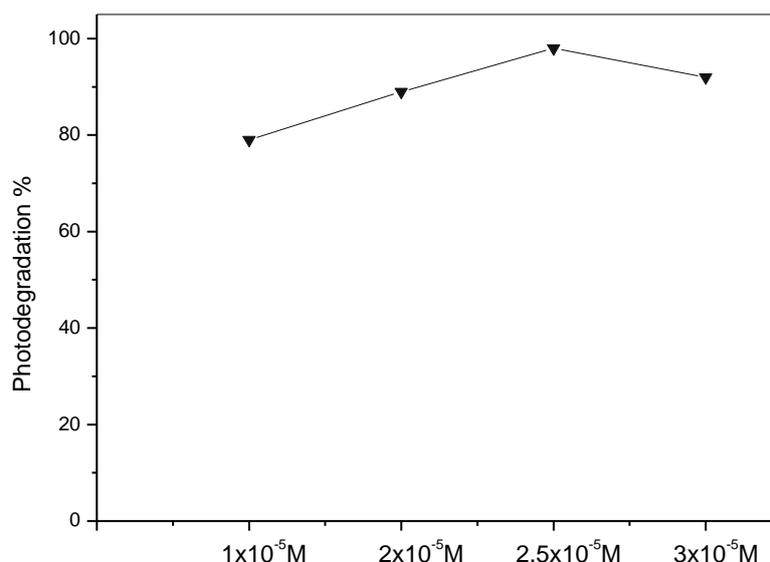


**Fig. 3.** SEM images of different titanium oxides prepared (a) commercial, (b) 65 nm, (c) 28 nm and (d) 200 nm, which its calcination temperatures are (b) 450 °C, (c) 500 °C and (d) 700 °C.

The SEM micrograph shows that the particles almost clustered and in the size range 500 nm for the commercial sample (Fig 3. a), while titanium oxide calcinated at lower temperatures 450 °C and 500 °C are in nanosized particles 65 nm and 28 nm, respectively (Fig. 3. b,c). For the sample calcinated at 700 °C (Fig. 3. d), it is observed that the nanosized particles are larger than observed at low temperatures 450 °C and 500 °C it reach 200 nm, This may be due to the phase transformation and/or else aggregate of the small particles to a large one.

#### *Effect of dye initial concentration*

The effects of the initial concentration of MB dye on the photocatalytic efficiency were investigated with concentrations  $1.0 \times 10^{-5}$  M,  $2.0 \times 10^{-5}$  M,  $2.5 \times 10^{-5}$  M, and  $3.0 \times 10^{-5}$  M (Fig. 4). From the curve, it is clear that the photodegradation percentage increases as the initial concentration increase from  $1.0 \times 10^{-5}$  M to  $2.5 \times 10^{-5}$  M and then decreases at  $3.0 \times 10^{-5}$  M.

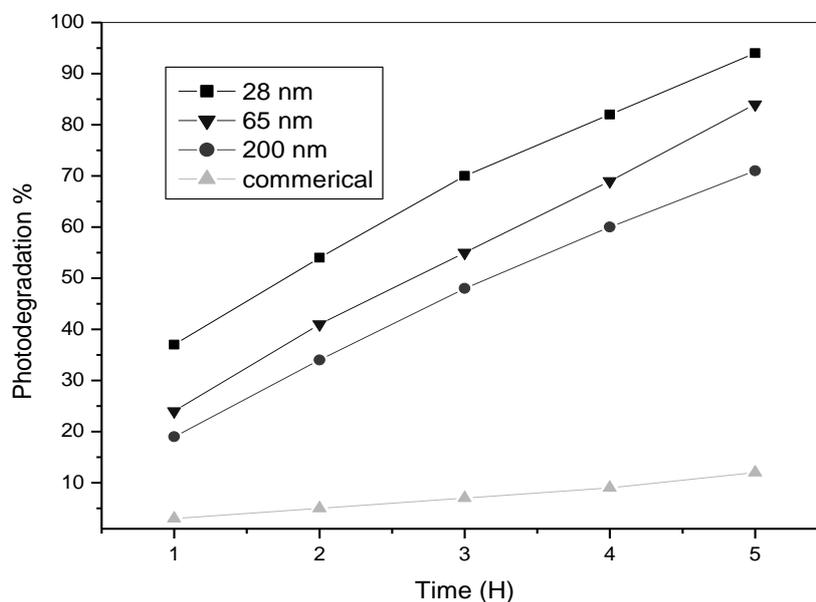


**Fig. 4.** Effect of MB dye initial concentration on the photodegradation percentage at 5 hr.

This may be explained by considering the high concentrations of dye, the deeper coloured solution would be less transparent to UV light and the dye molecules may absorb a significant amount of UV light causing less radiation to reach the catalyst and thus reducing the OH• radical formation. Since OH• radicals are of prime importance in the attack of the dye molecules, the lowering of OH• radicals would cause the photodegradation efficiency to decrease<sup>(16)</sup>.

*Effect of UV radiation time*

On increasing the radiation time, the degradation efficiency of dye increases. It has been reported that the photocatalytic reaction rate depends largely on the irradiation absorption of the photocatalyst leading to an increase in the degradation rate with increasing light intensity during photocatalytic degradation<sup>(17-20)</sup>. The high UV radiation intensity increases the photon influx entering the dye solution and consequently excites the TiO<sub>2</sub> particles in the media resulting in more OH• radicals being formed at the surface. As the reactive number of OH• radicals attacking the dye molecules increases, the photodegradation efficiency increases (Fig. 5).



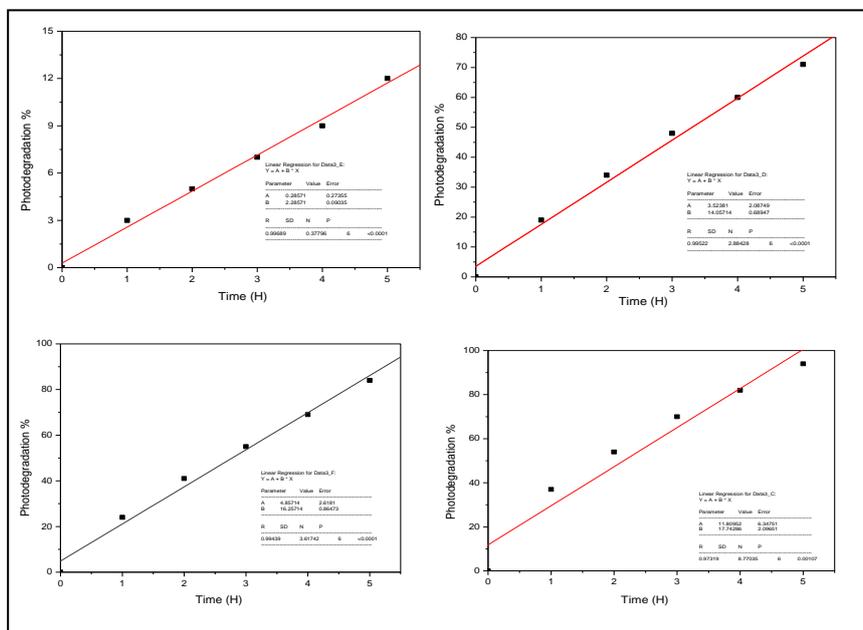
**Fig. 5.** The effect of irradiation time of MB dye by commercial and different of titanium oxides prepared under UV irradiation.

*Kinetics analysis*

To study the kinetics of the degradation the equation of the first-order kinetic expression was applied<sup>(21,22)</sup>.

$$\ln[C_t] = \ln[C_0] - k_{app}t,$$

where [C<sub>0</sub>] is the initial concentration of dye, [C<sub>t</sub>] is the concentration at time t, and k<sub>app</sub> is the apparent rate constant.



**Fig. 6.** photodegradation rates of MB dye degradation use under UV light irradiation for 1–5 hr for different titanium oxides prepared (a) commercial, (b) 65 nm, (c) 28 nm and (d) 200 nm, which its calcination temperatures are (b) 450 °C, (c) 500 °C and (d) 700 °C.

The obtained straight lines when  $\ln[C_t]$  was plotted against  $t$  for all samples confirmed the first-order kinetics of dye degradation [ The rate constants for MB dye degradation were listed in Table 1 for the different titanium oxides commercial, 65 nm, 28 nm and 200 nm, respectively.

**TABLE 1.** Photodegradation rates values and activation energies for for different titanium oxides prepared (a) commercial, (b) 65 nm, (c) 28 nm and (d) 200 nm, which its calcination temperatures at (a) 450 °C, (b) 450 °C, (c) 500 °C and (d) 700 °C .

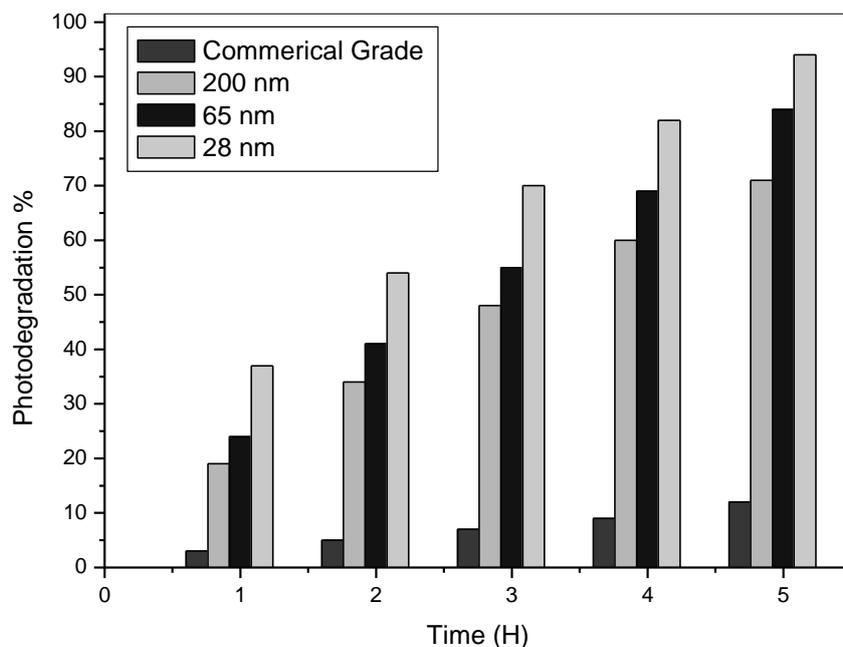
Titanium Type	Commercial	Nano 200 nm	Nano 65 nm	Nano 28 nm
Rate of Photodegradation (r)	2.28	14.05	16.25	17.74

From this table, it is observed that the rate of photodegradation increases from 2.28 to 14.05 (~ 5 times) when changes from commercial TiO<sub>2</sub> particles to that have particle size (200 nm) while it increases slightly as particle size of TiO<sub>2</sub> decreases from 200 nm to 28 nm.

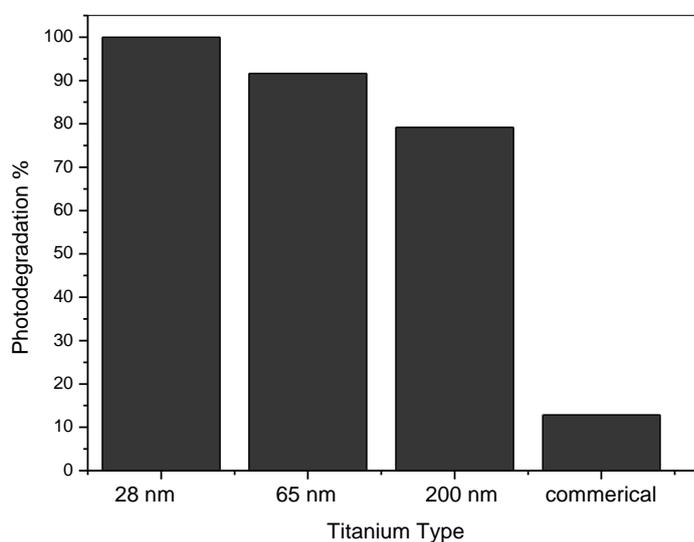
*Comparison between photocatalytic rates for MB by different samples of TiO<sub>2</sub>*

From the previous results, the diagram which plotted in Fig. 7 indicating the dependence of photodegradation percent on UV radiation time which is effected by the particle size of the TiO<sub>2</sub> samples (Fig. 7 and 8) respectively. These figures indicate the efficiency of the samples to photodegradation process for MB followed the following sequence TiO<sub>2</sub> (commercial) < TiO<sub>2</sub> (200 nm) < TiO<sub>2</sub> (65 nm) < TiO<sub>2</sub> (28 nm).

This sequence means that as the TiO<sub>2</sub> particle size decreases the efficiency of the particle increases, this may due to the increasing of the surface area which enhance the effect of UV radiation to work.



**Fig. 7.** Efficiencies of MB dye degradation use under UV light irradiation for 1–5 hr for different titanium oxides prepared (a) commercial, (b) 65 nm, (c) 28 nm and (d) 200 nm, which its calcination temperatures are (b) 450 °C, (c) 500 °C and (d) 700 °C.



**Fig. 8.** Comparison of photodegradation rates percentage of MB dye degradation use under UV light irradiation for 1–5 hr for different titanium oxides prepared (a) commercial, (b) 65 nm, (c) 28 nm and (d) 200 nm, which its calcination temperatures are (b) 450 °C, (c) 500 °C and (d) 700 °C.

### Conclusion

It is concluded from this study that the  $\text{TiO}_2$  as a semiconductor material exhibits a photodegradation effect of MB dye. Also, it is observed that the percent of the photodegradation process depends on the UV radiation time, the initial concentration of the dye and the particle size of  $\text{TiO}_2$ .

As the particle size increases the efficiency of photodegradation process by  $\text{TiO}_2$  for MB decreases, this may be due to the change in the surface area which controlled in the penetration of UV radiation through the  $\text{TiO}_2$  particles.

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### دراسات على التفكك الضوئي لصبغة الميثيل الأزرق بواسطة اكسيد التيتانيوم النانومتري

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تم دراسة التفكك الضوئي لصبغة الميثيل الأزرق بواسطة عينات من اكسيد التيتانيوم ذو الحجم النانومتري باستخدام اشعاعات فوق بنفسجية و شملت الدراسة أربع عينات من اكسيد التيتانيوم احدهم عينه تجارية و الثلاثة عينات الاخرى تم الحصول عليها بعمليات التسخين عند درجات حرارة مختلفة 450، 500، 700°م. تم دراسة النسبة المذابة لتفكك صبغة الميثيل الأزرق مع زمن التعرض للاشعة فوق البنفسجية، التركيز الاولي لصبغة الميثيل الأزرق .

دلت نتائج التوصيف للعينات المكلفة باستخدام طيف حيود الاشعة السينية و الميكروسكوب الالكتروني الماسح و النافذ انه تم الحصول على ثلاث عينات من اكسيد التيتانيوم حجمها الحبيبي 65، 28، 200 نانومتر وفقا لدرجات الحرارة سالفة الذكر.

كما تم دراسة ميكانيكية التفكك الضوئي في ضوء النتائج التي تم الحصول عليها من اعتماد النسبة المئوية للتفكك الضوئي على زمن التعرض للاشعة فوق البنفسجية و الحجم الحبيبي للعينات.