



Exploring Purification Property of TiO₂ Nanoparticles with Photo Degradation on EBT and MO

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Abstract

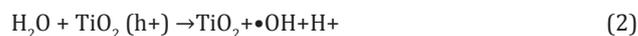
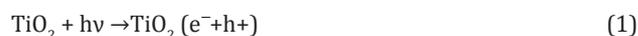
This study focused on a high photo catalyst activity of TiO₂ in addition to bleaching of different types of dyes. Titanium dioxide Nano particles were successfully synthesized by sol Gel method, then the gel has been dried at 400°C to obtain TiO₂ Nano powder. The synthesized Nano powder has been characterized by X-ray diffraction (XRD), Scanning Electron Microscope (SEM), Ultraviolet spectroscopy (Uv-Vis). A system of photocatalytic with UV- lamp (365nm) to activate a thin layer of TiO₂ particles on glass substrate was set up, and the effect of activated TiO₂ on degradation of methyl orange and Eriochrom black T as a model of organic pollutants were investigated in ppm concentration over period time of 6 hours. The results shown that Titanium dioxide nanoparticle shows a high efficiency to degradation of dyes. The highest percentages were 95.69%, 97.96% for MO and EBT respectively.

Keywords: (TiO₂ Nanoparticles; Photocatalytic; EBT; MO; Water purifier

Introduction

In the previous few years, there has been interesting in metal oxides particles like TiO₂ because of its unique properties Titanium dioxide gain the major axis of many studies and research. properties and applications of TiO₂ are controlled by its morphology, particle size, purity, crystal structure and phase, porosity and surface area [1]. Titanium dioxide is used as semiconductor in wide range of applications such as photosensor, photocatalysis, dyes sensitized solar cells, anti-reflective (AR) coating, optical filters, photovoltaic devices, UV light sensor and biomedical applications, etc [2]. Nanoparticles of TiO₂ also used as a pigment, a thickener and sunscreen in cosmetics and skin care products [3]. there has been three geometrical phases of TiO₂ anatase (tetragonal), rutile (tetragonal) and brookite (orthorhombic) [4]. The efficiency of photocatalytic materials, such as titanium dioxide to degrade organic contaminants in the air and water has been studied for more than 30 years [5]. The photocatalytic disinfection efficiency is attributed to the oxidative damage mainly induced by reactive oxygen species (ROS), like O₂•-, H₂O₂ and HO•. These reactive oxygen species are produced on the surface of TiO₂ when illuminated by photons with energy

greater than its band gap, so electron will excited from valance band to the conduction band thus creating an electron-hole pair. With holes (h+) and hydroxyl radicals (OH•) generated in the valence band, and electrons and superoxide anions (O₂•-) generated in the conduction band, irradiated TiO₂ photocatalysts can decompose and mineralize organic compounds by a series of oxidation reactions leading to carbon dioxide [6]. The mechanism of radical's generation (•OH and •O₂⁻) is presented as follows [7] :



One of the major advantages of TiO₂ is its ability to absorb greater portion of the solar light and able to remove many of organic pollutants under visible light irradiation. The irradiation of light onto the surface of the photo catalysts, with energy higher than the band gap energy, will produce electron hole pairs. These photo generated charges, through a series of reaction will produce radicals responsible for the degradation of the organic pollutants [8]. However, the rapid recombination of the photo generated electron hole pairs during the photocatalytic process limits the photocatalytic efficiency of TiO₂ nanoparticles. This study focused on the efficiency of a thin layer of titanium dioxide obtained from sol Gel method in anatase phase on glass substrate and the photocatalytic performance of the TiO₂ photo catalysts was evaluated by photo degradation of methyl orange, EBT under UV light irradiation.

Experimental

Materials and method of synthesis

The materials that have been used are: Titanium tetrachloride TiCl₄ (99.99%, BDH, England), Isopropyl alcohol (99.99%).

Method of synthesis: In synthesise of TiO₂ nanoparticles by sol-gel method, TiCl₄ was used as the precursor. Firstly 10 ml of

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TiCl₄ was added to 250 ml well dried conical flask, after that 100 ml of ethanol alcohol was added from a burette, the reaction was set up in a fume hood. Addition of alcohol was dropped by the drop at constant stirring to obtain more homogenous Nanoparticles. A pale yellow solution was obtained with gelatinized precipitate of TiO₂ then the sol Gel was vaporized at 80°C until dry Gel was obtained; the dry Gel was calcined for an hour and half in box furnace at 400°C to get titanium dioxide Nano powder. Figure 1 show TiO₂ Gel obtained before calcination.

Characterization of TiO₂ Nano particles: X-ray diffraction (XRD-5500 2kw type), shows the crystallinity shape of the synthesized nanoparticles at room temperature. Scanning Electron Microscopy (SEM, Tescan VEGA2 SB) have been used to identify the morphological (size and shape) of the TiO₂ nanoparticles that prepared from sol Gel method.

Photo catalytic system: A photo catalytic system was set up from the following components:

1. A six watts Herolab 365nm UV-Lamp to irradiating the MO, EBT solutions.
2. Air was bubbled into the solution by an air bump to insure continuous supply of oxygen.
3. A magnetic stirrer was stirred constantly to insure complete suspension of the catalyst.
4. A heating system, whereas the temperature was fixed in range of 60-80°C to increase the activity of the catalyst.

For the first hour, the experiment was performed in dark condition in order to evaluate the adsorption of (MO, EBT) on the titanium dioxide nanoparticles. After an hour, the UV light was switched on and at regular time intervals; 10 mL of aliquots were taken throughout the 6 hours of irradiation time and filtered using cellulose 0.40 μm membrane filter. The taken concentrations of the (EBT, MO) were then measured using PerkinElmer Lambda 35 UV-Vis spectrophotometer. All the photocatalytic degradation experiments were carried out in triplicate. The percentage

degradation and amount of degraded materials were calculated using equation 1 and 2, respectively:

$$\text{Photo degradation (\%)} = ((C_0 - C_t) / C_0) \times 100\% \quad (1)$$

$$\text{Amount of degraded (mg/g)} = ((C_0 - C_t) / m) \times V \quad (2)$$

Where C₀ and C_t is the concentration of (MO, EBT) initially and at time t, respectively, m is the mass of photo catalyst and V is the volume of material solution. Figure 2 show the schematic diagram of the photo catalytic system.

Result and Discussion

X-ray diffraction (XRD) analysis

Figure 3 shows the X-ray diffraction pattern, SQD concentrations and S-Q for photo catalyst (TiO₂) nanoparticles prepared by sol gel method. The S-Q shown that the purity of the

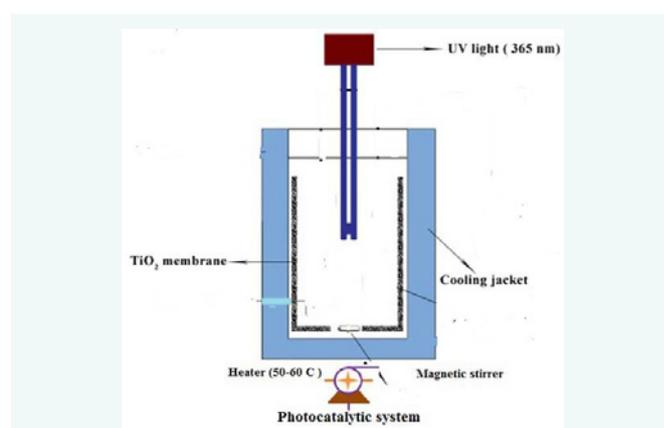


Figure 2 It shows the schematic diagram of the photo catalytic system.



Figure 1 TiO₂ Gel obtained from sol Gel method vaporized at 80°C.

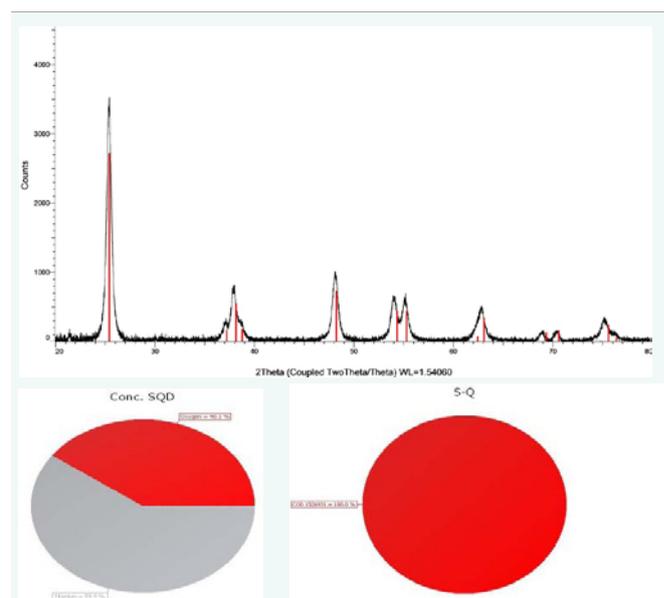


Figure 3 X-ray diffraction pattern, SQD concentrations and S-Q of TiO₂ particles prepared by sol gel method and calcined at 400°C.



samples 100%, and TiO₂ was anatase with tetragonal geometry shape has molar mass 77.96 g/mol the SQD shown the sample consist of 40.1% oxygen and 59.9% titanium elements.

Crystalline sizes of TiO₂ have been obtained from Scherrer's formula given by equation (1) [9]

$$D = \frac{k\lambda}{\beta \cos\theta}$$

At which K is a constant that depend on the crystallite shape (0.9 with the supposition of sphere-shaped particles), λ is the X-ray wavelength, β is the full width of the half maximum of the selected peak and θ is the Bragg's angle of diffraction of the peak [10].

Table 1 shows the sizes of Nanoparticles were identified at 2θ values 25.4°, 37.2°, 48.2°, 54.3°, 55.2° matches to the crystal planes of (101), (004), (200), (105) agreement with the standard X-ray diffraction pattern (JCPDS files No 21-1272).

The average of crystallite size for this TiO₂ sample was about 8.95 nm. This size was compared with the result reported by J.H. Leal *et al.* the crystallite size for anatase phase synthesized from TiCl₃ by simple high-temperature method was examined to be below 10 nm.

Scanning electron microscope (SEM)

SEM images of TiO₂ particles are shown in figure 4. Spherical particles with agglomeration were observed and the diameter of the gel particle was about 20nm. Whereas Figure 4 and 5 shown the image of TiO₂ nano powder calcined at 400°C.

Table 1: Crystal sizes of TiO₂ nanoparticles prepared from sol gel method calcined at 400°C.

Phase of obtained TiO ₂	0(DEG)2	D value	Grain size (nm)
100% Anatase	25.412	3.501	11.54
	37.209	2.414	8.95
	38.143	2.357	11.8
	54.334	1.885	17.54

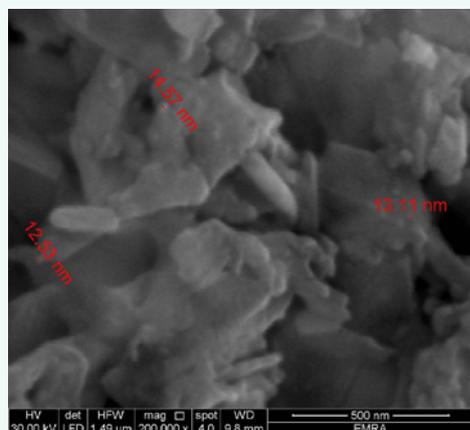


Figure 4 SEM image for TiO₂ gel prepared from sol-gel method.

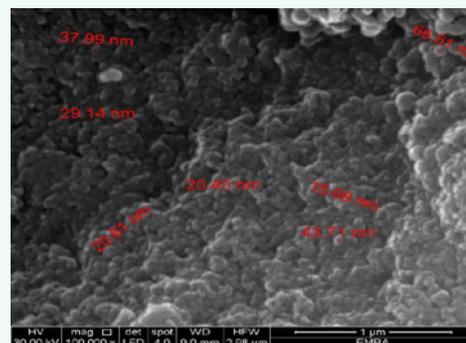


Figure 5 SEM image for TiO₂ nanoparticles calcined at 400°C.

Photo catalysis activity

Methyl orange (MO) and Eriochrome black T (EBT) degradation by TiO₂ nanoparticles: Methyl orange is a type of organic azo dye with a red colour in acid medium and yellow colour in alkaline medium. MO has a chemical formula C₁₄H₁₄N₃NaO₃S and IUPAC name: sodium 4-[(4-dimethylamino) phenylazo] benzenesulphonate. Eriochrome black T is a Complexometric indicator that is used in Complexometric titrations. in the water hardness determination process. It is an azo dye too with a chemical formula C₂₀H₁₂N₃O₇SNa and IUPAC name: Sodium 4-[2-(1-hydroxynaphthalen-2-yl) hydrazin-1-ylidene]-7-nitro-3-oxonaphthalene-1-sulfonate. Methyl orange (MO) and (EBT) are acidic dyes that are widely used in textile, printing paper, food and pharmaceutical industries and research laboratories [11]. Due to their mutagenic properties, it is very important to remove the MO and EBT from this industrial wastewater [12]. However, the dyes are difficult to degrade because of its stability towards light and oxidation [13]. As a result, various techniques are employed to remove the dye elements from water such as Physical, chemical and biological methods. But those methods are expensive and require posttreatment of the materials or solid wastes. Semiconductor photocatalytic oxidation technology has been introduced as an alternative method to remove the pollutant. TiO₂ is the most widely used photo catalyst due to its physical and chemical stability, non-toxic, and low cost [14]. One of the major advantages of TiO₂ is its ability to absorb greater portion of the UV- light and able to remove many of organic pollutants under visible light irradiation [15]. The irradiation of light onto the surface of the photo catalyst, with energy higher than the band gap energy, will produce electron hole pairs. These photo generated charges, through a series of reaction, would produce radicals responsible for the degradation of the organic pollutants (Figure 6,7,8) (Table 3).

The amount of MO, EBT degraded and the degradation percentage have been calculated by 1, 2 equations and the results obtained showed a high efficiency of TiO₂ nanoparticles to degrade the dyes. The percentage was increase with the time increased and the developed model predicted that the highest amount of MO and EBT were 23.99, 24.49 mg/g respectively

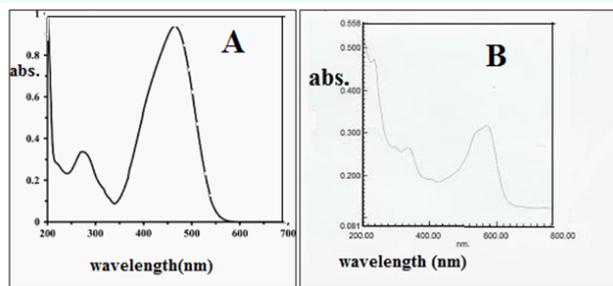


Figure 6 The absorption spectrum of A: 50 ppm of methyl orange (MO) B: 50ppm of Eriochrome black T (EBT).

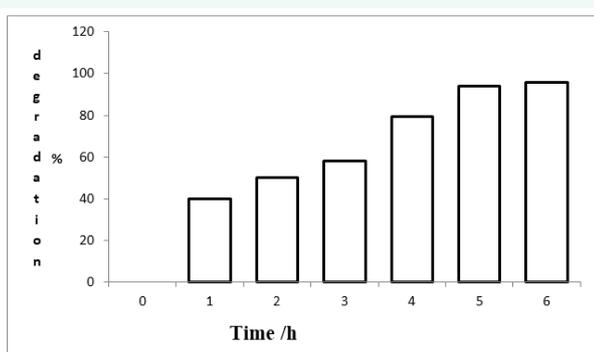


Figure 7 Photo degradation percentage of MO by TiO₂ nanoparticles at different time.

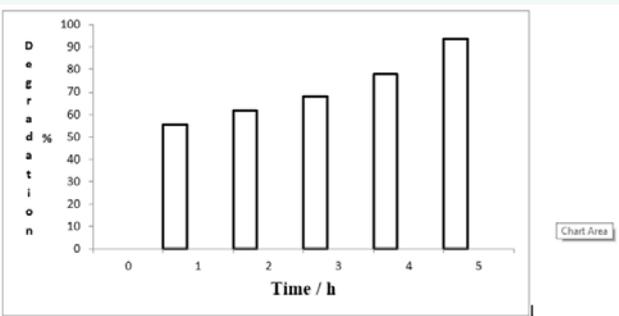


Figure 8 Photo degradation percentage of EBT by TiO₂ nanoparticles at different time.

with degradation percentage 95.69%, 97.96%. The solution concentrations of MO, EBT were 50ppm degraded by 1 gr of TiO₂ nanoparticles.

Conclusion

One gram of titanium dioxide nanoparticle was used to degrade 50ppm dyes solutions of methyl orange and eriochrom black T for 6 hours under 365nm UV lamp. The photo catalyst shows a high efficiency to degradation of dyes. The highest percentages were 95.69%, 97.96% for MO and EBT respectively.

Table 2: Amount of MO degraded (mg/g) and percentage of degradation by TiO₂ nanoparticles.

T(Time/h)	Absorbance	Amount of MO degraded (mg/g)	Percentage of degradation%
0	0.91	0	0
1	0.546	10	40
2	0.455	12.5	50
3	0.381	14.51	58.04
4	0.187	19.84	79.36
5	0.055	23.46	93.86
6	0.036	23.99	95.69

Table 3: Amount of EBT degraded (mg/g) and percentage of degradation by TiO₂ nanoparticles.

T(Time/h)	Absorbance	Amount of EBT degraded (mg/g)	Percentage of degradation%
0	0.32	0	0
1	0.142	13.84	55.36
2	0.122	15.39	61.58
3	0.102	17.01	68.06
4	0.07	19.5	78.02
5	0.019	23.45	93.82
6	0.006	24.49	97.96

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