

Synthesis of TiO₂ Nanoparticles and Their Photocatalytic Activity for Methylene Blue

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Abstract The Photocatalytic degradation of methylene blue dye (MB) was studied using Titanate nanoparticles catalyst under UV light in a tubular reactor. Titanate nanoparticles were synthesized by hydrothermal reaction using TiO₂ and NaOH as the precursors and calcinations at 500°C for 4 hr. The products were characterized with TEM and XRD. The parameters studied are Titanate nanoparticles catalyst dosage, initial concentration of dye and pH of the reaction mixture. The degradation of dye was found to be effective in the range: catalyst dose 0.10, 0.15, 0.20 g catalyst/ 400 mL of dye solution, initial dye concentration 5, 10, 15 ppm and pH of reaction mixture 1.4, 7, 12.6. Experimentation on different concentrations of TiO₂ nanoparticles showed that 0.2 g TiO₂/ 400 ml of effluent is the most suitable catalyst concentration. Photocatalytic processes were found to work better in basic medium and the present study showed that the best pH value was 12.6. The effect of the initial methylene blue concentration on the percentage degradation was also studied, demonstrating that the degradation of methylene blue generally increased when decreasing its concentration. The results showed that a percentage methylene blue degradation of 97.6% could be obtained when treating an effluent with 5 ppm of methylene blue for 90 minutes at 0.2 g TiO₂/ 400 ml of effluent and pH 12.6. This corresponds to 97.2% degradation when working on an effluent with 10 ppm methylene blue and 93%, when treating an effluent with 15 ppm of methylene blue for 90 minutes.

Keywords: hydrothermal reaction, Titanate nanoparticles, photocatalytic degradation, methylene blue

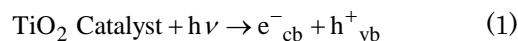
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1. Introduction

Around one million tons of synthetic dyes are produced each year and the global demand for these dyes is forecast to grow by about 3.9% through 2013. This predicts an exponential increase in water pollution which affects the entire ecosystem inclusive of plants, animals and humans. Most of these dyes are found to be toxic and carcinogenic to aquatic animals and plants. The discharge of colored dye effluents into water bodies has been an environmental problem of increasing concern. Dyes are being increasingly used in a number of industries, worldwide, including textile, chemicals, pharmaceuticals, foods, cosmetics and laboratories. Discharge of colored wastewaters from such industries creates serious problems to the environment. Color removal from textile dyeing effluents has been the target of great attention in the last few years, not only because of its toxicity but mainly due to its aesthetic effect, even at lower concentrations, compared to many other chemicals found in wastewater [1]. Therefore, the effective removal of dyes from aqueous systems becomes environmentally important. To date, a number of chemical, physical, and biological methods have been developed for removing dyes from wastewater. Among them, adsorption technique is believed to be one of the most effective and simplest processes [2], and

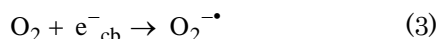
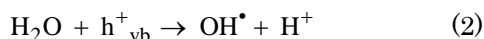
various adsorbents have been tested to remove dyes from water [2]. For example, activated carbon has been regarded as an excellent adsorbent and used widely. However, it was sometimes treated as one-off adsorbent due to the high regeneration cost [2]. This has led to the search for more efficient and cheaper alternate adsorbents.

Because of the recalcitrant nature of synthetic dyes, conventional biological treatment processes are ineffective and adsorption while coagulation practices result in secondary pollution. Consequently, a more promising technology based on advanced oxidation processes (AOPs) has been studied extensively for decolorization and degradation of textile dyes. The heterogeneous photocatalytic oxidation process developed in the 1970s is of special interest especially when solar light is used. The photocatalytic decolorization of a dye is believed to take place according to the following mechanism: when a TiO₂ catalyst is exposed to UV radiation, electrons are promoted from the valence band to conduction band and an electron-hole pair is produced (equation 1) [3].

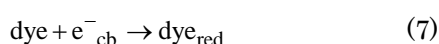
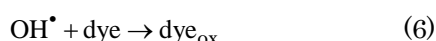
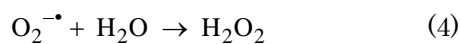


Where, e^-_{cb} and h^+_{vb} are the electrons in the conduction band and the electron vacancy in the valence band, respectively. Both these entities can migrate to the catalyst surface, where they can enter in a redox reaction with other species present on the surface. In most cases, h^+_{vb} can react easily with surface bound H₂O to produce OH[•]

radicals, whereas, e_{cb}^- can react with O_2 to produce superoxide radical anion of oxygen (equations 2 and 3) [3].



This reaction prevents the combination of the electron and the hole which are produced in the first step. OH^\bullet and $O_2^{\bullet -}$, can then react with the dye to form other species and are thus responsible for the decolorization of the dye (equations 4 - 7) [3].



Among the various semiconductor photocatalysts, TiO_2 has proved to be the most suitable catalyst for the widespread environmental applications because of its biological and chemical inertness, strong oxidizing power, non-toxicity and long-term stability against photo and chemical corrosion and Photocatalysis offers a promising solution as a clean, low-cost and environmentally friendly technology on both an energy and environmental basis; with one of its well-known applications being to degrade environmental contamination.

In recent year, there has been an increasing interest in the utilization of titanate nanostructures as titanate nanoparticles in environmental studies. It had been found that titanate nanostructures play the roles of adsorbent and photocatalyst simultaneously in the removal of dyes. Nano photocatalysis using nanostructured semiconductors constitute one of the emerging technologies due to its high catalytic efficiency. A number of methods for preparing nanostructure TiO_2 have been reported (e.g. ultrasonic technique, the sol-gel process and the hydrothermal process) and there are several methods available to synthesise Ti-O based nanostructures; for instance template, electrochemical.

The hydrothermal method has been suggested for commercial scale production without sacrificial templates. The hydrothermal reaction involves a heterogeneous chemical reaction in the presence of an aqueous solvent under high pressure and temperature in a closed system. As compared to template and sol-gel methods, hydrothermal synthesis is simpler and more effective, in that it can simultaneously provide a product with high quality and at a high yield. Post treatment following hydrothermal reaction; such as calcination and/or acid treatment, can be used to improve the photocatalytic properties of a material by promoting its crystalline conversion to a more active crystal phase or reducing surface defects. Although various techniques have been developed to fabricate titanate nanostructures and to improve their properties, unknowns remain regarding the impact of key synthesis conditions on particle properties and nanostructure formation. The influences of particle shape and morphology on its performance as a photocatalyst have not been extensively explored [4]. nanoparticles have good electrical, optical and magnetic properties that are different from their bulk counterparts

[5]. Titania nanoparticles have received much interest for applications such as optical devices, sensors, and photocatalysis [5]. There are several factors in determining important properties in the performance of TiO_2 for applications such as particle size, crystallinity and the morphology [5].

2. Experimental Sections

2.1. Materials

- Anatase TiO_2 catalyst with the following specifications: It is an analytical grade fine white powder having particle size of 0.05 mm and density of 0.94 g/cm³.
- Sodium hydroxide (NaOH, Oxford Laboratory)
- Hydrochloric acid (HCl, Elnaser Pharmaceutical Chemicals Co, Egypt)
- Deionized water
- Methylene Blue ($C_{16}H_{18}ClN_3S \cdot 2H_2O$) was used as a model pollutant in order to evaluate the photocatalytic performance of the synthesized catalyst.

2.2. Experimental Setup

Experiments were carried out in a tubular reactor consisting of a UV-A, 15W lamp, protected with a Quartz glass tube which is transparent for UV light, and enclosed in a stainless steel house. The reaction mixture passes in the annular space between the stainless steel pipe and the enclosed UV lamp for exposure to UV light and subsequent photodegradation. The stainless steel tube is 10 cm diameter and 40 cm long. This reactor is connected to a variable speed dosing pump to affect circulation of the reaction mixture in the tubular reactor.

2.3. Instrumentation

2.3.1. Instruments Used for the Photocatalytic Degradation Experiments:

The following instruments were used during the test runs:

Analytical balance (A Dventurer type), pH meter (Model pH- 206), centrifuge (auto bench centrifuge (80- 2)), muffle oven (Human Lab Instruments Co, Model No DMF- 03), magnetic stirrer (B&T Company) and spectrophotometer (PG Instruments LTD, Model T80UV-vis Spectrophotometer) used for measuring the concentration of dye solution.

2.3.2. Instrumentations Used for the Characterization of Titanate Nanoparticles Catalyst:

The crystalline phases of the products were determined by X-ray powder diffraction (X-ray, Model JSX- 60 PA, JEOL, and Japan). The morphologies of the samples were studied by a transmission electron microscope, TEM, (JEM 100 CX 11 instrument operating at 100 kV).

2.4. Procedure

2.4.1. Procedure for the Photodegradation Experiments:

A solution containing the proper concentration of the dye, e.g., 5, 10 and 15 ppm and dosage of Titanate

nanoparticles, 0.1, 0.15 and 0.2 g/ 400 ml of dye solution at pH values 1.4, 7 and 12.6 was prepared and exposed to ultraviolet light (UV-A) by passing it through the tubular reactor for a predetermined period of time. Samples are withdrawn periodically, every 15 minutes, and are centrifuged for precipitating Titanate nanoparticles powder. The clear solution is used for the absorbance measurements with UV- visible spectrophotometer at 664 nm (which is the maximum absorption wavelength of MB) to calculate the dye concentration with the aid of a calibration curve. The removal percent of MB was calculated by using the equation:

$$Y = (C_0 - C_t) / C_0 = (A_0 - A_t) / A_0,$$

where C_0 and C_t are dye concentration at initial and any time, respectively. The parameters A_0 and A_t are the absorbance of the MB solutions in the 664 nm wavelength at initial and any time, respectively.

2.4.2. Procedure for Preparation of Titanate Nanoparticles:

All the reactants and the solvents were of analytical grade and were used without further purification. In a typical procedure, 5g of pure anatase phase TiO_2 bulk-powder was mixed with 5N NaOH aqueous solution under constant magnetic stirring for 1 h a milky white solution appeared, which was then transferred to a Teflon-lined stainless steel autoclave with one liter capacity is shown in Figure 1 and heat treated at $160^\circ C$ for 16 hr. The white product was filtered and washed with 0.1 N HCl and washed several times with distilled water. The precipitates were finally calcinated at $500^\circ C$ for 4 h in air.



Figure 1. Schematic of the a Teflon-lined stainless steel autoclave

2.4.3. Procedure for Characterization of Titanate Nanoparticles

The crystalline phases of the products were determined by the X- ray powder diffraction technique. The corresponding X- ray diffraction patterns recorded agreement with the reported values of Joint Committee on Powder Diffraction Standards (JCPDS) card no. (37-0345). the final sodium titanium oxide are shown in Figure 2 which is agreement with the reported values of Joint Committee on Powder Diffraction Standards (JCPDS).

The Transmission Electron Microscope is used for studying the morphology of the nano structures. For the TEM observations, the powders were dispersed in 2-propanol ultrasonicated for 15 min. A few drops of this ultrasonicated solution were taken on a carbon-coated copper grid and examined.

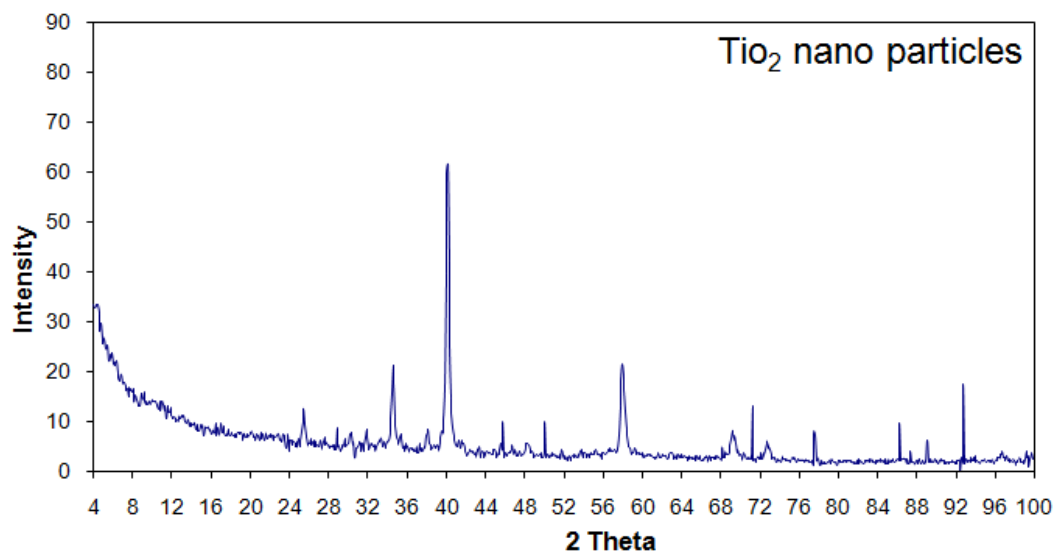


Figure 2. XRD Spectra of Titanate Nano particles synthesized

3. Results and Discussion

3.1. Characterization of the Titanate Nanoparticles Catalyst

The corresponding X- ray diffraction patterns recorded as prepared, nanoparticles after acid treatment and the final sodium titanium oxide nanoparticles is shown in Figure 2. which are basically in agreement with the

reported values in "Joint Committee on Powder Diffraction Standards (JCPDS) card No. (37-0345). the morphologies and composition of samples were observed using the transmitting electron microscopy (TEM). Figure 3 shows the TEM images of the samples formed in a 5 N NaOH solution at $160^\circ C$ for 16 h. The white product was filtered and washed with 0.1 N HCl and washed several times with distilled water. The precipitate was finally calcinated at $500^\circ C$ for 4 h in air.

During the reaction process, first titanium reacts with NaOH forming layered alkali titanate and H_2 which can be

found at the beginning of the reaction. These layered crystals are very thin and when a solution with the concentration

of 5 M was used. Dilute NaOH aqueous solution has a poor ability to form the tubular-shaped products.

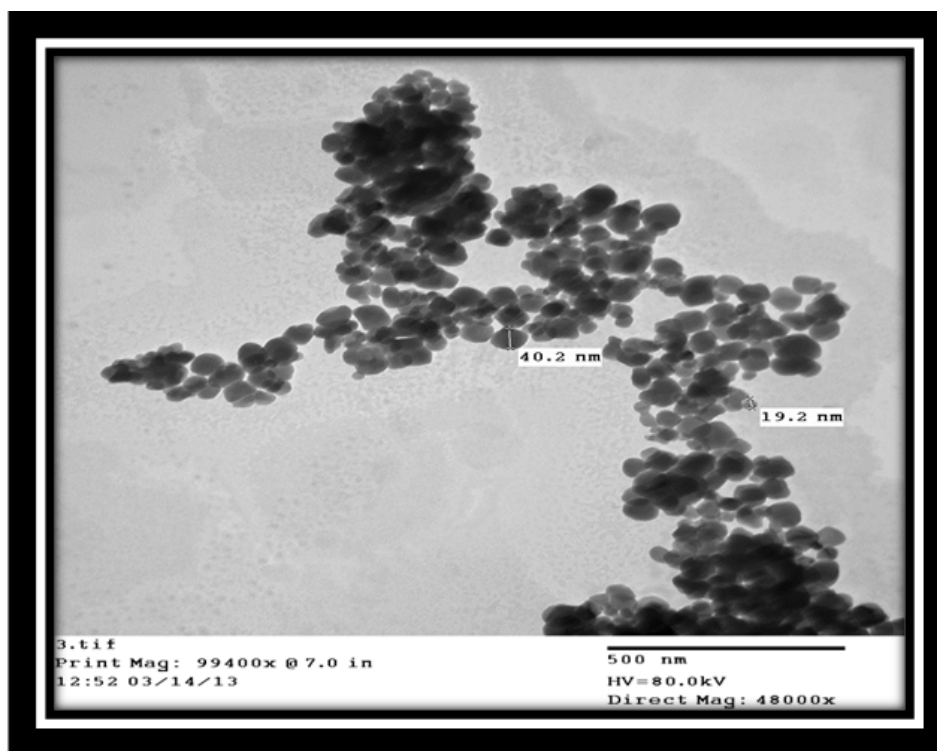


Figure 3. TEM image of the Titanate Nanoparticles synthesized

3.2. Photodegradation Study

The calibration curve of Methylene blue dye was obtained at 664 nm is shown in Figure 4 and will be used for determining the concentration of dye in the solution at different times. Figure 4 shows a plot of pollutant concentration versus absorbance. values are linearly

dependant on methylene blue concentration and increase with increasing its concentration. The Optical Density = $0.114 * \text{Concentration}$ and $R^2 = 0.981$.

The results of studying the operating parameters affecting the photodegradation of MB dye are discussed in the following sections.

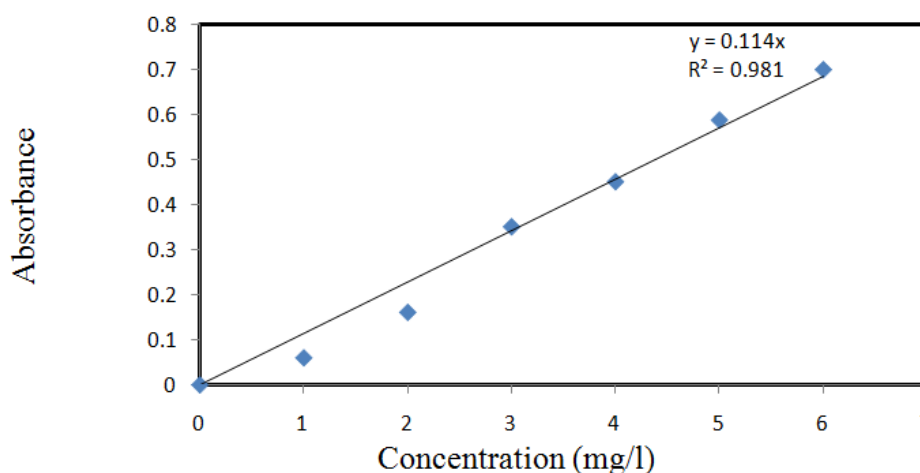


Figure 4. The Spectrophotometer calibration curve of Methylene Blue dye at $\lambda = 664 \text{ nm}$

3.2.1. Effect of Initial Dye Concentration

• Effect of Initial Concentration of Pollutant on Degradation at pH= 1.4:

The effect of initial concentration of dye solutions on the percentage removal was investigated at catalyst dosage 0.1 g/ 400ml of the dye solution for photocatalysis period of 90 min. The results are shown in Figure 5. As expected, there is a tradeoff between both photodegradation

conversion of MB and initial concentration of MB. The reason is that when the initial concentration of dye is increased, more and more dye molecules are adsorbed on the surface of TiO_2 . Since the existence of that large amount of adsorbed dye results in lack of direct contact with the holes or hydroxyl radicals, this might have an inhibitive effect on the dye degradation. Other possible reason for these results is the effect of UV screening of the own dye. In high dye concentrations a major amount of

UV tends to be absorbed by dye molecules. This reduces the efficiency of the catalytic reaction due to the decline in OH^\bullet and OH_2^\bullet concentrations. Another possible reason is the formation of the by-products during the degradation of mother dye molecules. Moreover the percentage removal increases rapidly at low MB concentrations and then changes slowly as the initial concentration increases [6]. The Methylene blue concentration is reduced after 90 minutes giving a value of 41.84% percentage degradation

at low initial Methylene blue concentration (e.g. 5 ppm) while this percentage was 33.79 and 11.34 % for relatively higher initial Methylene blue concentrations (i.e., 10 and 15 ppm of Methylene blue, respectively) at 0.1 g/ 400 ml of the dye solution. Tests on solutions with 5, 10 and 10 ppm Methylene blue are run at very close UV value 400 w/m^2 however, better results are obtained from the solution with 5 ppm Methylene blue. This indicates that the initial concentration of pollutant is the dominant factor [6].

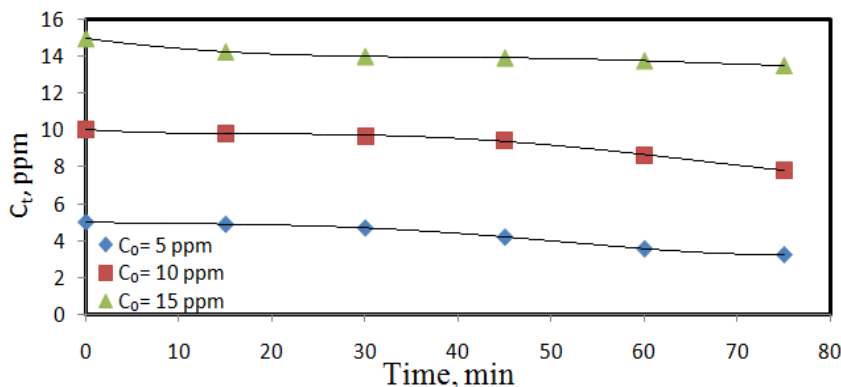


Figure 5. Effect of initial concentration of pollutant on its degradation, $C_0=5, 10, 15$ ppm, at 0.1 g $\text{TiO}_2/400\text{ml}$, and $\text{pH}=1.4$

• *Effect of Initial Concentration of Pollutant on Degradation at pH= 7:*

Figure 6 shows a plot of C_t for different initial concentrations versus time at pH 7 and 5, 10, 15 ppm dye concentrations, 0.1 g $\text{TiO}_2/400\text{ml}$. The curves clarify that

the degradation values increase with the decrease of the dye concentration. Percentage degradation of 56.56, 56 and 38.39% were obtained for initial dye concentrations 5, 10 and 15 ppm, respectively at pH value 7.

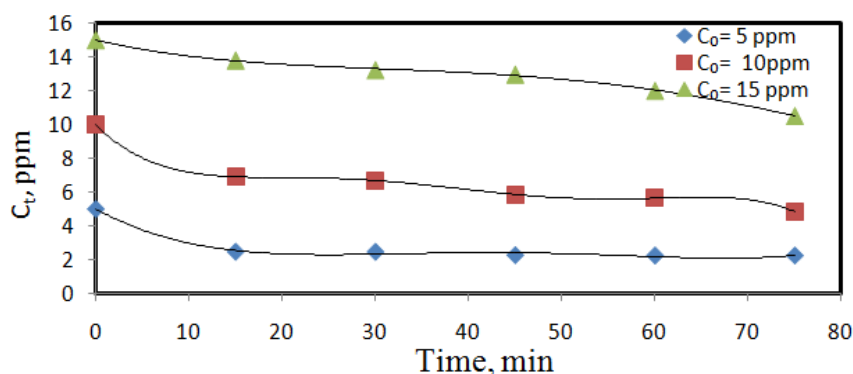


Figure 6. Effect of initial concentration of pollutant on its degradation, $C_0=5, 10, 15$ ppm, at 0.1 g $\text{TiO}_2/400\text{ml}$, and $\text{pH}=7$

• *Effect of Initial Concentration of Pollutant on Degradation at pH= 12.6:*

Figure 7 indicates that the percentage degradation of dye increases with decreasing the initial concentration of pollutant dye at 0.1 g $\text{TiO}_2/400\text{ml}$ and pH 12.6. 5 ppm

dye solution accomplished the highest percentage degradation at 0.1 g $\text{TiO}_2/400 \text{ ml}$ and pH 12.6. Percentage degradation values of 94.56, 94.15 and 90.133% were obtained for 5, 10 and 15 ppm dye solutions, respectively.

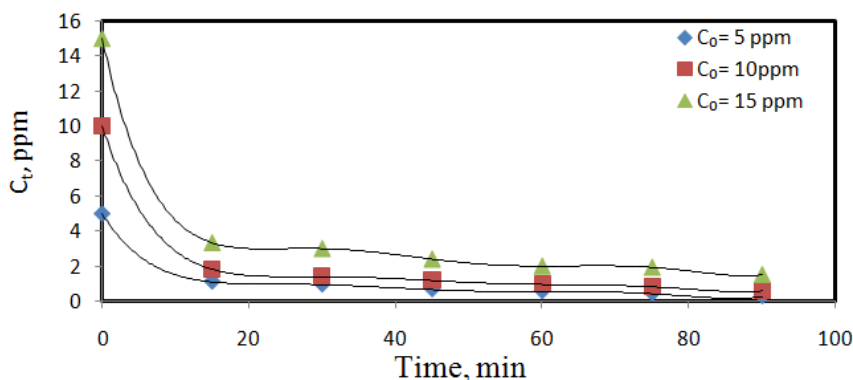


Figure 7. Effect of initial concentration of pollutant on its degradation, $C_0=5, 10, 15$ ppm, at 0.1 g $\text{TiO}_2/400\text{ml}$, and $\text{pH}=12.6$

3.2.2. Effect of Catalyst Dosage:

The effect of TiO_2 dosage on the MB removal was studied and the results are shown in Figure 8 for initial dye concentrations 5 ppm. The percentage degradation was determined at 90 minutes of reaction time. The most effective decomposition of MB was observed at 0.2 g/400 ml of TiO_2 . The curves show that increasing the catalyst concentration from 0.10, 0.15 and 0.2g nanoparticles catalyst /400ml of dye solution at 5 ppm dye solution increased the percentage of pollutant degradation from 94.56%, 96.48% and 97.58% for catalyst concentrations 0.1, 0.15 and 0.2 gm/400 mL solution, respectively, all at

pH value of 12.6. The reason of this observation is thought to be due to the fact that a higher fraction of dye molecules are adsorbed on TiO_2 [6]. Basically, the removal percentage of MB in the photocatalysis process increases with increasing catalyst dosage and then it reaches a constant value. Meanwhile, UV irradiation can also be used as an alternative energy source for nanoparticles catalyst to generate positive holes. Nanoparticles show a great tendency to aggregate due to high surface energy combined with their high surface area to volume ratio. The results show, the recommended amount of catalyst for photocatalytic degradation is 0.2g/400ml, as can be seen from these figures.

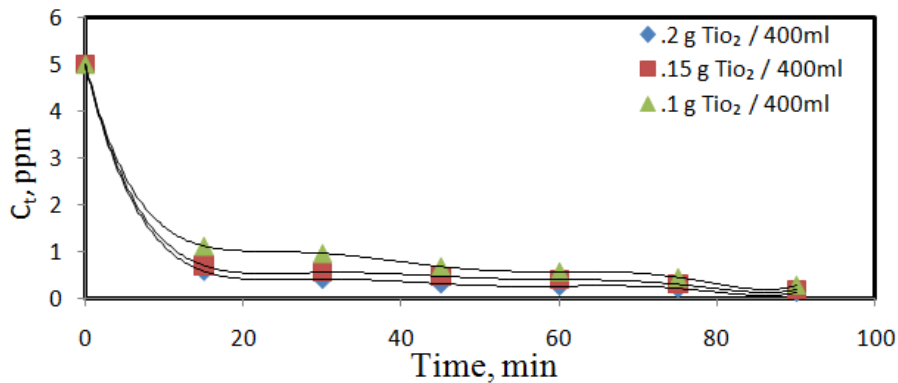


Figure 8. Effect of TiO_2 Nanoparticles concentration on pollutant degradation at $C_0=5$ ppm, and $\text{pH}=12.6$

3.2.3. Effect of PH:

Since pH of dye solution is a main parameter in the degradation progress, comparative experiments were performed at different pH values: one acidic pH (1.4), one basic pH (12.6) and one pH (7) at 0.1 g/400ml and 5 ppm dye solution. Increasing the pH value improves the removal percentage and the percentage degradation was 56.56, 41.84 and 94.56% at pH values 7, 1.4 and 12.6, respectively. The results are presented in Figure 9 for catalyst concentration 0.1 g/400 ml of dye solution. The pH influences the characteristics of the photocatalyst

surface charge, so pH of the solution is a significant parameter in performing the reaction on the surface of semiconductor particles. Point of zero charge (PZC) for TiO_2 particles is $\text{pH}(\text{PZC}) = 6.8$. The surface of TiO_2 has a negative charge in basic media ($\text{pH} > 6.8$), so there is electrostatic absorption between negative charge surfaces of TiO_2 and cationic dyes. As the pH of the system decreases, the number of surfaces with positive charge increases. The surface sites on TiO_2 do not tend to absorb the cations of dyes made by electrostatic repulsion. H_2SO_4 and NaOH were used for pH adjustment of dye solutions.

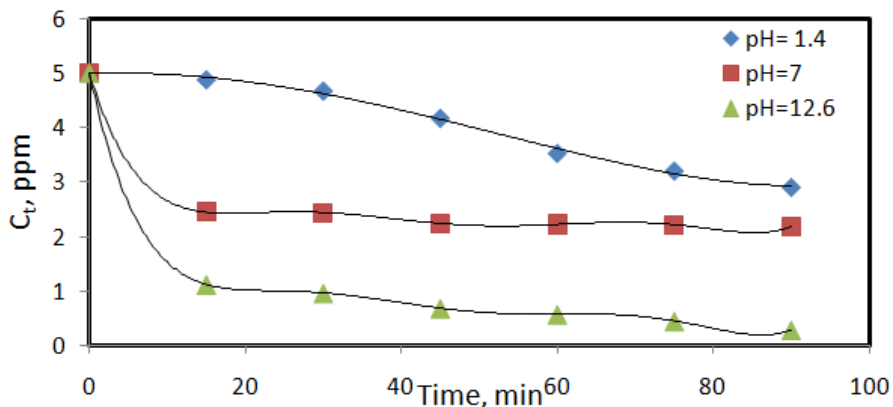


Figure 9. Effect of pH value on pollutant degradation at $C_0=5$ ppm and 0.1 g TiO_2 / 400ml

• Effect of pH in case of 10 ppm methylene blue solution and 0.1 g/400ml TiO_2 nanoparticles catalyst:

For an initial dye concentration of 10 ppm, the concentration decreased to 4.4 ppm after 90 min when the initial $\text{pH}=7$. This value of dye concentration at 90 min corresponds to 6.621 and 0.585 ppm when the initial pH values are 1.4 and 12.6, respectively.

Thus, it could be stated that alkaline media is highly recommended for running the photodegradation process. This is presented in Figure 10. It is noted that when using 5 ppm dye solution the rate of degradation in all cases of pH increased, compared to dye solutions 10 and 15 ppm.

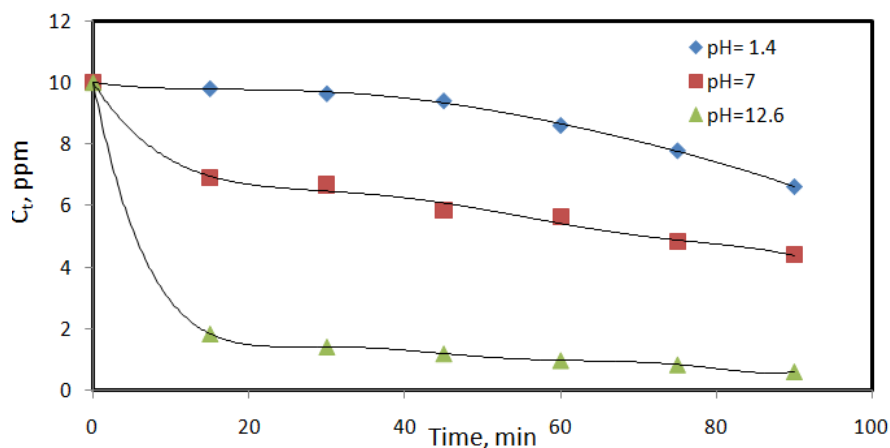


Figure 10. Effect of pH value on pollutant degradation at $C_0 = 10$ ppm, and 0.1 g TiO_2 / 400ml

- Effect of pH in case of 15 ppm of methylene blue solution and 0.1 g/ 400ml TiO_2 nanoparticles catalyst:

A percentage of methylene blue degradation of 90.1333 could be achieved after 90 minutes in an alkaline effluent

of pH=12.6. This percentage is higher than that obtained from pH 7 and 1.4 by 38.3933 and 11.34%, respectively. This is represented in Figure 11.

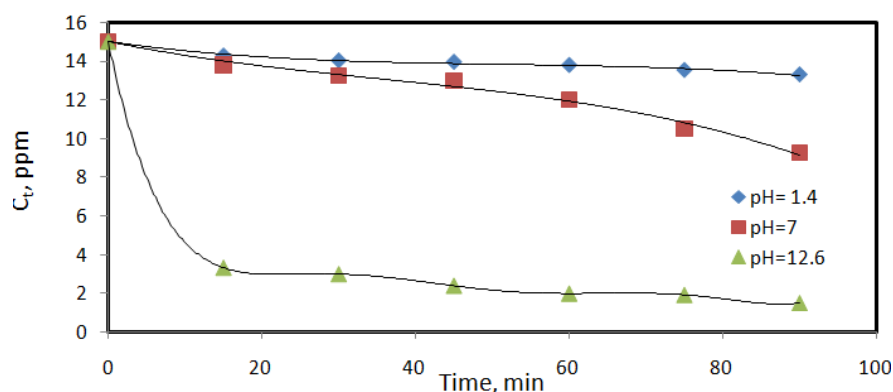


Figure 11. Effect of pH value on pollutant degradation at $C_0 = 15$ ppm and 0.1 g TiO_2 / 400ml

Acknowledgments

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