INVESTIGATION CATALYTIC ACTIVITY OF TiO_2 NANOPARTICLES PREPARED UNDER VARIOUS OPERATIONAL PARAMETERS ON THE REMOVAL OF MALACHITE GREEN

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ABSTRACT

Titanium tetraisopropoxide precursor was used to prepare TiO_2 nano-particles using sol-gel process. The impact of various operational parameters such as different ratios of water solvent and bath temperatures were examined and the optimum condition was determined. The prepared samples were analyzed by X-ray diffraction and Scanning Electron Microscopy (SEM). The catalytic activity of the prepared samples was studied on the removal of malachite green (MG) as pollutant.

Key words: TiO_2, Malachite Green, Contaminant, Catalytic Removal

1. INTRODUCTION

Although in the recent years the industrial growth and development have brought many advantages for the mankind, but it has exacerbated the environmental pollution. It has been caused by discharging wastes produced by various industries, factories and labs into the environment. Among various industries, dyeing industries play a significant role in polluting the environment, which it in turn is due to low efficiency of the dyeing process. Because a considerable part of dyes are wasted during the process. Therefore, removing dyes from the industrial wastes is very important and has convinced many researchers to work on this issue [1, 2].

Among various methods, the advanced oxidation processes in the presence of nanophotocatalysts is an effective process to degrade contaminants. During the past decade, the science of analyzing semi-conductive nanoparticles has been one of the newest and most controversial branches of science. TiO_2 is one of the most important recognized semi-conductors. TiO_2 is an inexpensive, very available and nontoxic semi-conductor. The mentioned characteristics along with its high photocatalytic activity have made it a good candidate for using in the industrial units. Xang *et al.* studied about photocatalytic degradation of methanol using Pt-TiO_2 and then determined the proper condition for degradation of contaminants [3]. Chen *et al.* found the synthetic relation between photocatalytic degradation of Ethyl acetate and ethanediol using TiO_2 [4]. Considerable studies have been done on synthesis of nano-photocatalysts. Researchers try to synthesize nano-particles with high efficiency and better performance through conducting tests in different conditions [5-14]. Gray *et al*. used titanium tetraisopropoxide precursor, hydrolysis with ethanol and sol-gel method in reflux condition to synthesize TiO_2 nano-particles in anatase and anatase-rutile phases and prepared nanoparticles with the diameter of 10-15 nm [15].

In this study, various ratios of water solvent and various bath temperatures were employed to prepare TiO_2 nanophotocatalyst. Then the photocatalytic activity's to remove MG as the contaminant was analyzed and good condition for removal process was determined.

2. METHODS AND MATERIALS

2.1. Materials

Titanium tetraisopropoxide, potassium hydroxide, propanol, ethanesulfonic acid 98%, methanol and malachite green were prepared from Merck (Germany). Deionized water was used for conducting all experiments and preparing all solutions.

2.2. Equipments

An ultrasonic bath (Elma T460/H), a spectrophotometer UV-VIS (Perkin Elmer Lambda) for measuring samples absorption intensity, a UV-C lamp (30W) made by Philips (Netherland) with the emission wavelength of 254 nm were used. A Philips Scanning Electron Microscopy (XL30), a centrifuge (Hcttich) and X-ray diffraction machine made by Siemens (D5000) were used to analyze the structure and morphology of samples.

2.3. Photo-reactor

A discontinuous photo-reactor system in a wooden chamber has been used to carry out practical works of the project. There are various tools in this system including wooden box, power supply, magnetic stirrer, UV-C lamp (30W), aeration system, crystallizer in various sizes.

2.4. Synthesis of TiO_2 non-particles

In this method, titanium tetraisopropoxide (TTIP) is added to methanol and the mixture is stirred in various bath temperatures under reflux condition for 4 hours. The water is dropped to the warm solution of methanol and titanium tetraisopropoxide with four hours of reaction time. Then the resulted suspension is desiccated in 85 °C for 12 hours and the prepared powder is calcined in 400 °C for 4 hours. After removing from the furnace, the suspension is homogenized completely in the mortar; the final product is TiO_2 nano-particle, the proper bath temperature and water's optimum molar ratio to titanium tetraisopropoxide and methanol were measured through conducting various experiments.

3. RESULTS AND DISCUSSION

3.1. Morphology of the nanoparticles synthesized

Figs. 1 and 2 show scanning Electron Microscopy was used to determine morphology of the synthesized nanoparticles.

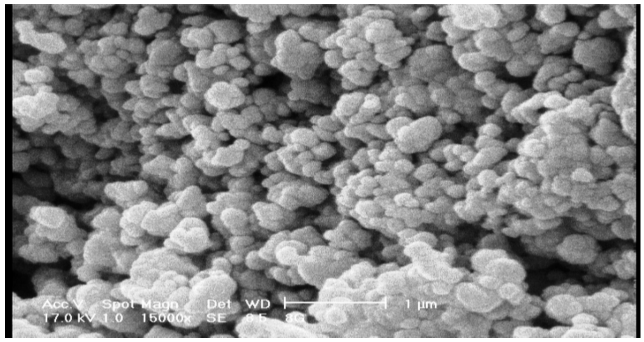


Fig. 1. *SEM image of TiO_2 photocatalyst prepared from TTIP precursor at bath temperature of 80 °C, calcination temperature of 400 °C, and calcination period of 4 h (OR: Methanol: H_2O 1:1:1)*

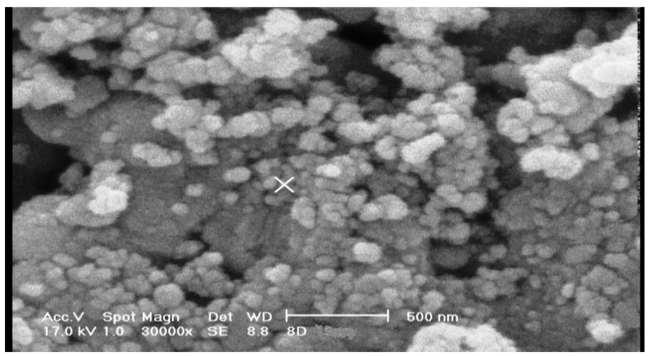


Fig. 2. SEM image of TiO_2 photocatalyst prepared from TTIP precursor at bath temperature of 60 °C, calcination temperature of 400 °C, and calcination period of 4 h (OR: Methanol: H_2O 1:1:75)

3.2. Study phase, size and activity of the synthesized nanoparticles

Hybrid phases and size of synthesized nanoparticles were analyzed using X-ray diffraction method. The average diametre of the synthesized particles can be measured by XRD ranges and Debye-Scherrer equation as follows [16]:

$$D= k\lambda/\beta \cos\theta \qquad 1$$

Where, k is a constant equal to 0.89; λ is the X-ray wavelength equal to 0.154056 nm, β is peak width at half-maximum, and θ is half of the diffraction angle.

When the synthsezied nano-particles have anatase and rutile phases, these phases are measured through the following equation [17]:

$$\chi = \frac{I_R}{0.8I_A + I_R} \qquad 2$$

Where, I_A and I_R indicate integrals of peak intensity for anatase and rutile phases.

Equation 3 was used in various tests to measure the removal percent.

$$\text{Removal percent} = (C_0 - C/C_0) \times 100 \qquad 3$$

3.2.1. The effect of various ratios of water solvent on crystalline structure and size of the nanoparticles synthesized from the TTIP precursor using sol-gel method

Fig. 3 shows the X-ray diffraction of the nanoparticles synthesized with various molar ratios of water solvent. The fig. shows that there is a certain peak at the 2θ=25.5 of anatase phase in various ranges of the X-ray diffraction; however, the peak widths are different.

Table 1 summarized phases and sizes of particles of the synthesized photo-catalysts. As the table indicates when the water solvent ratio is decreased, the size of the synthesized nano-particles is increased.

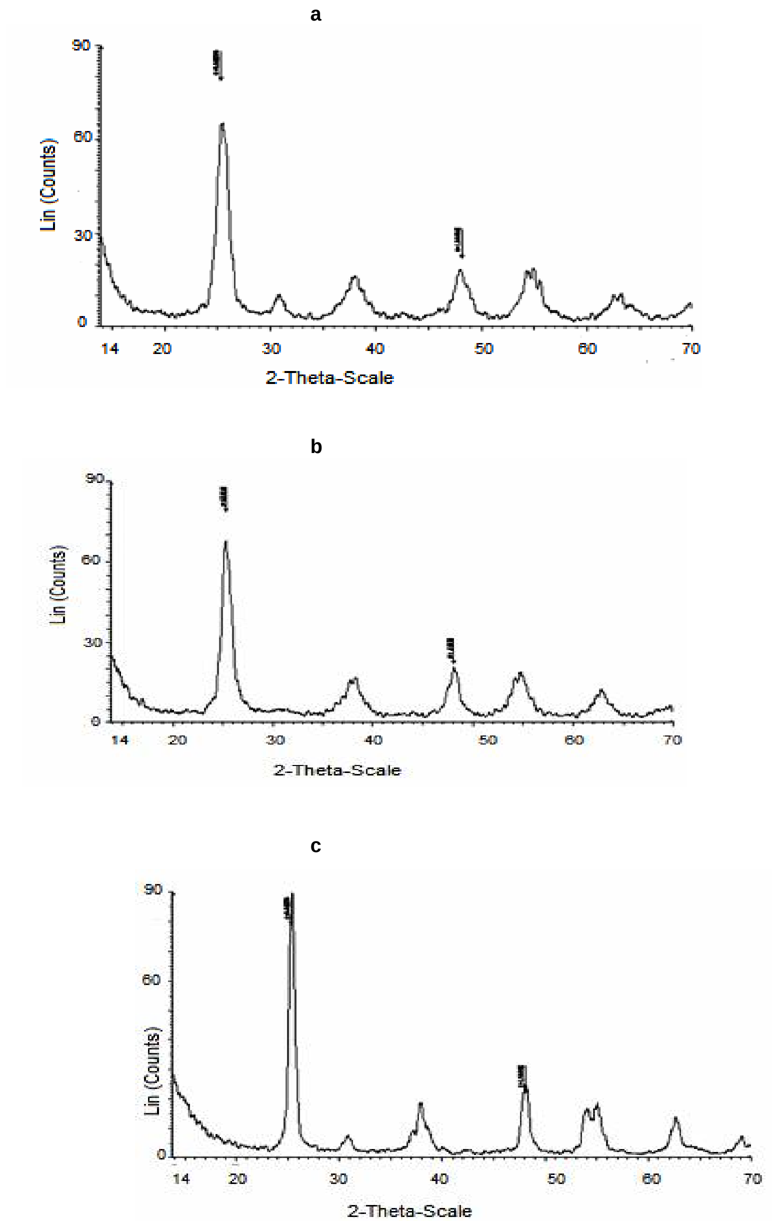


Fig. 3. *XRD range of TiO_2 phtocatalyst synthesized from TTIP precursor at bath temperature of 80 °C, calcination temperature of 400 °C, and calcination period of 4 h a:(OR: Methanol: H_2O 1: 1: 75), b:(OR: Methanol : H_2O 1: 1: 50), C:(OR:Methanol : H_2O 1: 1: 1)*

Table 1. Size and type of the prepared nanoparticles in various molar ratios of watersolvent

Particle size (nm)		Type of phase		Calcination temperature (°C)	OR: Methanol: H_2O
Rutile	Anatase	Rutile percent	Anatse percent		
-	12.37	-	100	400	1:1:75
-	12.8	-	100	400	1:1:50
-	14.7	-	100	400	1:1:1

3.2.1.1. The effect of various ratios of water solvent on activity of photocatalysts synthesized through sol-gel method

In order to analyze the photocatalytic activity of synthesized nanoparticles, MG was used as contaminant. Fig. 4 shows the results of photocatalytic activity of TiO_2 samples prepared in various ratios of watersolvent. The highest photocatalytic activity of samples is seen when the water solvent ratio is 75. As the results in Table 1 show, size of nanoparticles in this case is the smallest which justifies the higher activity of these nanoparticles.

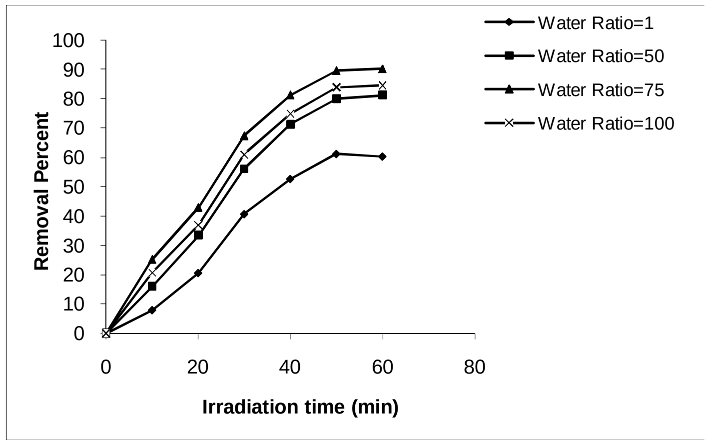
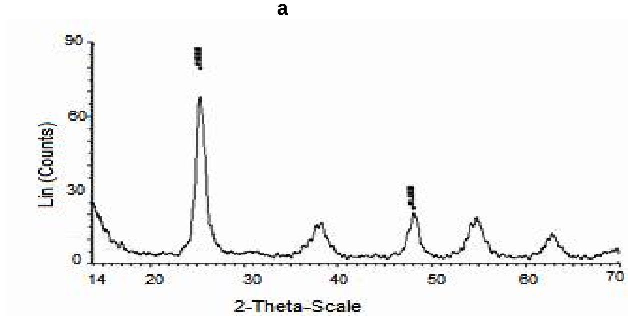


Fig. 4. *Diagram of MG removal percent in terms of radiation time in various watersolvent ratios at bath temperature of 80 °C, calcination temperature of 400 °C and calcination period of 4 h*

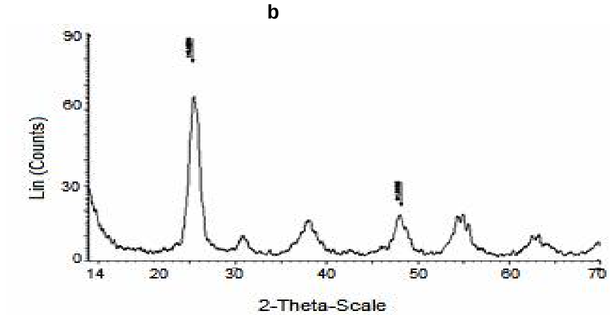
3.2.2. The effect of bath temperature in crystalline structure and size of photocatalysts synthesized from the TTIP precursor using sol-gel method

Bath temperature is another parameter examined in preparing TiO_2 photocatalyst nanoparticles. Fig. 5 shows the range of X-ray diffraction of the synthesized nanoparticles. There is a certain peak at the 2θ= 25.5 of anatase phase in various ranges of the X-ray diffraction and there is not a significant difference between peaks width. Table 2 summarizes phases and sizes of the particles of photocatalysts. This table reflects that when the bath temperature changes, the particles' size changes partially.

a



b



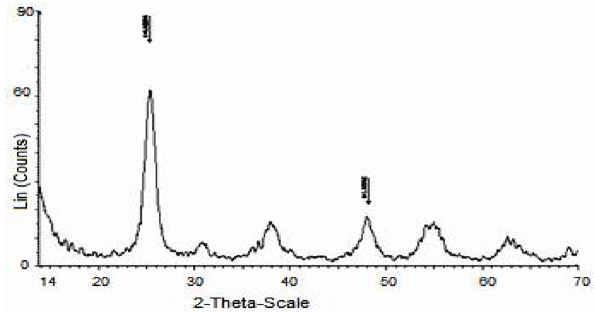


Fig. 5. *XRD range of TiO_2 photocatalyst prepared from TTIP precursor at bath temperatures of a: 60 °C, b: 70 °C, and c: 80 °C, calcination temperature of 400 °C, and calcination period of 4 h (OR: Methanol: H_2O 1:1:75)*

Table 2. Size and type of the prepared nanoparticles in various bath temperatures

Particle size (nm)		Type of phase		Calcination temperature (°C)	OR: Methanol: H_2O
Rutile	Anatase	Rutile percent	Anatse percent		
-	12.7	-	100	60	1:1:75
-	12.4	-	100	70	1:1:75
-	12.30	-	100	80	1:1:75

3.2.2.1. The effect of bath temperature on activity of the nanoparticles synthesized using sol-gel method

Fig. 6 has been developed through the results of photocatalytic activity of TiO_2 samples prepared in various bath temperatures. The highest activity of samples is seen in 80 °C. The results in Table 2 indicate that the particles size in this temperature is smaller than that in other temperatures.

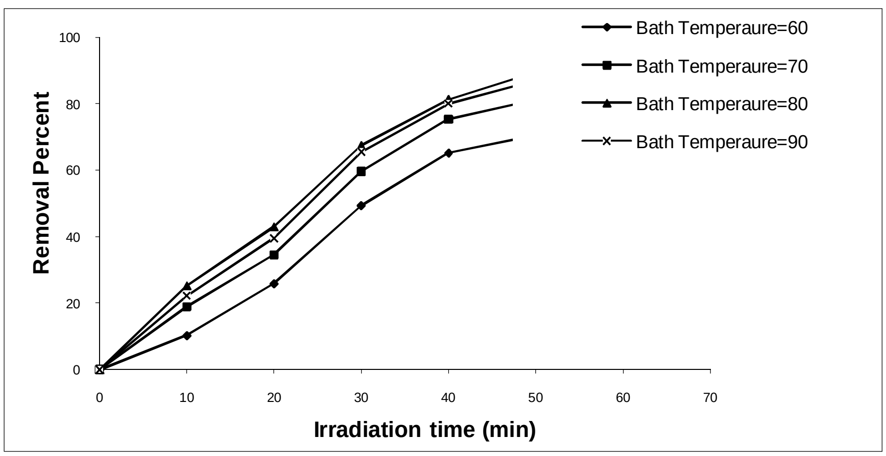


Fig. 6. *The diagram of MG removal percent in terms of radiation period in various bath temperatures, calcination temperature of 400 °C, and calcination period of 4 h (OR: Methanol: H_2O 1:1:75)*

4. CONCLUSION

Titanium oxide nanoparticles were prepared and their catalytic activity on the removal of malachite green was examined. Various effective parameters on the preparation TiO_2 nanocatalysts such as water solvent ratio and bath temperature were studied. The results demonstrated that the most effective parameter to prepare TiO_2 is calcination temperature. Phase conversion to each other occurred in various temperature of calcinations, changing calcinations temperature changes particles' size. The effect of calcinations temperature on catalytic activity of TiO_2 nanoparticles in various temperatures, from 400 to 800 °C indicated that calcination temperature has a direct relation with the photocatalytic activity. In most cases, increasing in the temperature causes a significant decrease in the activity of the TiO_2 nanoparticles. This reduction in activity may be due to the increased size of the nanoparticles and the increased rutile phase percent in such particles.

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