

## Synthesis, structural characterization and catalytic activity of TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> photo-composite

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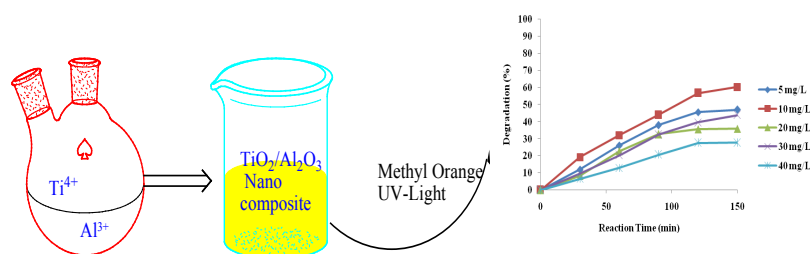
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### HIGHLIGHTS

- TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> nano-composite was fabricated by a chemical approach including TiCl<sub>4</sub>, Al(NO<sub>3</sub>)<sub>3</sub>, ethanol amine, ethyl acetoacetate and aqueous ammonia.
- Photocatalytic activity is higher for the TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> composite compared to TiO<sub>2</sub>.
- The TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> nano-composite displayed higher photocatalytic activity under acidic conditions.

### GRAPHICAL ABSTRACT



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### ABSTRACT

In this study, a chemical method including TiCl<sub>4</sub>, Al(NO<sub>3</sub>)<sub>3</sub>, ethanol amine, ethyl acetoacetate and aqueous ammonia were used for the fabrication of TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> nano-composite. The as prepared nano-composite was characterized applying the XRD, FE-SEM and TEM techniques. The photocatalytic behavior of TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> nano-composite was evaluated in the photo-catalytic degradation of methyl orange under UV irradiation technique. The effect of various parameters including catalyst dosage, dyes concentration, pH and temperature on the degradation of methyl orange was investigated. The degradation rate was efficiently increased as the concentration of catalyst was decreased. The optimum dosage of methyl orange was found to be 10 mgL<sup>-1</sup>. In addition, we found that pH can significantly enhance the photocatalytic degradation of methyl orange dye.

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## 1. Introduction

Energy shortage and environmental pollution are the main problem of the scientists especially when they work with homogeneous catalysts and to resolve these problems, a great deal of effort has been undertaken to develop highly effective heterogeneous based catalysts for their potential application in the reducing of chemical contaminants [1-3]. Metal oxides such as  $\text{TiO}_2$  and materials which are derived from them such as composites, ceramics and etc. are demonstrated to be effective ones for organic pollutant degradation and elimination [3-8].  $\text{TiO}_2$  involved composites and nano-composites represent one of the most widely utilized classes of metal oxides composites [3-8]. They are easily synthesized and form composites with various metal ions. Historically there have been many reports in the literature on their applications in catalysis, sunscreen lotions, solar cells, pigments, electrochemical electrodes, capacitors catalyst support and photo-catalysts [3-8]. Although researchers obtained various kinds of  $\text{TiO}_2$  contained composites, few efficient materials of these composites have been found to be used in photo-catalytic transformations as efficient catalysts. Therefore, for practical application, the development of new responsive photo-catalysts with the simplest preparation method and the most efficient photo-catalytic activity is needed.

Methyl orange an azo dyes is known to be non-biodegradable organic compound and thus has a crucial ecological problem for the environment. In fact relatively various kinds of industrial and synthetic azo dyes are carcinogenic and poses a potential threat to humans especially when discharged into water sources [9-12]. This could be the main reason for the received increasing attention of dyes removal from water sources. In recent years photo degradation processes have been developed and found to be a convenient method to treat wastewater and removal of azo dyes. Various photo-catalysts including metal oxides have been extensively studied for the photo degradation processes. It should be noted that high surface area and high adsorption capacity of photo-catalyst is an important impact because the rate of the photo degradation process increased when dyes well adsorbed on the surface of the photo-catalyst [13-15].

In recent years different structures of  $\text{TiO}_2$  were found to be efficient catalysts for the photo-catalytic degradation of methyl orange dyes. According to the literature surveys it was revealed that the characteristic properties and photo-catalytic activity of  $\text{TiO}_2$  are depended on several factors such as morphology, size

and crystalline structure of  $\text{TiO}_2$  and can be improved using  $\text{TiO}_2$  contained composites [15-19].

The objectives of this study were to investigate the preparation and characterization of  $\text{TiO}_2\text{-Al}_2\text{O}_3$  nano-composite *via* a chemical method and the influences of their catalytic activity in the Photo-catalytic degradation of methyl orange dye by UV irradiation technique.

## 2. Experimental

### 2.1. Material and instrumentation

All reagents were purchased from Merck and Aldrich and used without further purification. XRD data were collected from the synthesized powders for phase identification and determination of crystallite size by Philips TW3710 X'Pert diffractometers (for  $2\theta$  range from 0 to  $80^\circ$  with a step size of  $0.01^\circ$  ( $2\theta$ )) using  $\text{Cu-K}\alpha$  radiation. FE-SEM was taken by a Hitachi S-4160 photograph to examine the shape of the samples. TEM image was taken by a PHILIPS CM20 microscope to examine the shape and size of nano-composite.

### 2.2. Synthesis procedure

Two different solutions were prepared as follows: Solution A: for the preparation of solution A, at first  $\text{TiCl}_4$  (5 mmol) was added to a solution of methyl acetoacetate (30 mmol) and ethanol amine (90 mmol) in 50 mL of ethanol and the mixture was stirred at room temperature for 1h. Afterwards to this solution  $\text{Al}(\text{NO}_3)_3$  (25 mmol) was added and the resulted mixture was stirred at  $80^\circ\text{C}$  for 1h.

Solution B: Solution B was prepared by the mixing of n-hexane (30 mL), ethanol (20 mL), methyl acetoacetate (30 mmol) and the aqueous ammonia (5 mL).

Solution B was added to solution A slowly under vigorous magnetic stirring and the resulted mixture was stirred for 24h. Finally, the mixture was filtered washed with water for three times, dried and calcined at  $800^\circ\text{C}$  for 3h.

### 2.3. Photocatalytic degradation procedure

The photocatalytic degradation of the methyl orange solution was performed using a solution of the methyl orange substrate in water and  $\text{TiO}_2\text{-Al}_2\text{O}_3$  composite nano-powders as catalyst. The solution was stirred under UV irradiation (465 nm) with three 8 W ultraviolet lamp as a source in Pyrex flasks at room temperature. The absorption spectrum of the suspension mixture was measured periodically using a UV-visible spectrophotometer (Shimadzu, UV-2450, Japan) after cen-

trifugation to ensure the degradation of methyl orange solution. The cleavage of the azo bond of methyl orange leading to its bleaching was monitored by spectrophotometric analysis at 465 nm.

### 3. Results and discussion

The TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> composite nano-powders were synthesized by a chemical precipitation method.

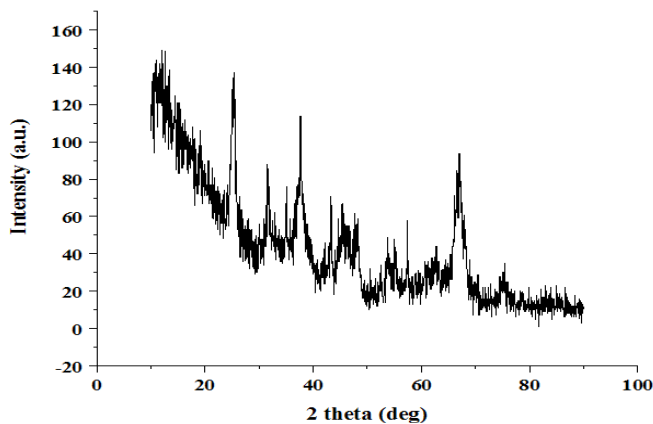
The as prepared sample was characterized with XRD, TEM and FE-SEM techniques.

The X-ray diffraction pattern of TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> composite nano-powders is shown in Figure 1. The XRD pattern shows that this composite has a two-phase structure: TiO<sub>2</sub> (anatase phase) and Al<sub>2</sub>O<sub>3</sub>. The diffraction peaks related to the TiO<sub>2</sub> phase of composite structure calcined at 500 °C are revealed at 2θ degrees of 25.33, 36.98, 37.81, 48.10, 53.92, 55.14, 62.75 and 75.13 (JCPDS file no.: 88-1175 and 84-1286). Whereas the characteristic peaks of Al<sub>2</sub>O<sub>3</sub> are 25.50, 35.11, 37.72, 43.29, 46.13, 52.52, 57.44, 66.47 and 68.16 (JCPDS file no.: 88-0826). Meanwhile these peaks are in conformity with tetragonal TiO<sub>2</sub> and rhombohedral Al<sub>2</sub>O<sub>3</sub>.

The average crystal size of the nanoparticles was calculated by the Debye–Scherer formula (1), and found to be 80 and 31 nm for TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> phases respectively.

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (1)$$

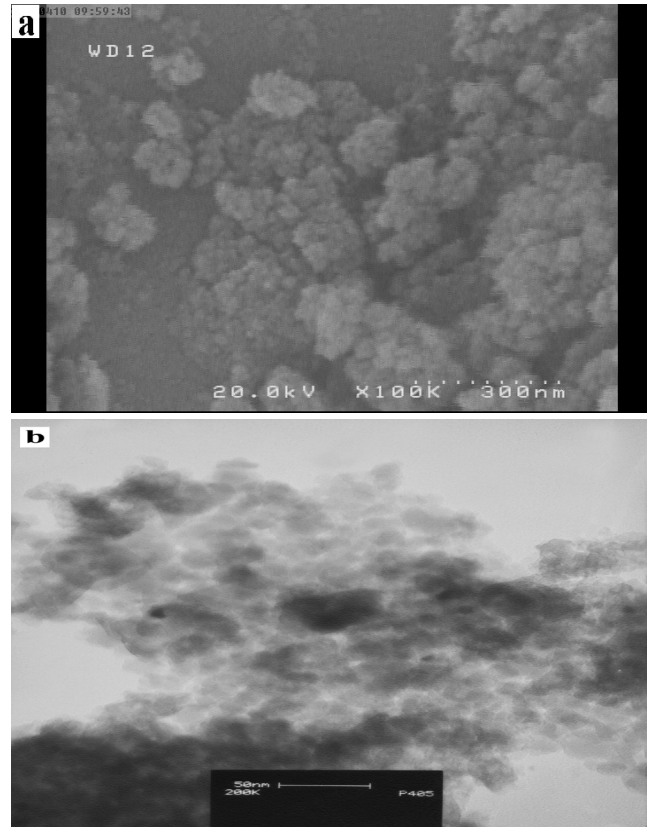
Where, k is the shape factor, D is the crystallite size, θ is the diffraction angle, β is the full width half maximum of diffraction angles in radians.



**Fig. 1.** XRD pattern of TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> composite nano-powder calcined at 800 °C.

The surface morphology and grain size of the as-prepared TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> composite nano-powders were characterized by FE-SEM and TEM techniques (Figure 2).

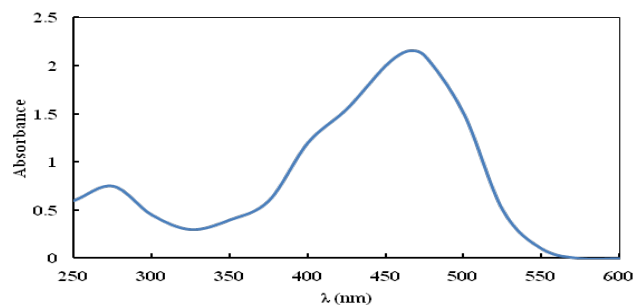
The FE-SEM image shows that the composite consist of uniform particles and TiO<sub>2</sub> homogeneously distributed on the surface of the alumina (Figure 2a). The TEM image shows that the particles in the composite nano-powder have good crystalline phases with a diameter less than 50 nm (Figure 2b).



**Fig. 2.** FE-SEM photograph (Figure 2a) and TEM image (Figure 2b) of TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> nano-composite.

#### 3.1. Photocatalytic activity

Photocatalytic degradation of methyl orange dye was investigated using the as-prepared TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> nano-catalyst by UV irradiation technique. The characteristic absorption peak of methyl orange solution was found to be 465 nm (Figure 3).



**Fig. 3.** The UV-vis spectrum of methyl orange in water.

Degradation of methyl orange was visualized by decrease in peak intensity within 150 min of incubation time and the concentration of it was calculated from the standardized calibration curve of absorbance vs. concentration.

The following equation was used for the evaluation of degradation rate:

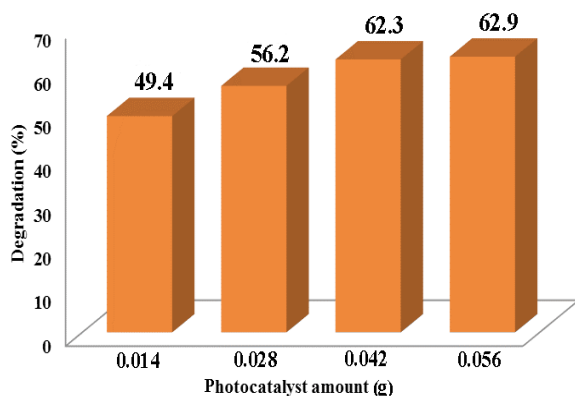
$$R = \frac{C_0 - C_t}{C_0} \times 100 \quad (2)$$

Where R is degradation rate,  $C_0$  and  $C_t$  are the concentrations of the methyl orange solution at UV irradiation time 0 and t, respectively.

It was inferred from control experiments that presence of both  $\text{TiO}_2$ - $\text{Al}_2\text{O}_3$  composite and UV light is necessary for photo-degradation.

### 3-2- Effect of catalyst amount

Initially, the effect of catalyst concentration on the methyl orange degradation was investigated and the results are shown in Figure 4. It is revealed that the methyl orange degradation increased with increasing in the catalyst amount at a range of 0.014 -0.042 g. Afterwards due to reducing of the light penetration into the suspension, a decreasing in the methyl orange degradation was occurred.



**Fig. 4.** Photo-catalytic degradation of methyl orange: effect of catalyst dosage.

Next, in order to find the optimum of the methyl orange dosage, various concentration of methyl orange including 5, 10, 20, 30 and 40  $\text{mgL}^{-1}$  was investigated. The results are shown in Figure 5. From Figure 5 it was revealed that the concentration of methyl orange decreased with time but degradation rate seem to be decreased. It should be due to this fact that organic material adsorbed on the surface of the catalyst and deac-

tivated it [20]. Due to the higher yield of degradation, 10  $\text{mgL}^{-1}$  was chosen as optimum dosage.

The kinetic studies shows that the photo-degradation of methyl orange follow from the pseudo-first order kinetics and nearly linear relation of  $\text{Ln}(C_0/C)$  vs. t was observed (Figure 6). Since  $C_0$ , C and t are initial concentration of methyl orange, concentration after photo-degradation, and the time of photo-degradation respectively. Langmuir-Hinshelwood model was also used to describe the photo-degradation process. The nearly linear relationship between  $\text{Ln}(C_0/C)$  and t indicating that the photo-degradation of methyl orange follows first-order kinetics. It was observed that this relationship follows from the below equation:

$$\text{Ln}\left(\frac{C_0}{C}\right) = Kt \quad (3)$$

Which k is the constant of the reaction rate and can be determined from the straight-line slope of the fitted values by means of linear regression. The k values are showed in Figure 6 and are 0.004, 0.005, 0.003, 0.004, 0.002 for the 5, 10, 20, 30, 40  $\text{mgL}^{-1}$  of methyl orange respectively.

The increasing of the k values with methyl orange concentration is good matched with the results shown in Figure 5.

### 3.3. Effect of pH levels on the photo-degradation of methyl orange

It is believed that the pH level can influenced the photo-catalytic of metal oxides such as  $\text{TiO}_2$ . This is due to the amphoteric behaviour of metal oxides. In fact the pH level influences the surface charge properties of metal oxides. Thus reactions which take place on the surface of metal oxides occurred via different mechanism at different pH values. At the basic condition the surfaces of most metal oxides are negatively charge whereas in acidic condition is positive [21-24].

For a wide pH value range, methyl orange molecules save their negative charges. Therefore, the ability of methyl orange to adsorb on the surfaces of metal oxides increased when the solution pH value is in acidic condition [21, 25].

In order to clear this means, the effect of acidic and basic media on the photo-degradation of methyl orange was investigated. Increasing and decreasing of pH was done by the using of NaOH and HCl for basic and acidic condition respectively. The results are

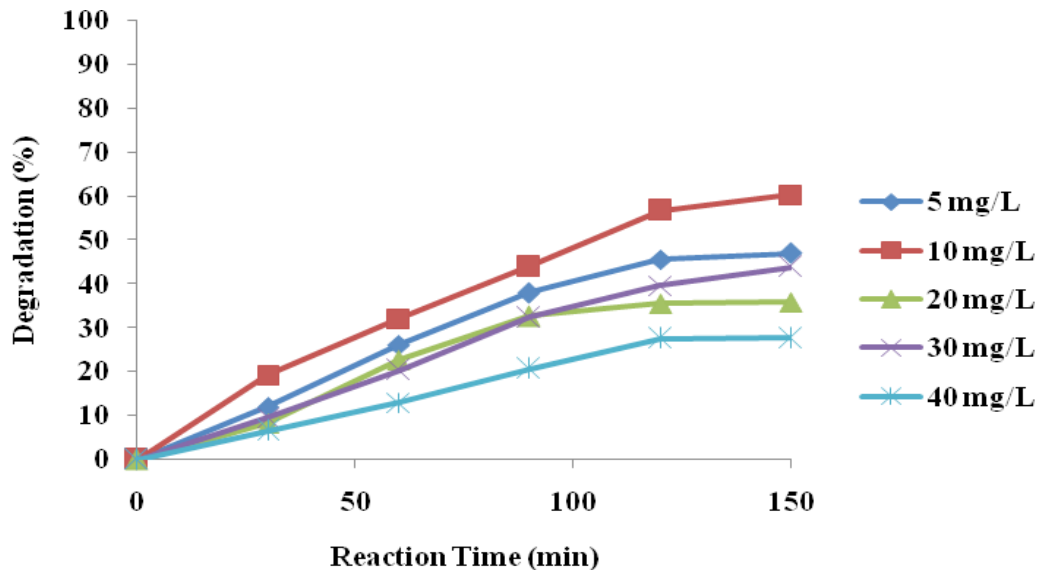


Fig. 5. Photo-catalytic degradation of methyl orange: effect of dye concentration.

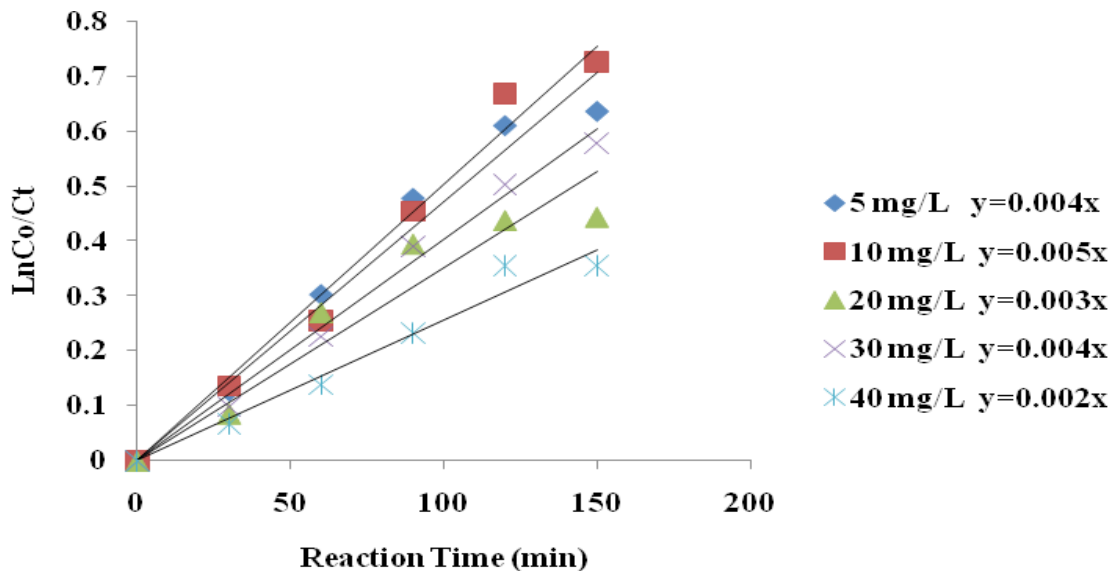


Fig. 6. Plot of  $\ln(C_0/C_t)$  versus effect of methyl orange dosage.

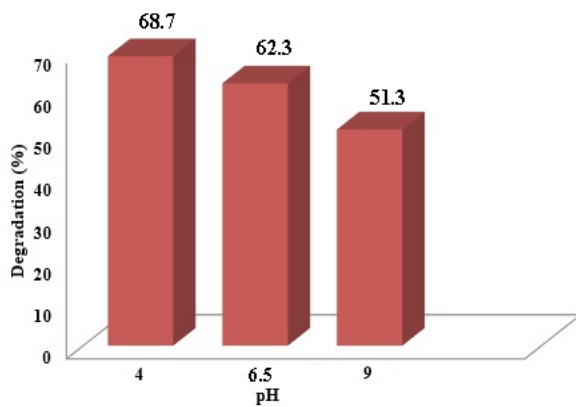


Fig. 7. Photo-catalytic degradation of methyl orange: effect of initial pH solution

in acidic medium. A remarkable decrease in the photo-degradation of methyl orange was observed with increase in the pH into basic condition.

The kinetics of the photo-degradation of methyl orange at basic and acidic pH levels was investigated and the observed rate constants are shown in Figure 8. It was revealed that the kinetics was followed from the pseudo-first order kinetics. Under acidic conditions, the photo-degradation rate was moderately increased; while it was delayed at basic conditions summarized in Figure 7.



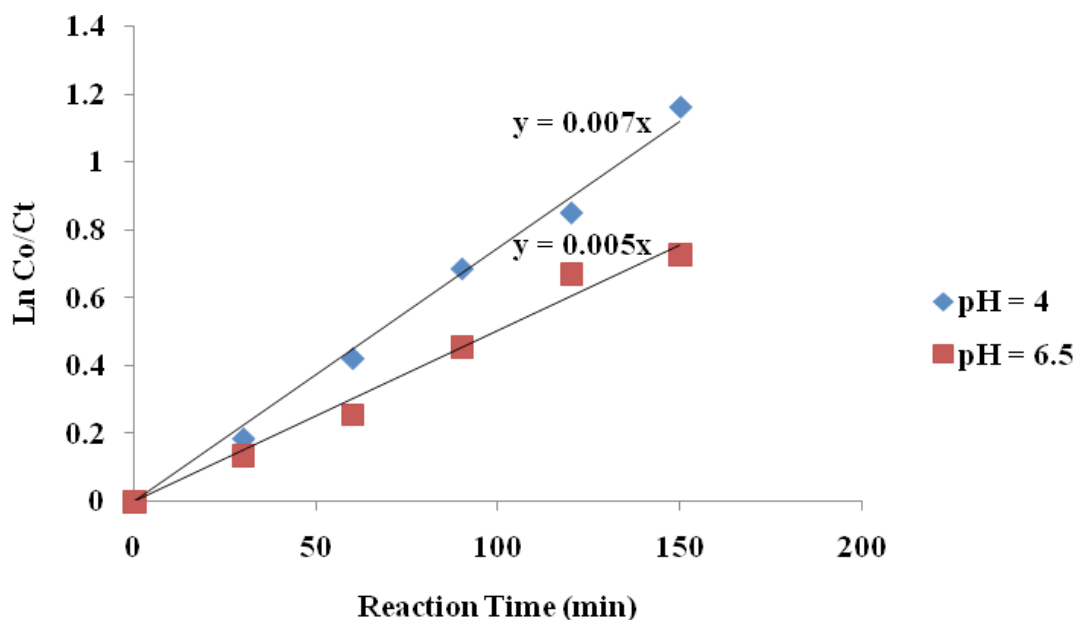


Fig. 8. Plot of  $\ln(C_0/C_t)$  versus time for the degradation of methyl orange: effect of initial pH solution.

From Figure 7 it is revealed that the photo-degradation of methyl orange increased.

#### 3.4. Effect of temperature on the photo-degradation of methyl orange

The effect of temperature on the photo-degradation of methyl orange over  $\text{TiO}_2\text{-Al}_2\text{O}_3$  composite nano-powder was also investigated at the temperature range of 25 to 50 °C. The results are summarized in Figure 9. It is revealed that photo-degradation of methyl orange is not efficiently changed with increasing temperature in the reaction. The results indicated that temperature is not promoting photo-degradation of methyl orange.

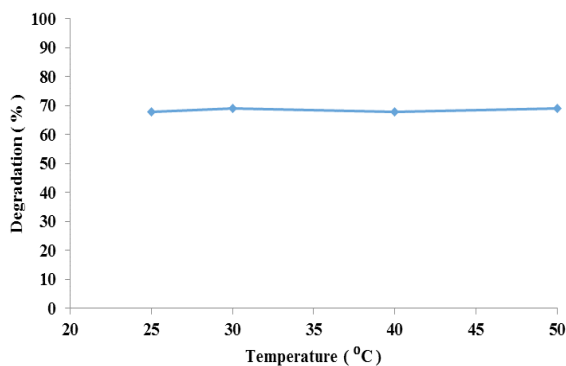


Fig. 9. Photo-catalytic degradation of methyl orange: effect of temperature.

#### 3.5. $\text{TiO}_2\text{-Al}_2\text{O}_3$ nano-composite versus $\text{TiO}_2$

With the comparison between the obtained results of  $\text{TiO}_2\text{-Al}_2\text{O}_3$  nano-composite and  $\text{TiO}_2$ , it was observed that the rate of the photo-catalytic degradation of methyl orange over  $\text{TiO}_2$  increased when it was loaded in the composite structure (Figure 10). The increasing acidity of  $\text{TiO}_2$  surfaces when it mixed with other metal oxides create more OH radical necessary for photo-oxidation reactions due to higher affinity of absorbing more hydroxyl groups or  $\text{H}_2\text{O}$ , resulting in enhancement of photo-catalytic activity. Also the more acidity of  $\text{TiO}_2\text{-Al}_2\text{O}_3$  nano-composite than  $\text{TiO}_2$  increased the absorbance of methyl orange molecules and thus improves the photo-catalytic degradation rate [26-29].

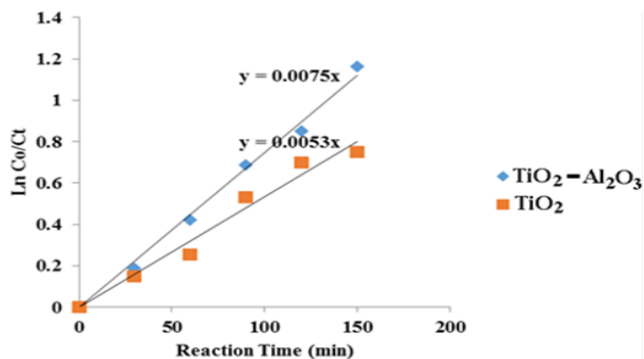


Fig. 10. Comparison results between the catalytic activities of  $\text{TiO}_2$  and  $\text{TiO}_2\text{-Al}_2\text{O}_3$ .

#### 4. Conclusions

The present work concentrated on the chemical preparation of TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> nano-composite using ethanol amine and ethyl acetoacetate precursors. The synthesized nanoparticles have been characterized using Powder XRD, FE-SEM and TEM techniques. The photocatalytic behavior of the as prepared sample was evaluated by methyl orange degradation. It was revealed that photocatalytic activity of TiO<sub>2</sub> is lower than its TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> composite. The TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> nano-composite showed higher photocatalytic activity under acidic conditions. Implying different concentrations of catalyst showed that the catalyst played a key role in the photo-catalytic degradation of methyl orange.

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