

## Preparation, Characterization of TiO<sub>2</sub> Nanoparticles by Electrodeposition Method and Using as Catalyst in Photocatalytic Degradation

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**Abstract:** In order to get of catalyst inexpensive and effective application for photodegradation, TiO<sub>2</sub> powder which were prepared by the electrodeposition method simple and inexpensive and using surfactants such as (Glycerin (GLY), Polyvinyl Alcohol (PVA), Poly (N-Vinylpyrrolidone) (PVP)) that help the growth and nucleation of suspended particles. These particles were distinguished by (Atomic Force Microscopy (AFM), X-Ray Diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM), EDS and High Resolution Transmission Electron Microscope (HRTEM), these particle was obtained reached to the about 40 nm, in order to demonstrate the photodegradation efficiency of the titanium dioxide in the removal of the organic Malachite Green oxalate (MG) dye, the catalyst was used in both cases the standard Titanium Oxide (TiO<sub>2</sub>, 80 vol% anatase +20 vol% rutile) from (US research nanomaterials, Inc) and prepared TiO<sub>2</sub> calcination at 700°C to converted from anatas phase to TiO<sub>2</sub> anatase/rutile phase and the parameters such as amount of catalyst, concentration of dye, pH of dye sol and temperature were calculated. Pseudo first order reactions according to, the Langmuir-Hinshelwood can be obtained from results photocatalytic reactions. Parameters such as: Energy activation (Ea), Enthalpy of activation ( $\Delta H^0$ ), entropy of activation ( $\Delta S^0$ ) and free energy of activation ( $\Delta G^0$ ) were calculated the activation energy equal to (56.73±1) and (37.49±1) kJ/mol for (MG) dye inpresence TiO<sub>2</sub> NPs in tow case standard and prepared, respectively.

**Key words:** Electrochemical deposition of TiO<sub>2</sub>, photochemical processing, thermodynamic, kinetic, mechanism, nanoparticles

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### INTRODUCTION

Nanoparticles especially metal oxides like titanium and zinc oxides play a crucial role in degradation of dyes. Photocatalytic degradation is the process of degradation of toxic metals and an alternative biological degradation process (Byrne *et al.*, 1998). The titanium dioxide has multiple crystallographic phases such as rutile and anatase phase. The rutile phase has fast recombination rate and excited only in visible light. But the anatase phase excited only at UV lights and slow recombination rate. The reason for the mixed production of two phases is used to increase the photocatalytic property of the titanium oxide (Hurum *et al.*, 2003, 2005, 2006). Recently, variety of methods has been used for the synthesis of titanium dioxide nanoparticles such as aerosol pyrolysis, calcinations and surfactant based colloidal synthesis (Ahonen *et al.*, 1999; Li and Ishigaki, 2001; Ding and Liu, 1997; Zhang *et al.*, 2001; Yang *et al.*, 2001; Chemseddine and Moritz, 1999; Yin *et al.*, 2001; Chae *et al.*, 2003).

### MATERIALS AND METHODS

**Experimental:** This method is simple and useful for generating nanoparticles. This approach includes using two electrodes, anode and cathode plates made of Titanium (Ti) with high purity reaches to 99.99% with scale (2 cm width×3 cm length×1.5 mm thick) from (99% Fluka Analytical, Swiss) the two electrode rinsed by acetone with deionized water, the two electrodes are placed facing each to other in a vertical way with a distance 2 cm between anode and the counter electrode, the electrical cell that contains 100 mL Deionized Water (DW) obtained from (Faculty of Pharmacy, University of Kufa, Iraq). The electrolysis has been employed with the temperatures (60°C) with continuous various voltages, the current passed in the circuit has been monitored with a voltmeter. Additionally, the production of nanoparticles in a way of electrochemical reduction in changing the polarity of the direct current between the electrodes during electrolysis process in order to obtund the better precipitation (Liao *et al.*, 2000). Electrolyte was used to preparing TiO<sub>2</sub> NPs (0.745 g/100 mL, 1 M) KCl (99%

**Table 1: Chemical, solutions and working conditions applied in the experiment of TiO<sub>2</sub> NPs powder electrodeposition of KCl solutions**

Chemicals	PVP	PVA	Glycerin
KCl	0.74 (g/100 mL)	1 M	1 M
Deionized water	0.7 (µsec/cm)	0.7 (µsec/cm)	0.7 (µsec/cm)
Glycerin	(1g/100 mL)	-	10 (mL)
PVA	(1g/100 mL)	-	-
PVP	(1g/100 mL)	10 (mL)	-
pH	7	7	7
Temperature	50-60°C	50-60°C	50-60°C
General current density	500 (A/m <sup>2</sup> )	500 (A/m <sup>2</sup> )	500 (A/m <sup>2</sup> )
(Titanium) anode area	12 (cm <sup>2</sup> )	12 (cm <sup>2</sup> )	12 (cm <sup>2</sup> )
Current density	0.6 (A)	0.6 (A)	0.6 (A)
Voltage-time	(V)/(min)	19.2 (V)/60 (min)	17.1 (V)/60 (min)
			18.3 (V)/60 (min)

Thomas, India) at pH (7). A power supply under study, DC applied by power supply (potentiostat/galvanostat) (China) was utilized to supply and measurement with more precision current additives like Glycerin (GLY), Polyvinyl Alcohol (PVA), Poly (N-Vinylpyrrolidone) (PVP) (CDH-India), material listed in Table 1. Afterwards, the white color of titanium dioxide powder was washed repeatedly with deionized water numerous times by using centrifugal (4000 rpm) several time and then wash twice with 99% ethanol and then dry in an oven 60°C for 1 h, latter store the deposited TiO<sub>2</sub> in tightly blocked vials, store in a vacuum container contain a silica gel powder (Murray *et al.*, 2005).

## RESULTS AND DISCUSSION

### AFM measurements of TiO<sub>2</sub> powder electrodeposition:

The AFM analysis of precipitated TiO<sub>2</sub> powder shows in Table 2 that the root mean square roughness (sq) is 9.73 nm, i.e, the surface roughness of TiO<sub>2</sub> with stabilizer glycerin which has packs with more heights than other sample with deferent stabilizer such as PVP and PVA, the results accordingly the roughness profile as the following, TiO<sub>2</sub> with glycerin >PVP>PVA, surface roughness of samples depends on operating conditions.

It was found that the average granularity cumulation distribution of diameter for nanoparticles TiO<sub>2</sub>. When using 10 mL of PVP is 61.37 nm, the parameters are also, listed as (Fig. 1-3a-c) in Table 2 where it is clear that the sample is prepared with PVA>Glycerin>PVP (Gadelmawla *et al.*, 2002).

### X-ray measurements of TiO<sub>2</sub> powder electrodeposition:

The purity and crystal phases of TiO<sub>2</sub> nanopowder were examined by X-ray diffraction, XRD data come from using a Shimadzu 6000 diffractometer equipped with Cu K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ) (at 50 kV and 40 mA) in a scan range ( $2\theta$ ) from 20°-80° shows the XRD patterns for titanium dioxide nanoparticles which were nancrystalline in nature of TiO<sub>2</sub> which prepared by electrodeposition at room temperature, XRD patterns of the as-prepared

samples with different conditions were shown in Fig. 4a is found to be crystalline and possesses anatase structure as it shows few peaks of anatase (101) and (004), X-ray diffraction analysis reveal that TiO<sub>2</sub> nanopowder are amorphous if the temperature sample is lower than 300°C (Yahya, 2010).

The diffraction peaks are in good agreement with those given in JCPD data card (JCPDS No. 21-1272 and 21-1276) for TiO<sub>2</sub> anatase and rutile as shown in Fig. 4 a, b. It is observed that the intensities of the peaks of few TiO<sub>2</sub> planes increased slightly with the increase of annealing temperature. In addition, the location of the (101) peaks is shifted to lower  $2\theta$  angles from  $2\theta = 25.27^\circ$  to  $2\theta = 25.11^\circ$ . The pronounced anatase TiO<sub>2</sub> characteristic diffraction peaks  $2\theta = 25.25^\circ$  (101) and  $48.0^\circ$  (200) were found in the patterns, all the peaks in the XRD patterns can be indexed as anatase and rutile phases of TiO<sub>2</sub> and the diffraction data are in good agreement with data reported by Vijayalakshmi and Rajendran (2012) (Chen *et al.*, 2004). From Fig. 4b, the X-ray diffraction patterns of the optimum TiO<sub>2</sub> NPs prepared by using electrochemical method have been TiO<sub>2</sub> prepared. It has been calcination to a temperature of 700°C to convert from TiO<sub>2</sub> anatas amorphous phase to crystallized phase TiO<sub>2</sub> anatas/rutile that corresponds to the standard sample shown in Fig. 5, used in photodegradation process.

### SEM, TEM and EDS measurements of TiO<sub>2</sub> (NPs) electrodeposition with GLY, PVP, PVA:

The SEM micrograph of the prepared TiO<sub>2</sub> nanoparticles, spherical and uniformly distributed particles can be seen, largest particles in figure may be aggregates from smaller particles (Reddy *et al.*, 2010). The value of particle size observed in SEM and TEM image, good agreement with the results obtained from XRD, significantly important of spherical shape not only for the design of surface area and surface properties but also for accuracy the electronic structure, for visible light spectrum more active for photocatalytic activity better by observing SEM an image, we find nanoparticles distributed regularly in the shape of

Table 2: AFM measurements of TiO<sub>2</sub> powder electrodeposition of KCl solutions by using PVA, Glycerin  
CSPM imager surface roughness analysis (amplitude parameters)

TiO <sub>2</sub>	PVP	PVA	Glycerin
Roughness average (sa) nm	2.3400	0.5680	8.4300
Root mean square (sq) nm	2.7800	0.6560	<b>9.7300</b>
Surface skewness (Ssk)	-0.2330	-0.0543	<b>0.0319</b>
nm surface kurtosis (sku) nm	<b>2.1100</b>	1.8400	1.8100
Sku = (3) mesokurtic, <(3) leptokurtic, >(3) platykurtic	<b>2.1100</b> >	1.8400>	1.8100
Peak-peak (sy) nm	11.100	3.0700	34.100
Ten point height (sz) nm	11.100	2.8500	34.100
<b>Hybrid parameters</b>			
Mean summit curvature) ssc (1/nm)	-0.0107	-0.0023	-0.0430
Root mean square slope (sdq) (1/nm)	0.1790	0.0390	0.6440
Surface area ratio (sdr)	1.5800	0.0767	18.700
<b>Functional parameters</b>			
Surface bearing index (sbi)	4.4900	1.2000	4.3000
Core fluid retention index (sci)	1.3900	1.4600	1.5100
valley fluid retention index (svi)	0.1100	0.0744	0.0666
Reduced summit height (spk) nm	0.2810	0.1330	4.6000
Core roughness depth (sk) nm	8.5700	2.1200	28.3000
Reduced valley depth (svk) nm	2.0700	0.1840	1.1600
<b>Spatial parameters</b>			
(density of summits) Sds (1/um <sup>2</sup> )	335.00	277.00	366.00
Fractal dimension	2.1200	2.7000	2.1100
Avg. diameter nm	61.37	103.45	69.27
Voltage (V)	19.2	17.1	17.9

Bold values are significant

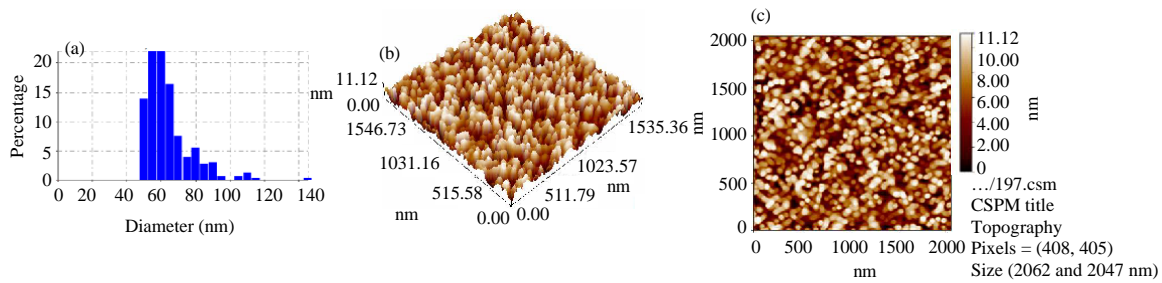


Fig. 1: AFM images of TiO<sub>2</sub> powder electrodeposition of KCl solutions with PVP (10 mL). Avg. diameter: 61.3 nm: a) Granularity cumulation distribution chart; b) 3-Dimensional image and c) 2-Dimensional image

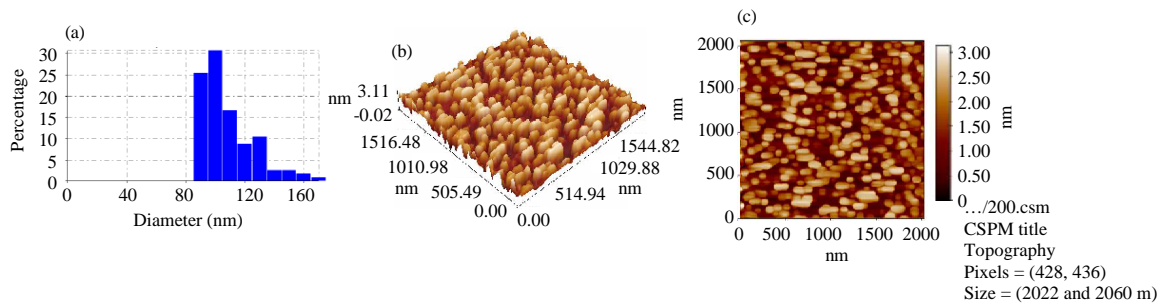


Fig. 2: AFM images of TiO<sub>2</sub> powder electrodeposition of KCl solutions with PVA (10 mL). Avg. diameter 103.45 nm: a) Granularity cumulation distribution chart; b) 3-Dimensional image and c) 2-Dimensional image

circular spherical particles, spherical in shape and without aggregation (Fig. 6) (Narayana *et al.*, 2011). The TEM image of TiO<sub>2</sub> appear spherical for all particles, narrow shape and distribution is displayed with a size of 40-80 nm. The EDs was recorded in the binding energy

region of 0-15 keV is shown in Fig. 6-8. The spectrum peak is reveal the atomic % of Ti and O, the present composition of Ti and O reveals that, the formation of non-stoichiometric TiO<sub>2</sub> which is superior for photocatalytic applications.

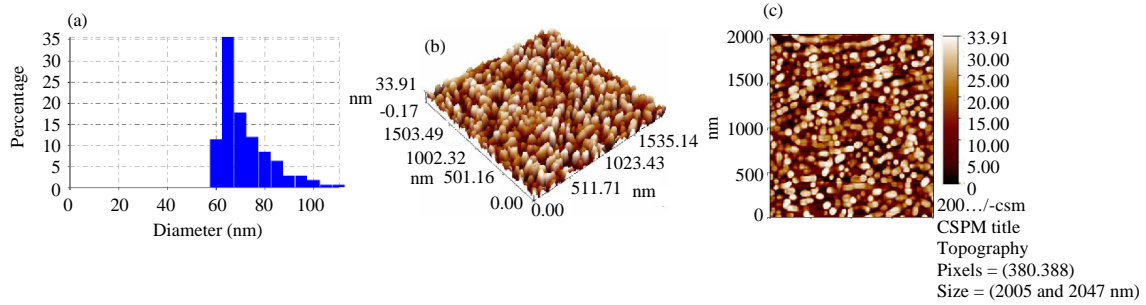


Fig. 3: AFM images of TiO<sub>2</sub> powder electrodeposition of KCl solutions with GLY (10 mL). Avg. diameter: 69.27 nm: a) Granularity cumulation distribution chart; b) 3-Dimensional image and c) 2-Dimensional image

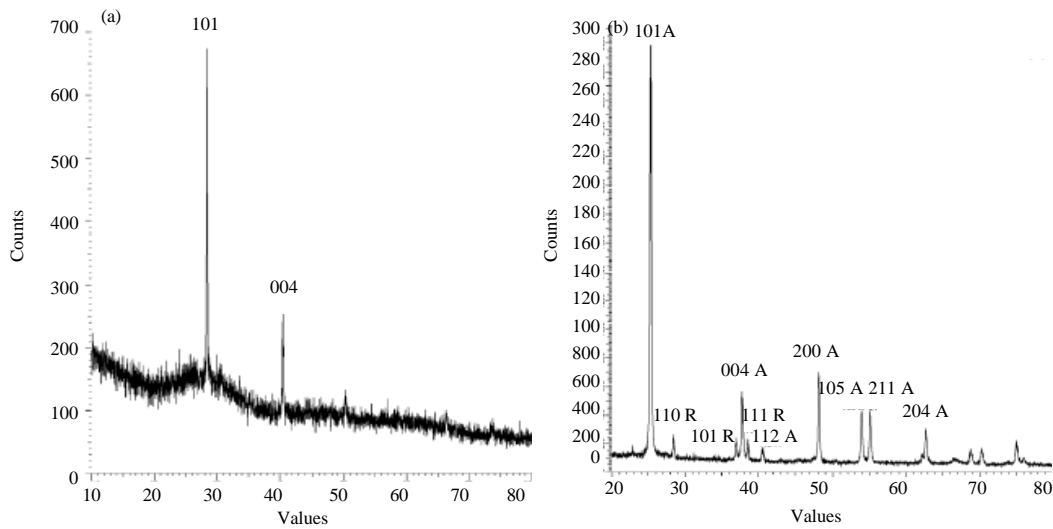


Fig. 4: X-ray images of TiO<sub>2</sub> nanopowder amorphous phase: a) Calcination at 700°C for 1 h and b) Electrodeposition of KCl solutions

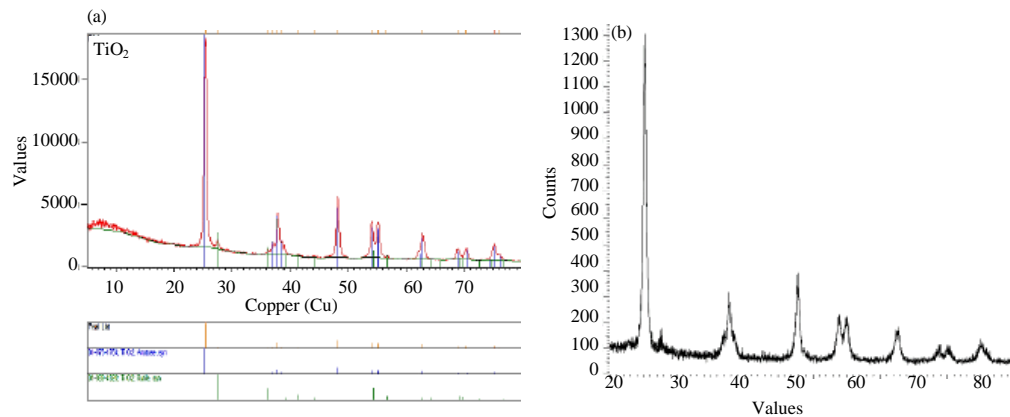


Fig. 5: X-ray images of TiO<sub>2</sub> nanopowder (anatase/rutile) standard, from USA, US Research Nanomaterials, Inc

**Photodegradation of MG by TiO<sub>2</sub> as catalyst:** In order to prove the potential of TiO<sub>2</sub> oxide from electrical way as a catalyst in the destruction of organic pollutants from pigments, wastewater or textile plants and to the

increasing demand for highly efficient and inexpensive catalysts, Malachite Green oxalate (MG) dye under studied with absorption about (617 nm) and good stability with visible light (Jiang *et al.*, 2015). MG which is specific

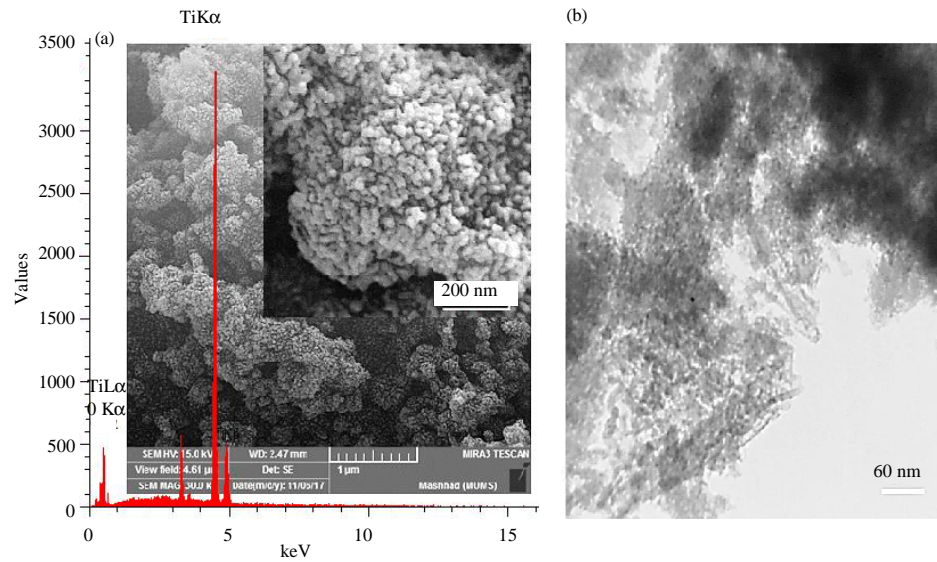


Fig. 6a, b: SEM, TEM and EDS images of TiO<sub>2</sub> NPs electrodeposition in KCL (0.1) M with GLY (10 mL), vigorous stirring (Ti = 30.25 wt.%, O = 69.75 wt.%)

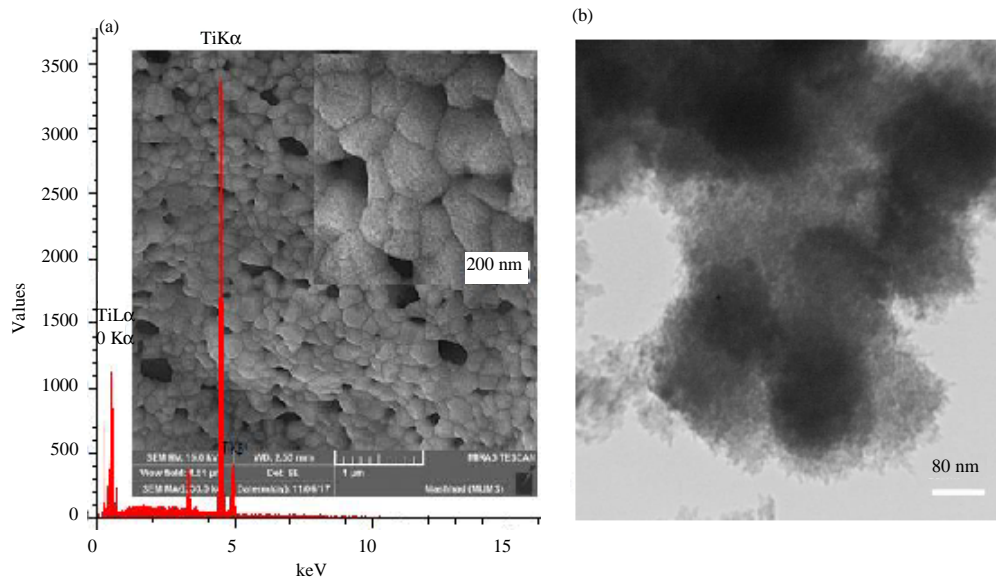


Fig. 7a, b: SEM, TEM and EDS images of TiO<sub>2</sub> NPs electrodeposition in KCL (0.1) M with PVA (10 mL), vigorous stirring (Ti = 35.53 wt.%, O = 64.47 wt.%)

as a basic dye which is an great water soluble dye relationship to triphenylmethane family M.wt. 927.01 g/mol (Alderman, 1985; Sawa and Hoten, 2001; Vijayalakshmi and Rajendran, 2012; Culp *et al.*, 1999). The homely photoreactor equipment mercury lamp-Philips-Holland (250 W) without cover glass as a source for UV irradiation (Shimadzu UV 1650 PC Japan) was used to decide the declination degree of the (MG) dye solutions (LAB) tech, hot plate Korea. The space of

lamp and solution glass is 15 cm. The test occur at 25°C and closed compartment to block escape of harmful radiation the suspension pH values were adjusted at desired level using (0.01) N NaOH or (0.01) N HCl solutions were measured via. pH meter-Hanna tool, the water mixture was stirred magnetically during the amount of dye adsorbed and reduced was determined by change in the absorbance of (MG) dye using Eq. 1:

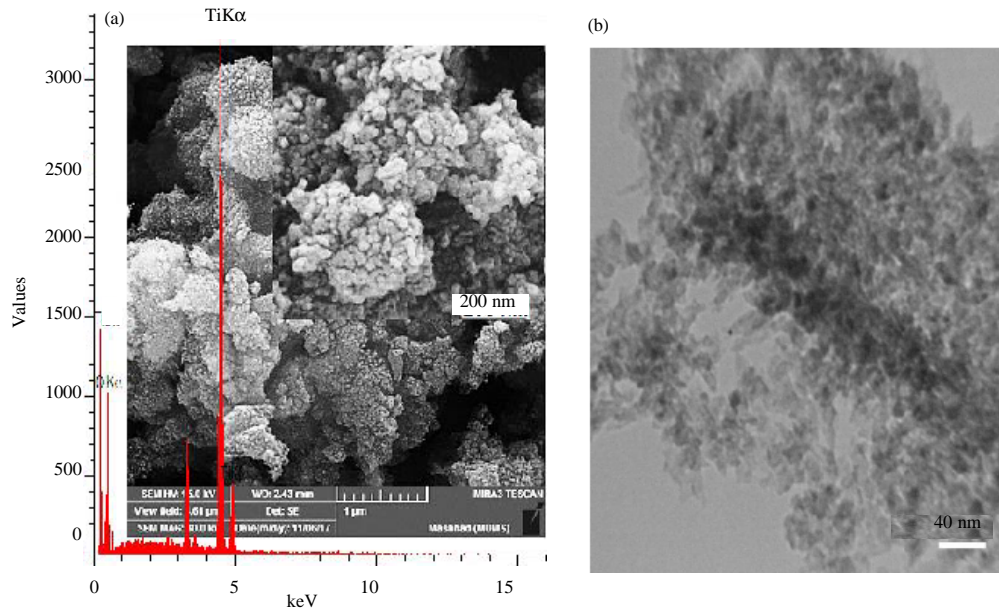


Fig. 8a, b: SEM, TEM and EDS images of TiO<sub>2</sub> NPs electrodeposition in KCL (0.1) M with PVP (10) mL, vigorous stirring (Ti = 52.84 wt.%, O = 47.16 wt.%)

$$(D\%) = \left[ \frac{C_o - C_a}{C_o} \right] \times 100\% \quad (1)$$

Where:

D% = The Degradation ratio

C<sub>o</sub> = The initial Concentration of dye solution

C<sub>a</sub> = The Concentration of dyes after adsorption by the catalyst

**Dark reaction of MG dye in presence TiO<sub>2</sub> catalyst:** In dark reaction performed tests in the lack of ultraviolet beam employ TiO<sub>2</sub> as a catalyst as show in Fig. 9, no deterioration in the loss of ultraviolet ray as results show where gave adding stimulation a slight change in the dye concentration in an incubation time slightly pigment concentrations decrease, after limited period of time. It becomes fixed where the monolayer configuration on the surface of the catalyst because no active sites useful for extra adsorption, so, no additional lessening in dye concentrations was observed. Thus, the yield obtained of the absorption taste confirm the low concentration of solutions (MG) is due to the absorption of dyes over catalysts, then no degradation of dyes was found. The conclusion show that the balance occurs after (90 min). The percentage of decomposition efficiency is calculated at (29.05 and 39.425%) for the TiO<sub>2</sub> (standard, prepared calcination at 700°C), respectively.

**Photodegradation of MG dye solution by UV irradiation in catalyst absence:** The photodegradation of MG dye solution by UV irradiation in catalyst absence as in Fig. 10

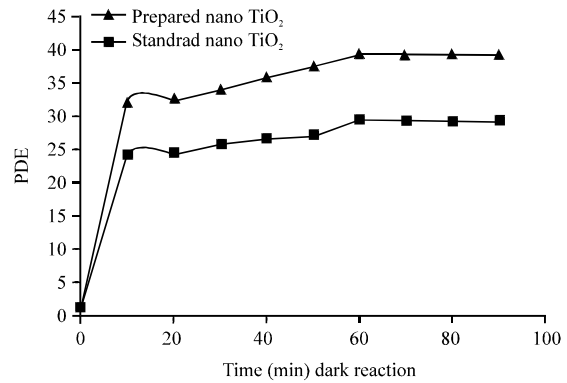


Fig. 9: The degradation efficiency of MG with (standard anatase/rutile, prepared anatase/rutile calcination at 700°C from TiO<sub>2</sub> catalyst, absence the UV radiation

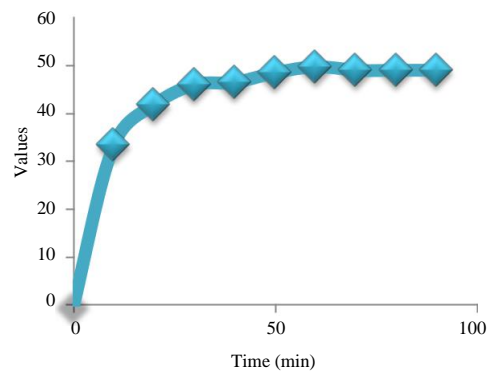


Fig. 10: The photodegradation efficiency of MG dyes without the catalyst

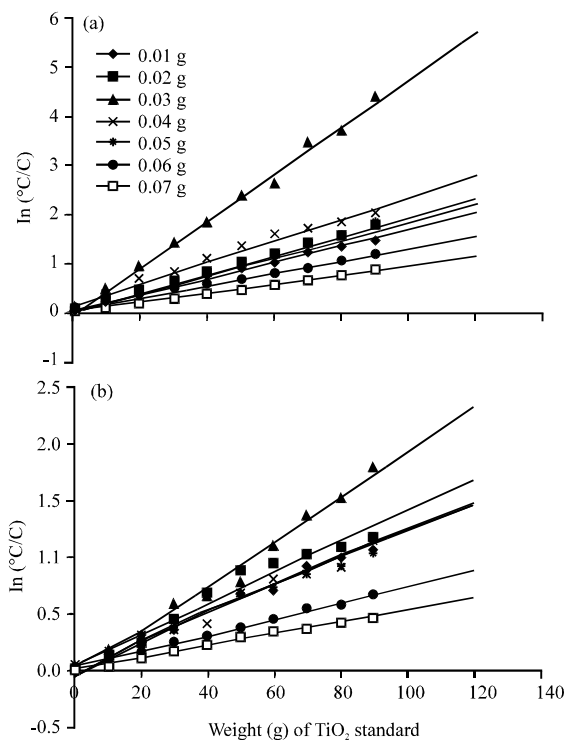


Fig. 11a): Effect of weight of  $\text{TiO}_2$  (standard) on photodegradation efficiency of MG and b) Effect of weight  $\text{TiO}_2$  (prepared) on photodegradation efficiency of MG

can be determined result after 90 min of UV treating, the Photodegradation Efficiency (PDE %) can be observed (49.75%) take effect by the ultraviolet radiation in catalyst absence.

**Effect of  $\text{TiO}_2$  mass on the rate of degradation of MG dye:**

The influence of amount catalyst onto photocatalytic degradation for MG dyes, light power (250 W) at (25°C) and variable the mass of  $\text{TiO}_2$  NPs for both (standard, prepared) in range (0.01-0.07) g in 100 mL from 4 ppm of MG dye. If the concentration of photocatalyst crosses certain optimum value in the suspension then the penetration of light through the suspension reduces that causes decrease in the rate of decolourization of dye (Kartal *et al.*, 2001; Neppolian *et al.*, 2002). Thus, for executing any continuous research, the catalyst dose optimization is required before starting any photolysis process. Through Fig. 11a, b, for  $\text{TiO}_2$  NPs for both (standard, prepared). The following is illustrated, the best weight of  $\text{TiO}_2$  is 0.03 for tow catalyst. Photodegradation efficiency for  $\text{TiO}_2$  NPs for both (standard, prepared) which is equal to 98.74 and 83.2%, respectively.

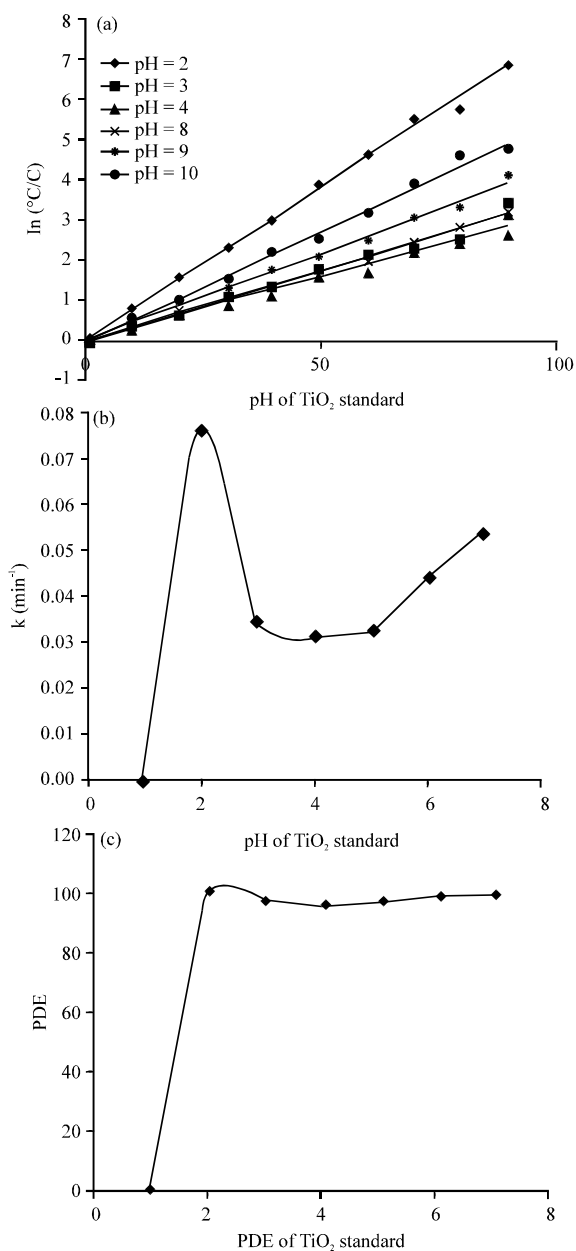


Fig. 12a-c): Influence of pH on photocatalytic degradation efficiency of MG with 0.03 g  $\text{TiO}_2$  (standard)

**Effect pH of  $\text{TiO}_2$  on the rate of degradation of MG dye:**

By studying the changes in pH solution in the range of 2-10 by maintaining other test conditions fixed, dye concentration of 4 ppm, light power (250 W), catalyst dose (0.03) g, at (25°C). The results observed in Fig. 12a, b. The influence of the initial solution pH on the removal of MG by  $\text{TiO}_2$  NPs,  $\text{TiO}_2$  is amphoteric in aqueous solution (Neppolian *et al.*, 2002), the higher the

Table 3: The values of rate constant, kinetics and thermodynamic parameters for the photocatalytic degradation of MG dye at (303-318) K with (0.03) g of TiO<sub>2</sub> standard, prepared)

T (K)	1/T	K (sec <sup>-1</sup> )×10 <sup>5</sup>		ln K		Ea (kJ/mol)		ΔH <sup>0</sup> (kJ/mol)		ΔS <sup>0</sup> (kJ/mol/k)		ΔG <sup>0</sup> (kJ/mol)	
		-----		-----		-----		-----		-----		-----	
		TiO <sub>2</sub> prepared	TiO <sub>2</sub> standard	TiO <sub>2</sub> prepared	TiO <sub>2</sub> standard	TiO <sub>2</sub> prepared	TiO <sub>2</sub> standard	TiO <sub>2</sub> prepared	TiO <sub>2</sub> standard	TiO <sub>2</sub> prepared	TiO <sub>2</sub> standard	TiO <sub>2</sub> prepared	TiO <sub>2</sub> standard
303	0.00330	4.166	4.330	-10.085	-10.047	-	-	34.979	54.215	-	-	96.488	96.029
308	0.00324	5.833	9.166	-9.749	-9.297	-	-	34.937	54.174	-	-	97.461	96.719
313	0.00319	7.660	12.200	-9.476	-8.987	-	-	34.896	54.132	-	-	98.435	97.409
318	0.00314	11.160	18.600	-9.100	-8.589	-	-	34.854	54.090	-	-	99.408	98.099

dissolution rate of the pollutant was observed at higher the acidic reaction medium than the neutral and basic mean, increased catalyst effectiveness can be explained when the medium is acidic because the catalyst surface is positively charged, this leads to the attraction of pollutant-negative aggregates to the surface of the catalyst and increases adsorption, thereby, increasing the disintegration of the pollutant as well as increasing the attraction of negative hydroxyl ions that can be transformed into the free hydroxyl radical caused by hole that are responsible for the disintegration of the pollutant, it can be seen that the adsorption percentage maintained very high (99.89%), (90.49%) at pH = (2) and (99.15%), (89.38 %) at pH = (10), for both TiO<sub>2</sub> NPs (standard, prepared), respectively.

**Effect of MG dye concentration on the rate of degradation in presence TiO<sub>2</sub> NPs:**

The influence of primary dye concentration on the photocatalytic degradation rate can be calculated by maintenance all other test conditions stable at light power (250 W), the pH = (2) at (25°C), (0.03) g for TiO<sub>2</sub> NPs for both (standard, prepared) and changing the primary dye concentration in domain (1-7) ppm as in form Fig 13a, b, the results show that with the reduced concentration of the dye, the rate of photo degradation increases this is because increasing the concentration of the primary dye reduces the length of the photon path into the solution, thereby, reducing the number of photons reaching the catalyst surface and hence, rate of formation hydroxyl radicals and super oxide ions (O<sup>2-</sup>) is reduce because of the lower surface area exposed to the excitation, the rate of photolysis decreases (Hustert and Zepp, 1992; Daneshvar *et al.*, 2008).

**Effect of temperature on photocatalytic degradation efficiency of MG dye with 0.03 g TiO<sub>2</sub> catalyst:**

In range of temperature (303-318) K, the effect of temperature on dye removal was studied by keeping other experimental conditions constant at dye concentration of 1 ppm, light intensity equal to 250 W, TiO<sub>2</sub> for both (standard, prepared) catalyst dosage was 0.03 g, pH dye solution

equal to (2) as in Fig 14a,b, the results are listed in Table 3, the temperature is directly proportional to the disintegration of the pollutant where the photodegradation is increased by increasing the reaction temperature.

**Thermodynamic, kinetic studied of plot ln (k) vs. 1/T:**

Experimental data obtained through thermodynamic investigation were analyzed. Thermodynamic parameters such as standard free energy change (ΔG<sup>0</sup>, kJ/mol), thermal content change (ΔH<sup>0</sup>, kJ/mol) and entropy change (ΔS<sup>0</sup>, kJ/mol/k) were determined expressed in Eq. 2-4:

$$\ln A = \ln \frac{KBT}{h} + \frac{\Delta S^0}{R} \tag{2}$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{3}$$

$$\Delta H^0 = E_a - RT \tag{4}$$

Brief the thermodynamic parameters determined at different temperatures ranging from (303-318) K. The positive value of ΔH<sup>0</sup> substantiated the endothermic nature of the dye sorption process. The negative ΔS<sup>0</sup> values suggest the decreased randomness at solid-liquid interface and reflect favorable condition for the removal MG dyes from solutions. These results indicate that the degradation efficiency not significantly affected with the increase of temperature, according to MG reduced the rate of most reactions varies with temperature in such a way that:

$$k = Ae^{-E_a/RT} \tag{5}$$

The activation energy E<sub>a</sub> was calculated from the Arrhenius plot of lnk vs. 1/T the slope of linear plot is equal to -E<sub>a</sub>/R as show in Fig. 15a, b, the entropy of activation ΔS<sup>0</sup> was calculated from Eq. 2 (Daneshvar *et al.*, 2008). The activation energy for photodegradation and decontamination in MG solution using the titanium dioxide catalyst in the (303-318) K temperature range was (56.734±1) and (37.498±1) kJmol<sup>-1</sup>, respectively.



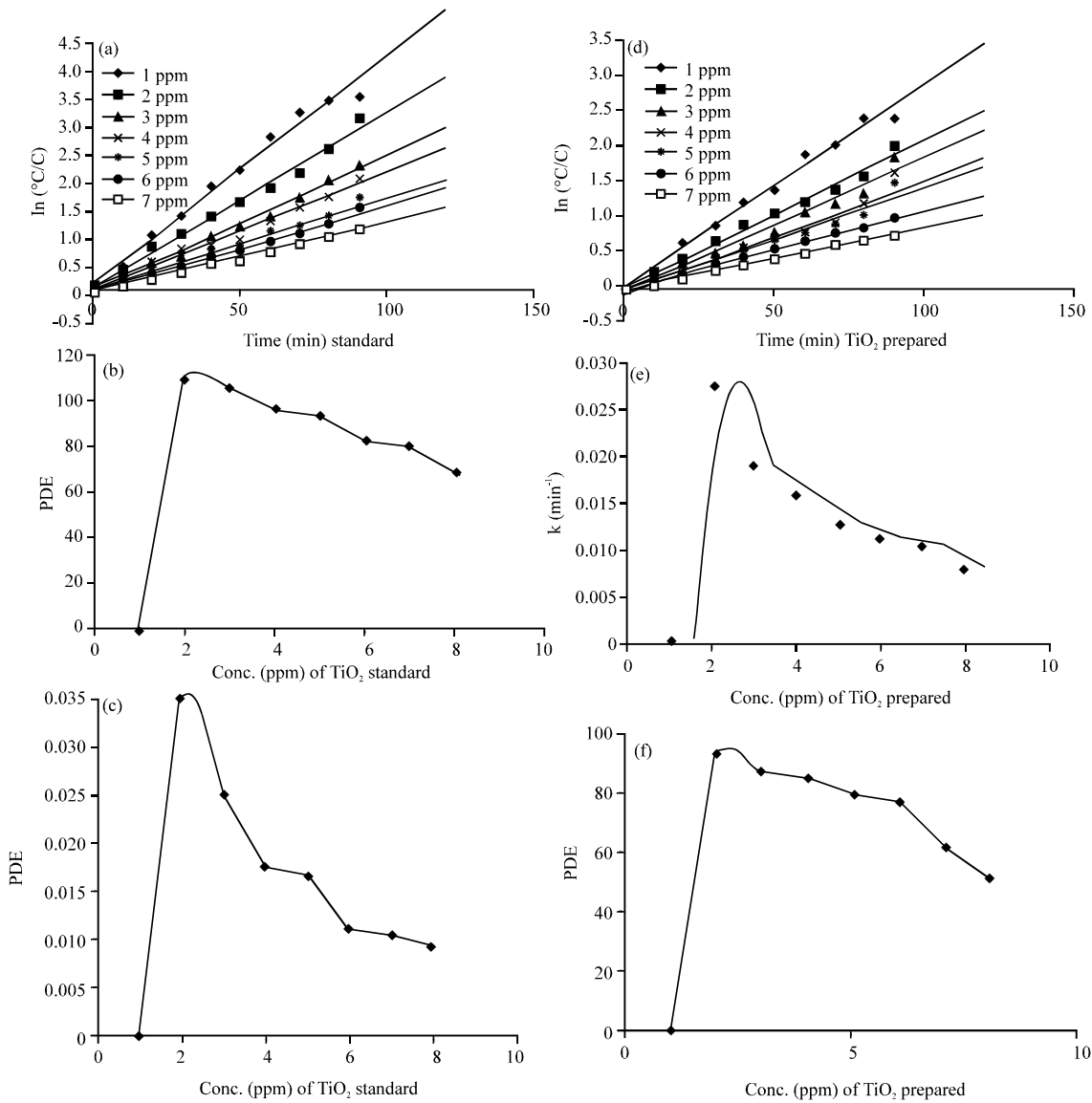


Fig. 13a-c): The variable in photocatalytic degradation efficiency for MG dye with concentration in presence (0.03) g of  $TiO_2$  (standard) and d-f) The variable in photocatalytic degradation efficiency for MG dye with concentration in presence (0.03) g of  $TiO_2$  (prepared)

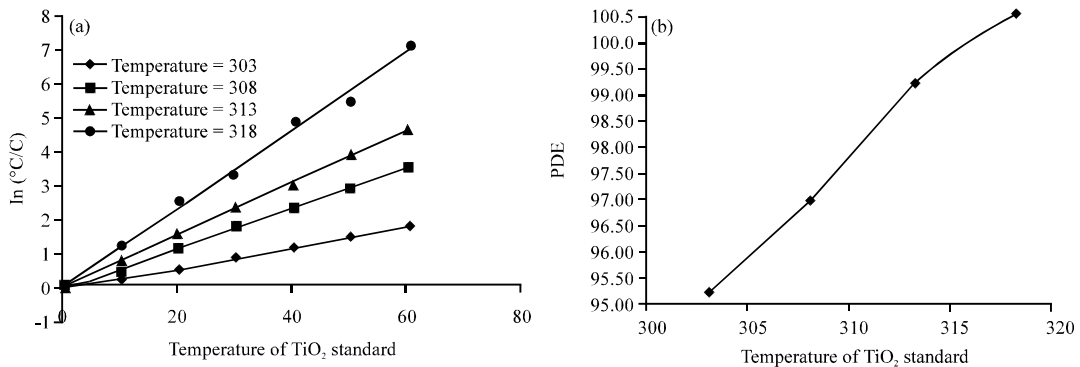


Fig. 14: Continue

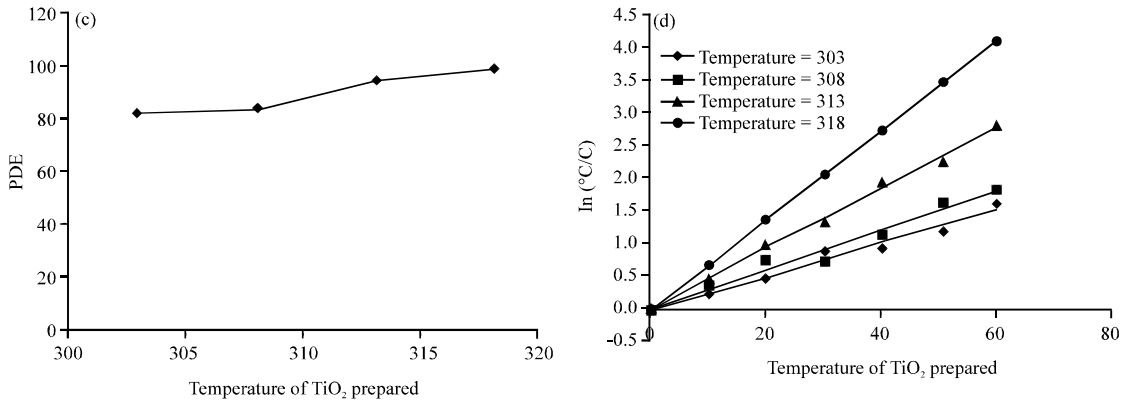


Fig. 14a, b): Effect of temperature on photocatalytic degradation efficiency of MG dye with 0.03 g TiO<sub>2</sub> standard and c-d): Effect of temperature on photocatalytic degradation efficiency of MG dye with 0.03 g TiO<sub>2</sub> prepared

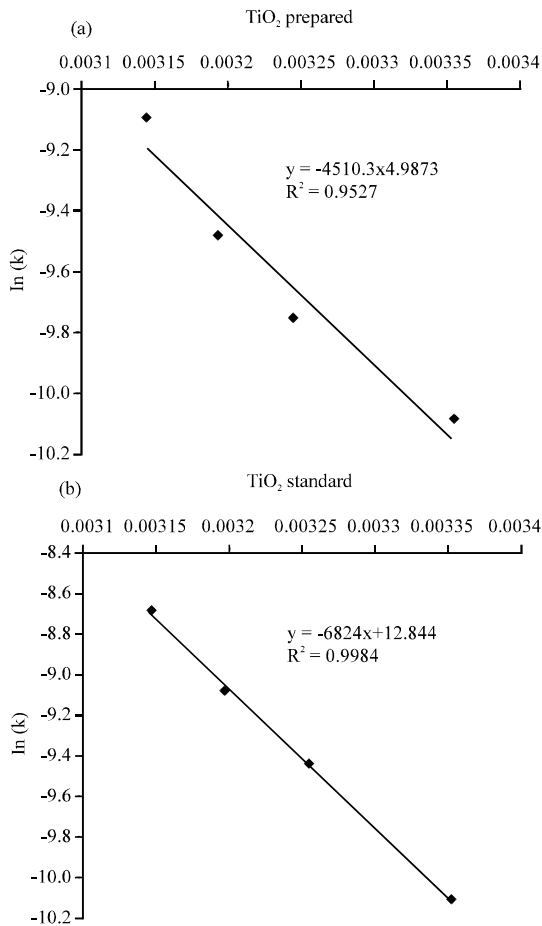


Fig. 15a, b): Arrhenius plot of MG dye (0.03) g TiO<sub>2</sub> standard and prepared

### CONCLUSION

By electrochemical can be prepared successfully TiO<sub>2</sub> nanoparticles, inexpensive, simple and high-precision way

to control the size and shape of the nanometer. To improve the catalytic performance of photocatalysis and to increase crystallization, the prepared powder was calcination to 700°C, to converted from anatase phase to TiO<sub>2</sub> anatase/rutile phase, for comparison with standard Titanium Oxide (TiO<sub>2</sub>, 80 vol% anatase+20 vol% rutile) from (US research nanomaterials, Inc), the result indicates that (E<sub>g</sub>) which was referred to as 56.73, 37.49 for both prepared and standard, respectively, the thermodynamic parameters of the degradation of MG solutions and titanium oxide refer to the positive  $\Delta H^0$  certain on endothermic reaction, the positive  $\Delta G^0$  result indicate that the non-spontaneous reaction, entropy of activation  $\Delta S^0$  is negative less randomly, the reactive species such as hydroxyl radical and superoxide anion have been produced from the heterogeneous photocatalytic reaction. The results of the fragmentation of the dye by the catalyst were CO<sub>2</sub> and H<sub>2</sub>O.

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