

# Electrochemical-assisted photodegradation of dye on TiO<sub>2</sub> thin films: investigation on the effect of operational parameters

Zulkarnain Zainal\*, Chong Yong Lee, Mohd Zobir Hussein, Anuar Kassim, Nor Azah Yusof

*Department of Chemistry, Faculty of Science, Universiti Putra Malaysia, 43400 UPM Serdang,  
Selangor Darul Ehsan, Malaysia*

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## Abstract

Electrochemical-assisted photodegradation of methyl orange has been investigated using TiO<sub>2</sub> thin films. The films were prepared by sol–gel dip-coating method. Several operational parameters to achieve optimum efficiency of this electrochemical-assisted photodegradation system have been tested. Photoelectrochemical degradation was studied using different light sources and light intensity. The light sources chosen ranged from ultraviolet to visible light. The effect of agitation of the solution at different speeds has also been studied. Slight improvement of photodegradation rate was observed by applying higher agitation speed. Investigation on the electrode after repeated usages show the electrode can be reused up to 20 times with percentage of deficiency less than 15%. The study on the effect of solution temperature indicated that the activation energy of the methyl orange degradation is 18.63 kJ mol<sup>-1</sup>.

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## 1. Introduction

In the last two decades, numerous studies have been performed on heterogeneous photocatalysis process, which has emerged as a promising advanced oxidization technology for water purification. It has attracted considerable attention from researchers due to the prospect of complete mineralisation of the pollutants into harmless compounds [1–3]. In addition, the availability of abundance and inexpensive catalyst with non-toxicity, high photoactivity and high stability (biologically and chemically) features have accelerated the research activities in this field. Among the semiconductors, titanium dioxide (TiO<sub>2</sub>) has been proven to be an excellent photocatalyst material, which many organic substances have been shown to be oxidatively or reductively degraded [4–9].

The high degree of recombination between photogenerated electrons and holes in semiconductor particles is a ma-

ior limiting factor for photodegradation process [10,11]. In photoelectrochemical method, TiO<sub>2</sub> is immobilised onto conducting substrates, on which electrical bias potential can be applied. The application of the external potential can drive away the photogenerated electron to counter electrode, which could minimise the charge recombination process [12,13]. Another advantage of using the immobilising technique is that the electrode can be easily recycled, while in suspension or slurry system costly post-filtration processes are required.

TiO<sub>2</sub> (anatase) is a semiconductor that has bandgap energy of 3.2 eV, where only the light with wavelengths below 380 nm can be absorbed to generate the electron–hole pairs. It is known that <5% of the solar energy reaching the surface of the earth is ultraviolet light [14]; therefore, significant photodegradation efficiency is difficult to be achieved by natural sunlight in short irradiation period. This factor places some limitations on the application of this technology in the treatment of wastewater, since artificial light sources need high electrical power and are

\* Corresponding author. Tel.: +603 89466810; fax: +603 89435380.  
E-mail address: zulkar@fsas.upm.edu.my (Z. Zainal).

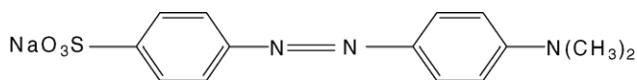


Fig. 1. Chemical structure of methyl orange.

expensive. Besides that, the efficiency of controlling the parameters such as solution agitation and temperature in aqueous pollutants in real wastewater treatment also seems to determine the photoreactor efficiency.

In this paper,  $\text{TiO}_2$  films were fabricated by sol–gel dip-coating method. This study was undertaken to investigate the effects of light source, light intensity, agitation, electrode repeated usage and solution temperature on photoelectrochemical degradation process of a model pollutant, methyl orange dye. Methyl orange (Fig. 1) was selected as model dyeing pollutant because azo-dyes are among the largest group of colorants used in a variety of industrials such as textile and paper [15]. The collected data will provide useful information in designing a photoreactor with optimum efficiency.

## 2. Experimental

### 2.1. Preparation of precursor solutions

The precursor solution for  $\text{TiO}_2$  sol was prepared using the system that containing titanium tetraisopropyl-orthotitanate, polyethelene (glycol) (molecular weight,  $M_w = 2000$ ), diethanolamine, ethanol and water as reported by Kato [16–18]. Modifications were made on chemical molar ratio and adding sequences. The molarity of alkoxide in the ethanol was  $0.94 \text{ mol/dm}^3$ . The molar ratio of diethanolamine to the alkoxide was one. The concentration of polyethylene glycol and water to alkoxide was 6 and 0.8 wt.%, respectively. The polyethelene glycol solution was dissolved in the ethanol solution before adding other chemicals in the following sequences; diethanolamine, titanium tetraisopropyl orthotitanate and water. The mixture was stirred in a sealed condition for several hours at room temperature. The resulting sol–gel was clear and transparent.

### 2.2. Preparation of $\text{TiO}_2$ thin films

The titanium plates ( $5 \text{ cm} \times 2 \text{ cm}$ ) were used as the conductive supporting materials for  $\text{TiO}_2$ . The plate was polished by silicon carbide paper (Bioanalytical system PK-4 polishing kit) and later cleaned with acetone in an ultrasonic bath for 15 min. The treated Ti plate was dried in an oven at  $100^\circ\text{C}$  for 15 min and then dip-coated with sol–gel solution and left to dry at room temperature. The coated electrode was heated at  $100^\circ\text{C}$  for 5 min in an oven followed by subsequent dip-coating. An area with a size of  $1.5 \text{ cm} \times 2.0 \text{ cm}$  at the top was left uncoated to provide the area for the electrical connection. This step was repeated several times until the amount of  $\text{TiO}_2$  catalyst loaded was approximately 2.00 mg. Finally, the plate

was annealed at  $500^\circ\text{C}$  in a Thermolyne 21100 furnace for 2 h.

### 2.3. Analytical measurements

The photoelectrochemical measurements were carried out in the two-compartment cell equipped with a quartz plane window as shown in Fig. 2. The anode and cathode electrodes were separated by Polytetrafluoroethylene (PTFE)  $0.45 \mu\text{m}$  membrane. The working electrode was a  $\text{TiO}_2/\text{Ti}$  plate and the counter electrode was a platinum plate ( $1 \text{ cm}^2$ ). All the potentials were specified to the Ag/AgCl reference electrode, which was connected to the assembly via a salt bridge. The electrode potentials and photocurrents were recorded using AMEL general-purpose potentiostat–galvanostat Model 2049. All the potentials were fixed at 1.0 V during photodegradation experiment. Meanwhile, a potensioestat EG&G Princeton Applied Research (PAR) VersaStat driven by model 270 Electrochemical Analysis System software with PC control was used for linear sweep voltammetry (LSV) measurement. The temperature of the reactor solutions was maintained at 313 K throughout the experiments by using a water jacket circulation system around the cell (except during the study on the effect of solution temperatures). The light source was placed 8 cm away from the sample. Photoreactor cell (total volume of  $140 \text{ cm}^3$ ) was filled with  $120 \text{ cm}^3$  methyl orange solution containing 0.1 M NaCl as a supporting electrolyte. The samples were withdrawn every 30 min thereafter for a period of 120 min. The concentration of the methyl orange in the solution was determined by measuring the absorbance values using UV–vis Perkin-Elmer Lambda 20 Spectrophotometer at 464.5 nm.

## 3. Results and discussion

### 3.1. Effect of different type of light source

In the studies reported elsewhere, various types of lamps were used as illumination source ranging from visible to near UV light [19,20]. The light source used is an indicator to evaluate the operating cost and the efficiency of photoreactor. Three types of lamps were chosen as light sources namely halogen (Tungsten type, 300 W) fluorescent (energy save type, 15 W equal to 75 W) and near UV lamp (100 W). Halogen lamp was chosen because it closely resembles sunlight. Meanwhile, fluorescent lamps are widely used for household and industrial purpose provide a cheap and energy saving alternative.

Fig. 3 shows the effect of various types of light source towards photoelectrochemical degradation of methyl orange dye. The experimental results are reported as ratio of ( $C/C_0$ ) versus illumination time ( $t$ ), where  $C_0$  is the initial concentration of dye and  $C$  is the concentration at  $t$  minute. The dye concentration was determined through standard calibration curve of absorbance (recorded at  $\lambda_{\text{max}} = 464.5 \text{ nm}$ ) versus

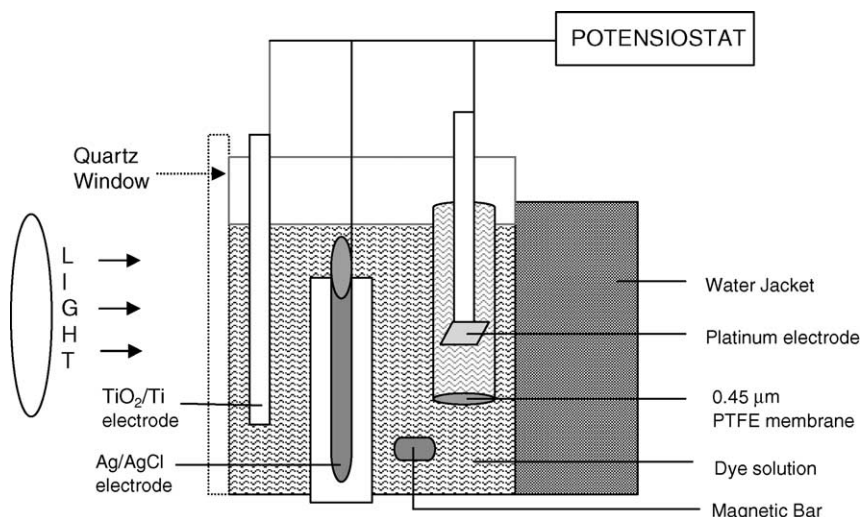


Fig. 2. The experimental set-up for the photoelectrochemical degradation process from cross-sectional view.

concentration. Control experiment was carried out by illumination of methyl orange solution in the absence of TiO<sub>2</sub>, which shows no changes of dye concentration for period of 120 min irradiation times.

The photoelectrochemical degradation rate using UV lamp with power of 100 W is almost equivalent to a 300 W halogen lamp. This is due to UV radiation that possesses higher intensity of photon with energy equal or higher than TiO<sub>2</sub> bandgap ( $E_g$ ). Thereby, more electrons were excited from the valence band to the conduction band. In this study, TiO<sub>2</sub> has bandgap energy about 3.2 eV (~380 nm) as indicated by UV–vis absorption spectrum in Fig. 4. In conjunction with this, only small amount of photon energy generated

by halogen lamp, which possesses longer wavelength, was suitable for electron excitation. However, probably due to high intensity of the halogen lamp its performance is comparable to the near UV lamp.

Besides that, the mechanism of photodegradation using light with energy less than  $E_g$  will be different from that taking place using light with energy more than  $E_g$  of TiO<sub>2</sub>. The former excite the dye compounds directly, while the latter generate electron–hole pairs [14]. In another study, the photoassisted degradation of dyes preadsorbed on the surface of TiO<sub>2</sub> particles with visible light was reported [21], where the photoreaction system was almost water free and only the molecules that were in direct contact with the TiO<sub>2</sub> surface (the molecules at monolayer or submonolayer coverage) underwent photodegradation. This suggests that the high-energy component of the light plays an important role in generating electron–hole pairs for the photodegradation reaction.

On the other hand, a 15 W fluorescent lamp shows almost equal photoelectrochemical degradation rate with a 50 W

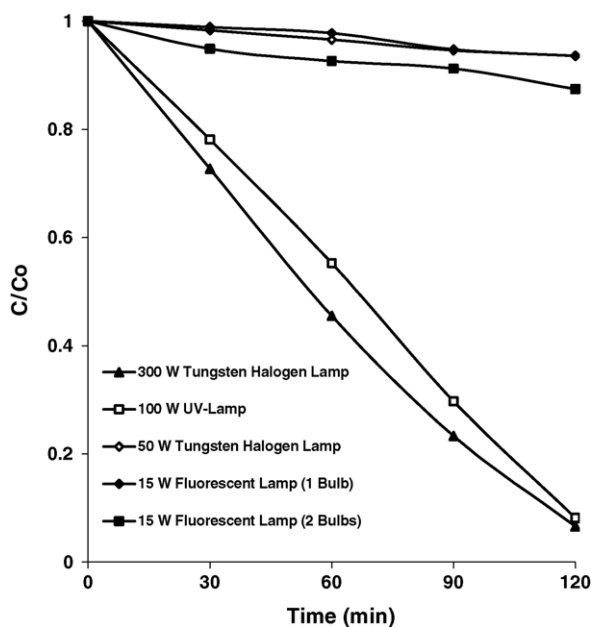


Fig. 3. The methyl orange degradation dependence on different types of light source.  $C_0 = 10$  ppm, containing 0.1 M NaCl; potential = 1.0 V.

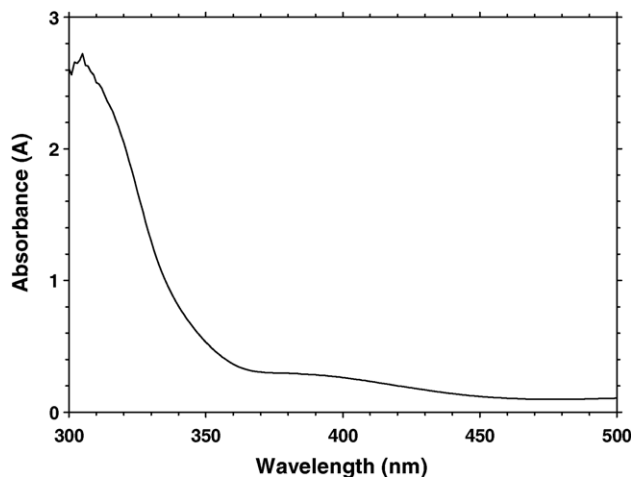


Fig. 4. UV spectra of TiO<sub>2</sub> thin film coated on ITO glass.

Table 1

Apparent first-order kinetic rate constants, half times and correlation factors for the photoelectrochemical degradation of methyl orange illuminated with different types of light with medium stirred speed

Type of lamp	Apparent rate constant, $k_{app}$ ( $\times 10^{-3} \text{ min}^{-1}$ )	Half time, $t_{1/2}$ (min)	Correlation factor, $R^2$
Tungsten halogen lamp 300 W	21.9	31.6	0.93
Ultraviolet Lampl 100 W	19.9	34.8	0.90
Tungsten halogen lamp 50 W	0.6	1155.0	0.99
Fluorescent lamp 15 W (1 bulb)	0.6	1155.0	0.96
Fluorescent lamp 15 W (2 bulbs)	1.0	693.0	0.96

halogen lamp. Therefore, the fluorescent light was irradiating more photon with suitable energy for excitation. This result may also be attributed to fluorescent lamp exhibits with energy saving feature. An increase in the photoelectrochemical degradation rate was observed when two fluorescent bulbs were used. The Langmuir–Hinshelwood first-order kinetic rate constant as shown in Table 1 was increased by almost two-fold when two fluorescent bulbs were used.

### 3.2. Effect of light intensity

The intensity of a 300 W halogen lamp irradiation was varied from without illumination to full light intensity using a dimmer. A lux meter was used to determine the percentage of the light intensity. The results indicate that dye degradation rate increased with light intensity as shown in Fig. 5. At lower light intensity, the reaction pathway seems to follow strictly the mechanism for visible light as discussed. Nevertheless, at high intensity more photons with energy larger than  $E_g$  of  $\text{TiO}_2$  are generated, which leads to more electron–hole pairs on the  $\text{TiO}_2$  surface. This produces more hydroxyl radical

on the surface or bulk solution to involve in the oxidation of dye molecules. Furthermore, direct oxidation may also occur for dye molecules, which are in direct contact with the  $\text{TiO}_2$  surface.

As seen in inset in Fig. 5, the kinetic constant of photoelectrochemical degradation shows exponential relationship with the light intensity percentage. This observation suggests there is a possibility to drastically promote the degradation rate by increasing the light intensity to a certain level where significant concentrations of electron–hole pairs were generated.

### 3.3. Effect of agitation

The rate of photodegradation is affected not only by the electrode reaction itself but also by the transport of species to and from bulk solution. This transport can occur by diffusion, convection or migration. Migration is an essential electrostatic effect that arises due to the application of voltage which creates a charged interface on the electrodes. Any charged species near the interface will either be attracted or repelled from it by electrostatic forces.

In this study, the effect of migration can be neglected. This is due to the presence of supporting electrolyte (0.1 M NaCl), which acts to transport almost all the current in the cell and reduce the cell resistance. Consequently, the effect of the electrical field is limited to a small distance from the electrode. Therefore, mass transport due to the diffusion and convection of the dye molecules to the interface may affect the overall efficiency.

Diffusion is the natural movement of species in solution, without the influence of electrical field. Thus, the species can be charged or neutral. In normal circumstances, the rate of diffusion depends on the concentration gradient as expresses by Fick's first law [22]:

$$J = -D \frac{\delta c}{\delta x} \quad (1)$$

where  $J$  is the flux of species,  $\delta c/\delta x$  the concentration gradient in solution and  $D$  the proportionality constant known as the diffusion coefficient.

There is no significant concentration gradient in the bulk solution due to the homogenous distribution of dye molecules in the solution. However, concentration gradient exists at the interface between the electrode surface and

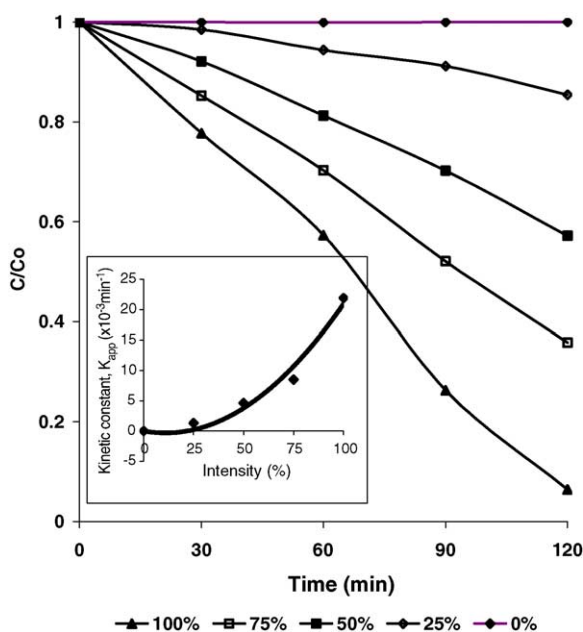


Fig. 5. The methyl orange dye degradation dependence on percentage of light intensity.  $C_0 = 10$  ppm, containing 0.1 M NaCl; potential = 1.0 V. Inset shows the first kinetic order constant vs. percentage of light intensity applied.

the solution during the photoelectrochemical degradation experiment. Dye molecules near to the electrode surface reacted with the reactive holes from the semiconductor leading to decrease of dye concentration at that region. On the other hand, hydroxyl radicals attacked the dye in the bulk solution far from electrode surface also resulting in the decrease of dye concentration [23]. Therefore, the variation of the concentration gradient is widely dependent on whether the reaction is more dominant at the electrode surface or to the bulk solution. If both the reaction occurred at the same rate, no concentration gradient was established.

Another type of mass transport is convection, which results from the action of a force on the solution. This could be due to a pump, flow of gas, stirrer and gravity. There are two forms of convection; natural and forced convection. The natural convection occurs in any solution is generated by small thermal or density differences and acts to mix the solution in a random, therefore unpredictable manner. Thus, in this study the photo reactor cell was equipped with water jacket to keep the temperature thermostated with the aim of avoiding big thermal gradient.

Beside thermal effect, we try to draw out the natural convection effects from an electrochemical experiment by deliberately introducing convection into the cell. Magnetic stirrer was placed in the bottom of the cell to agitate the reactants. This form of convection is termed forced convection. Fig. 6 depicts a slight increase of photocurrent, when higher agitation rates were applied. The sinusoidal curves could be observed for stirred solution compared to a smooth line for unagitated solution for both in dark and under illumination. From Fig. 7, we observe that the degradation curves shifted to slightly lower  $C/C_0$  value indicating better degradation when agitated. By agitating the solution, more dye molecules will be introduced and brought near to the surface of the electrode. On the other hand, hydroxyl radical produced at the surface can react more randomly with the dye in bulk solution.

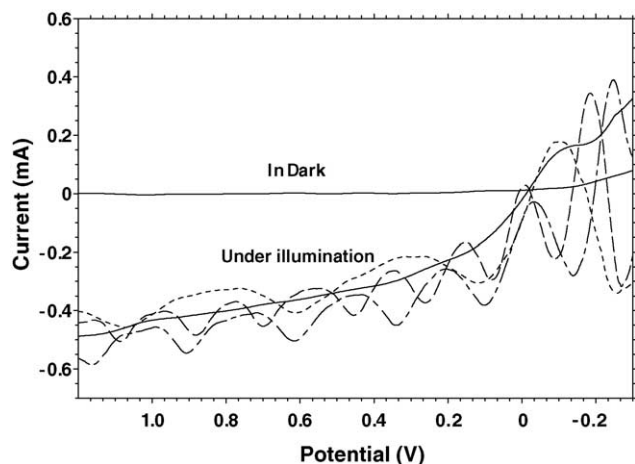


Fig. 6. The effect of agitation speed on photocurrent under illumination of 300 W halogen lamp.  $C_0 = 10$  ppm, containing 0.1 M NaCl. (—) Without stirred, (···) slow, (---) medium, (-·-·-) high.

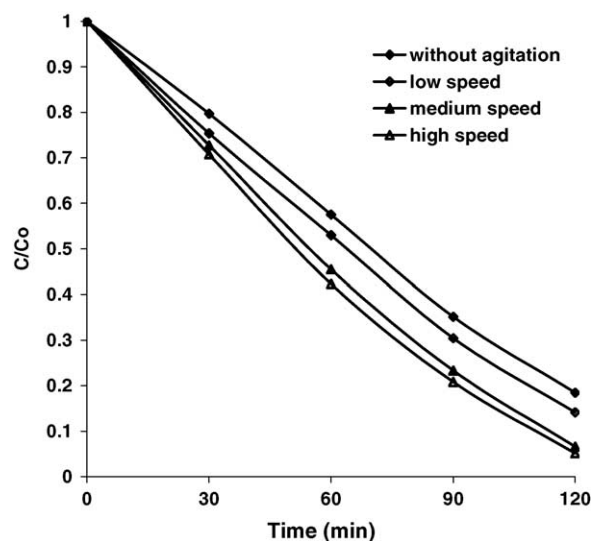


Fig. 7. The methyl orange dye degradation process dependence on agitation.  $C_0 = 10$  ppm, containing 0.1 M NaCl; potential = 1.0 V; illumination = 300 W halogen lamp.

#### 3.4. Effect of electrode repeated use

The electrode performance upon repeated usage has great significance in justifying the effectiveness of the electrode. If the electrode shows good ability to be repeatedly used, there is a good possibility for it to be applied in actual wastewater photoreactor.

In this study, the electrode was tested for total 20 runs for treatment of methyl orange solution with an anodic bias potential of 1.0 V as shown in Fig. 8. The result indicates that only a slight decrease in degradation efficiency was observed. The decrease in the efficiency may be due to the factor such as dissolution of the photocatalyst, development of insulation layer and poisoning of the catalyst surface by impurities

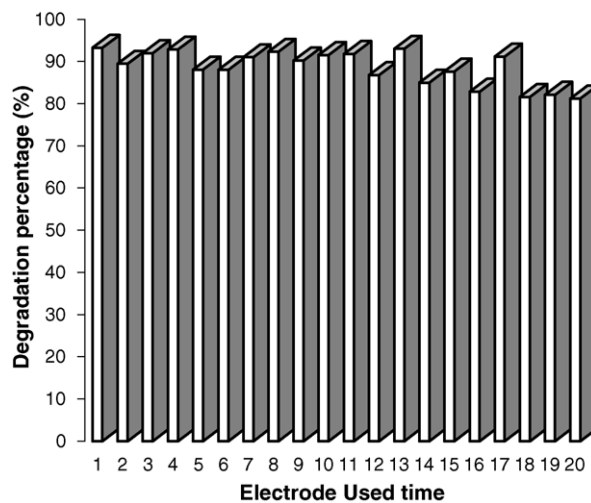


Fig. 8. The electrode repeated usage performance for total 20 times.  $C_0 = 10$  ppm, containing 0.1 M NaCl; potential = 1.0 V; illumination = 300 W halogen lamp.



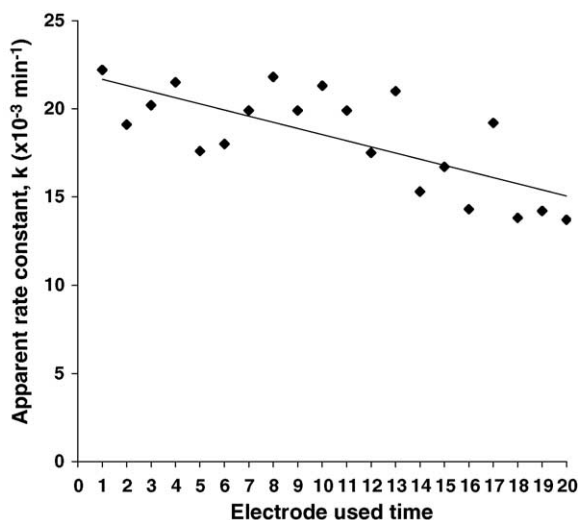


Fig. 9. Graph kinetic constant vs. electrode repeated usage time.

participating in a stoichiometric fashion in product formation [24]. However, high degradation percentage for 4, 8, 10, 13, 15, and 17 repetitions may be attributed to the increase in the surface area, chemical composition and the presence of bound water in the reused catalyst.

The performance of the electrode after repeated use widely depends on the factors that activate or deactivate the electrode efficiency as discussed. Fresh electrode not necessarily shows better performance than the reused one and vice versa. Fig. 9 shows the graph for first-order kinetic rate constants versus the electrode used times. The general trend is shown by the straight line, which indicates that the electrode suffered only a slight decrease in the overall performance after been repeatedly used.

### 3.5. Effect of photoreactor temperature

The dependence of photoelectrochemical degradation process on the temperature of methyl orange solution ranges from 298 to 318 K was studied. An increase of photoelectrochemical degradation process with increasing temperature was observed. Table 2 shows increasing of pseudo first-order kinetic rate constants with temperature.

Arrhenius suggested that the rate of most reactions varies with temperature in such a way that [25]:

$$k = Ae^{-E_a/RT} \quad (2)$$

Table 2

Apparent first-order kinetic rate constants, half times and correlation factors for the photoelectrochemical degradation of methyl orange at different solution temperatures using 300 W halogen lamp with medium stirred speed

Temperature $T$ (K)	Apparent rate constant, $k_{app}$ ( $\times 10^{-3} \text{ min}^{-1}$ )	Half time, $t_{1/2}$ (min)	Correlation factor, $R^2$
298	14.8	46.8	0.94
303	17.7	39.2	0.93
308	19.1	36.3	0.93
313	21.9	31.6	0.93
318	24.0	28.9	0.95

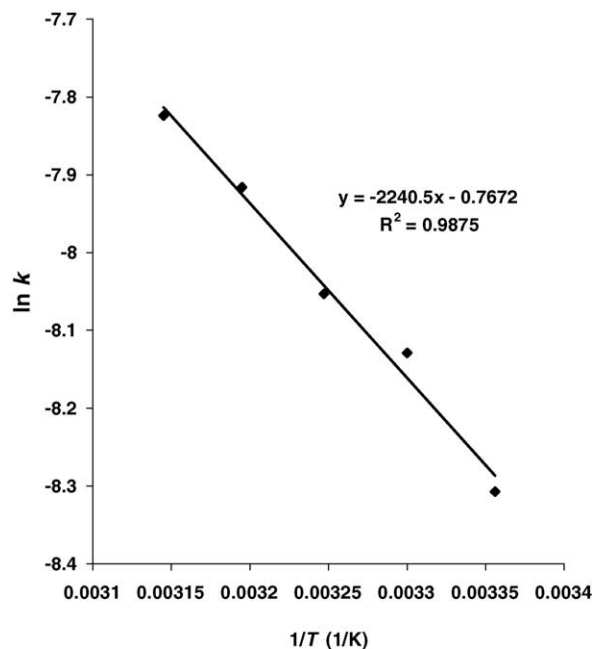


Fig. 10. An Arrhenius plot for methyl orange in photoelectrochemical degradation process.

where  $k$  is the rate constant,  $A$  is the frequency factor or pre-exponential factor, and  $T$  is the temperature (K).

Taking natural logarithm of both sides of Eq. (3) resulted in the following equation.

$$\ln k = -\frac{E_a}{R} \times \frac{1}{T} + \ln A \quad (3)$$

In this experiment, the rate constants were determined from the first-order kinetic graphs. The values of the rate constants are listed in Table 2. A linear plot of  $\ln k$  versus  $1/T$  was obtained as shown in Fig. 10 with the slope value of  $2240.5 \text{ K}^{-1}$ . The overall activation energy obtained was  $18.63 \text{ kJ mol}^{-1}$ . This value is quite similar to the activation energy reported by Chen et al. [26] where the value was found to be  $18 \text{ kJ mol}^{-1}$  for  $\text{TiO}_2$  suspension. An increase of activation energy on immobilised  $\text{TiO}_2$  compared to suspension is similar to observation for 4-chlorophenol as shown in Table 3. However, only a slight difference in the activation energy for methyl orange is observed compared to the one in suspension system. This suggests that the electrochemically-assisted photodegradation system applied in this study successfully reduce the activation energy for photodegradation reaction.

Table 3  
Comparison of activation energy obtained in this study with the findings in literatures

Reactant	TiO <sub>2</sub> catalyst	E <sub>a</sub> (kJ mol <sup>-1</sup> )	T (K)	Researcher(s)
Methyl orange	Suspension	18	300–318	Chen and Chou [26]
Methyl orange	Immobilised	18.63	298–318	This work
4-Chlorophenol	Suspension	16	288–328	Mills and Morris [27]
4-Chlorophenol	Immobilised	20.6	283–333	Hofstadler et al. [28]

The activation energy obtained is small, which indicates that the photocatalytic reaction is less temperature dependent. This is due to irradiation is the primary source of electron–hole pair generation as the band gap energy is too high to be overcome by thermal activation. Therefore, the effect of temperature is most likely due to the increase in collision frequency of the dye and the hydroxyl radical molecules [29]. Furthermore, an increase in temperature helped the reaction to compete efficiently with electron–hole recombination [30].

#### 4. Conclusion

The results indicate the importance of the operational parameters towards obtaining high photoelectrochemical degradation rate. Types of light sources as well the intensity significantly influenced the photoelectrochemical degradation. Agitation acts to promote the degradation rate by bringing more dye molecules closer to the electrode surface and hydroxyl radical produced at the interface can also react more randomly with the dye in the bulk solution. The film showed only slight decrease in the performance after repeated usage. The activation energy of photoelectrochemical degradation of methyl orange in aqueous solution was found to be 18.63 kJ mol<sup>-1</sup>, which is comparable to the value obtained in suspension system.

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