

Electrochemical-assisted photodegradation of mixed dye and textile effluents using TiO₂ thin films

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Abstract

Mixed dye consists of six commercial dyes and textile effluents from cotton dyeing process were treated by electrochemical-assisted photodegradation under halogen lamp illumination. Two types of effluents were collected which are samples before and after undergone pre-treatment at the factory wastewater treatment plant. The photodegradation process was studied by evaluating the changes in concentration employing UV–vis spectrophotometer (UV–vis) and total organic carbon (TOC) analysis. The photoelectrochemical degradation of mixed dye was found to follow the Langmuir Hinshelwood pseudo-first order kinetic while pseudo-second order kinetic model for effluents by using TOC analyses. The chemical oxygen demand (COD) and biochemical oxygen demand (BOD) values of mixed dye and raw effluents were reported. Photoelectrochemical characteristic of pollutants was studied using the cyclic voltammetry technique. Raw effluent was found to exhibit stronger reduction behaviour at cathodic bias potential but slightly less photoresponse at anodic bias than mixed dye.

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1. Introduction

Rapidly growing of human population increased the demand on variety of goods and products. This trend catalyzed the industrialization process which released tremendous environmental harmful by-products during manufacturing processes. Textile plants, particularly those involved in finishing processes are among the major source of water pollution. Large amounts of effluents that containing appreciable quantities of organic compound that is not easily to be treated chemically and biologically are released as wastewater. This is mainly due to the dyestuffs are designed to be resistant to chemical fading and light induced fading. In addition, the stability of their molecular structure also leads to resistant to aerobic microbial degradation [1]. Thus, there is a great challenge towards the treatment of textile effluents.

Dyeing wastewaters are conventionally treated by biological, physical and chemical techniques such as biological oxidation

[2,3], adsorption [4] and reverse osmosis [5]. Nevertheless, these processes involved high operational cost and some of it is not resulting in total degradation of the pollutants. Therefore, new method for treatment of textile effluents, which is cheaper and more efficient are required. Recently, the development of advanced oxidation processes in wastewater treatment field seems to fulfill these criteria. Heterogeneous photocatalysis which needed only suitable semiconductor and light source appeared as an emerging destructive technology leading to the total mineralisation of most of the pollutants [6–8]. TiO₂ is the most widely investigated semiconductor since it exhibits unique and excellent properties such as high corrosion stability, high photocatalytic efficiency and its photogenerated holes are highly oxidizing [9,10].

TiO₂ can be employed either in suspension mode or immobilized on a substrate [8,11,12]. Although most works have used TiO₂ suspension due to its high photodegradation efficiency, nevertheless the costly and difficult post-treatment process to recover and reuse the semiconductor set a limitation towards application of this system. Therefore, wide varieties of techniques for immobilization of TiO₂ on suitable substrate have been developed such as chemical vapor deposition, sol–gel and electrophoretic coating [13–15].

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Another interesting feature about this technique is the additional electrochemical method could be applied. In this approach, a bias potential is applied across a photoanode on which the catalyst is supported, resulted the photogenerated electron to be driven away to counter electrode. Thus, photodegradation efficiency improved through more effective separation of photogenerated charges by increasing the lifetime of electron–hole pairs, consequently increases the quantum yield of the TiO₂ process [16,17]. This electrochemical approach also increases mass transfer of negatively charged species toward the positive TiO₂ working electrode via electromigration through electrostatic effect. This helps in reducing mass transfer limitation imposed by the reduction of catalyst surface area to volume ratio encountered when using an immobilized catalyst [18].

In spite of several advantages, there are relatively less studies reported on photodegradation of textile dye using immobilized TiO₂ through electrochemical method compared to non-electrochemical system [19–21]. In addition, most of the findings reported used commercially available dyes as model pollutants [22,23]. Therefore, it is equally important to evaluate the feasibility of this method to treat the real textile effluents. In the previous works, we reported the effect of operational parameters and supporting electrolytes in electrochemically assisted photodegradation system on a commercial dye as model pollutant [24,25]. In this paper, we extend our work to study the applicability of electrochemical-assisted photodegradation process for the treatment of mixed dyes and textile effluents using TiO₂/Ti photoanode. Two types of effluents that are raw and effluent undergone pre-treatment at factory wastewater treatment plant were collected. The TOC, Total Inorganic Carbon (TIC), BOD, COD and decolourisation of these pollutants are reported.

2. Experimental

2.1. Materials

All chemicals, tetraisopropyl orthotitanate (>98% Ti, Merck-Schuchardt), ethanol (Analytical reagent grade, R.G HmbG Chemical), diethanolamine (Acros Organics), polyethylene glycol (molecular weight, $M_w=2000$, Fluka Chemika), methyl orange (BDH chemicals Ltd.), methylene blue (BDH chemicals Ltd.), reactive blue 2 (Aldrich), naphthol blue black (Aldrich), direct red 81 (Aldrich) and rhodamine 6G (Aldrich) were used without further purification. All solutions in this experiment were prepared using deionized water (Milipore Alpha Q system, 18.2 MΩ cm).

2.2. Source of effluents

The mixed dye used consists of mixture between methyl orange (MO), naphthol blue black (NBB), reactive blue 2 (RB 2), methylene blue (MB), direct red 81 (DR 81) and rhodamine 6G (Rh 6G). The 300 ml of 1000 ppm mixed dye stock solution was prepared by mixing each 50 ml of 1000 ppm stock solution for six mentioned dyes. The dye solution was stirred continuously for 3 min using magnetic bar. The prepared dye solution

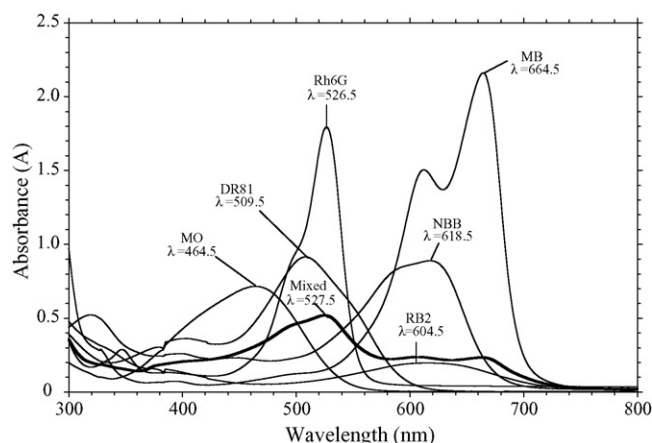


Fig. 1. UV–vis absorption spectra of six types of dyes and mixed dye.

was transferred and sealed in volumetric flask and kept overnight in the dark to attain equilibrium and to avoid preactivation by room light or sunlight. Then, 10 ppm mixed dye was prepared from the stock solution with addition of 0.1 M NaCl as supporting electrolyte. The UV–vis spectra of mixed dye and other six dyes (10 ppm) are shown in Fig. 1.

The textile effluents were collected from a local textile factory. The effluent was stored at 0 °C in volumetric flasks and used without previous filtration. Two types of textile effluents were obtained namely raw and pre-treated. The raw textile effluent refers to the original disposal from the textile furnishing and finishing process while textile effluent with pre-treatment had undergone coagulation–flocculation and biologically treatment at the factory wastewater treatment plant. For both effluents, 0.1 M NaCl was added as supporting electrolyte.

2.3. Preparation of TiO₂ thin films

The TiO₂ sol–gel solution was prepared using the method described previously [24,25]. The titanium plates (5 cm × 2 cm) were used as the conductive support materials for TiO₂. 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 °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 °C for 5 min in oven followed by subsequent dip-coating. An area with size of 1.5 cm × 2.0 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 TiO₂ catalyst loaded was approximately 2 mg. Finally, the plate was annealed at 500 °C in a Thermolyne 21100 furnace for 2 h.

2.4. Analytical measurements

The photoelectrochemical measurements were carried out in the two-compartment cell equipped with a plane quartz window. The anode and cathode were separated by polytetrafluoroethylene (PTFE) 0.45 μm membrane. The working electrode was a TiO₂/Ti plate and the counter electrode was a platinum plate

(1 cm²). All the potentials were specified against 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 the photoelectrochemical degradation process. Meanwhile, a potentiostat EG&G Princeton Applied Research (PAR) VersaStat driven by model 270 Electrochemical Analysis System software with PC control was used for cyclic voltammetry (CV) 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. Tungsten halogen projector lamp (Osram, 300 W and 120 V) was used as the light source. The lamp has a spectral emission ranging from 360 to 830 nm. It was placed 8 cm away from the sample. The photoreactor cell was filled by 120 ml of methyl orange solution and supporting electrolyte. The samples were withdrawn every 30 min for a period of 150 min. The concentration of dye in the solution was determined by measuring the absorbance values using UV/Vis Perkin Elmer Lambda 20 Spectrophotometer. The existences of organic carbon in the samples before and after photoelectrochemical degradation for every 30 min were determined using ANATOC Series II Total Organic Carbon Analyzer. COD was measured using dichromate standard method while BOD was measured after 5 days of incubation at 20 °C [26]. For COD, the interference from chloride could give rise to higher COD values than the real values because chloride might be oxidized by dichromate. Thus, sufficient amount of mercury sulphate was added to eliminate the chloride interference since mercury generates very stable complexes with this anion [27]. Deviation of COD values between the samples in the presence (after treated with mercury sulphate) and absence of sodium chloride was found to be about 5%.

2.5. Control sets of experiment

In order to verify the photoelectrochemical degradation of the samples, three sets of control experiments were carried out. All controls were run for 150 min. First set of control was direct illumination of tungsten halogen lamp in the absence of TiO₂. This is important to test the dye degradability under light exposure. The second set was photocatalyzed degradation of the samples without electrochemically assisted. By this control experiment, the synergy or overlapping effect of electrochemically assisted photodegradation could be examined. The third set of the control was by applying the potential of 1.0 V to the TiO₂ electrode but without illumination to examine whether direct electrochemical oxidation of the samples occurred at that particular potential.

The results obtained show that in those three sets of control conditions, no significant change in dye concentration was observed. The samples seem stable under the irradiation of halogen lamp in both cases of presence and absence of TiO₂ thin film. Although a drop in concentration should be observed in the presence of TiO₂, a very small amount of photocatalyst (~2 mg) on the Ti substrate compare to the volume of the solution (120 ml) limit the detecting sensitivity of photodegradation reaction. The other important feature was no oxygen or air was

supplied throughout the experiment. This could largely affected the photodegradation efficiency as the supply of molecular oxygen to the TiO₂ surface is well known as the rate limiting step, especially in preventing the charge recombination [28,29]. The third set of the control could well explain the reason for applying 1.0 V was to avoid the effect of direct electrochemical oxidation of the samples. From our observation, direct electrochemical oxidation occurred at the potential near to 1.5 V. This was further supported by the cyclic voltammetry result as shown in Fig. 8.

3. Results and discussion

3.1. Decolourisation analysis

Fig. 2 shows the UV–vis absorption spectra of mixed dye recorded for every 30 min obtained from photodegradation using TiO₂ electrode by applying potential of 1.0 V and illuminated with halogen lamp. The spectra show the appearance of several minor peaks beside maximum absorbance at 527.5 nm. This was due to the integration between various dyes structures. Besides that, the decrease in absorbance with time during degradation process was observed. Rapid drop occurred for the first 30 min which decolourised the dye to half of its original value. Further irradiation resulted in slower depreciation of the absorbance values probably due to low possibility of dye molecules to be attacked by oxidizing agents or adsorbed on holes at low concentration.

Fig. 3 shows the UV/vis absorption spectra for industrial textile effluents (raw and pre-treated) recorded at different time intervals. The changes of absorbance could only be recorded until 250 nm for the raw sample due to high concentration of effluent. On the other hand, the pre-treated effluent could reach until 200 nm with clear absorbance peaks. The changes of absorbance value as a function of C/C_0 are shown in the following section (Fig. 4). C/C_0 value for raw sample was based on 280.0 nm while 228.0 nm for sample with pre-treatment. Comparatively, pre-treated sample show more obvious change in the

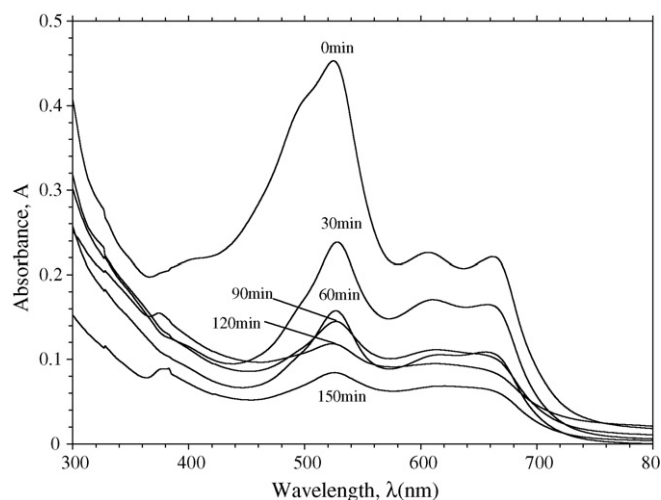


Fig. 2. UV–vis absorption spectra of mixed dye recorded at different time intervals.

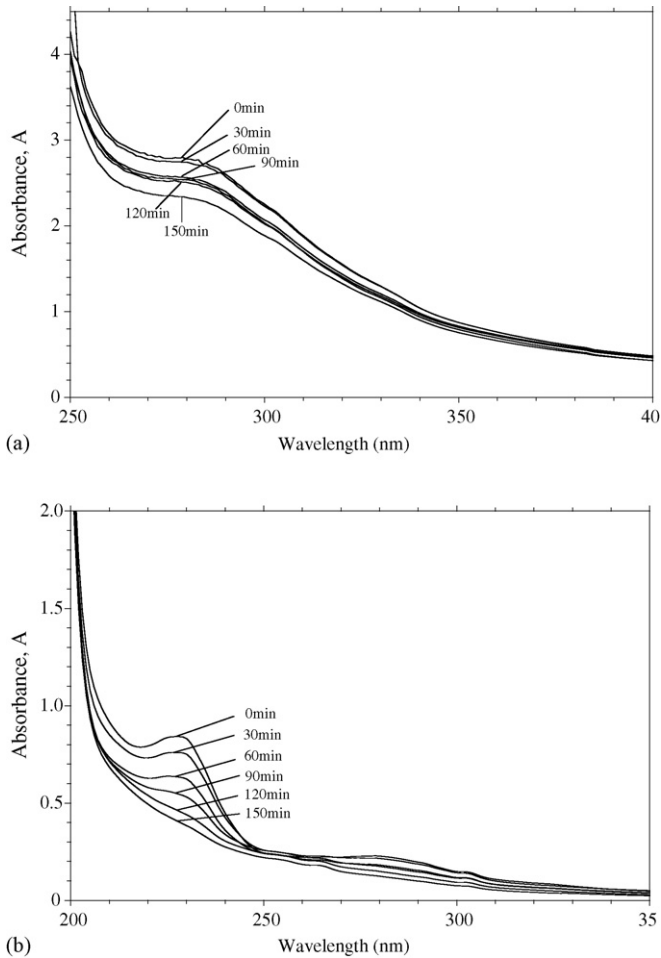


Fig. 3. UV/vis absorption spectra of textile effluents: (a) raw and (b) with pre-treatment recorded at different time intervals.

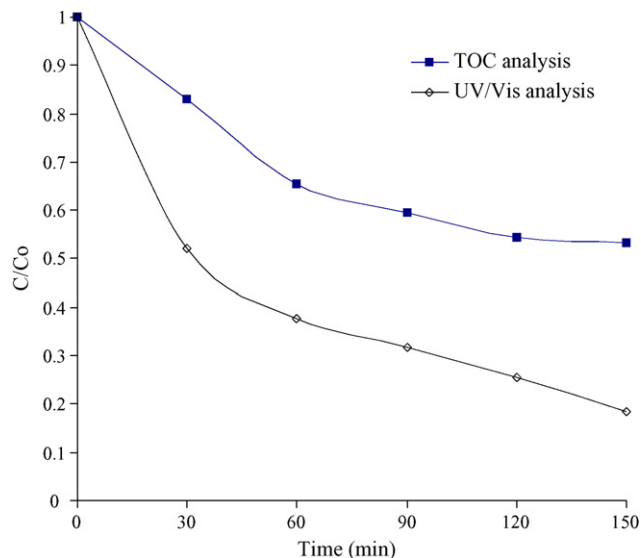


Fig. 4. Depletion in TOC and change in absorbance (UV/vis analysis) as function of irradiation time for mixed dye.

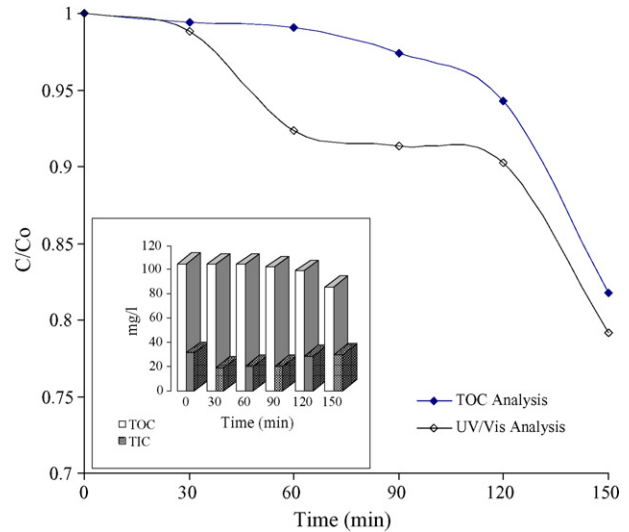


Fig. 5. Depletion in TOC and change in absorbance values (UV/vis analysis) as a function of irradiation time for raw effluent. Inset shows the changes of TOC and TIC contents.

absorbance than the raw sample. Highly concentrated raw effluent show rather slow change due to smaller amount of effluent that had been degraded compared to total concentration in the solution.

3.2. TOC analysis

Kinetic analyses for mixed dye were carried by TOC analysis to investigate the rate of mineralisation, i.e. conversion of organic substances into inorganic species. This is of course the utmost importance in practical environmental applications of the detoxification techniques, as degradation intermediates may even be more toxic than the starting substrates [30]. The kinetic results were obtained by monitoring the changes in substrate concentration by employing UV–vis spectroscopic analysis and decrease in TOC content as a function of irradiation time.

All the concentrations are taken as ratio of the initial concentration (C/C_0). The decrease in initial concentration ratio for both curves should be the same and parallel. However, UV/vis absorbance analysis is based on the solute absorbance. Thus the intermediates existence will reduce the C/C_0 value of the curve relatively causing the differences between TOC and UV/vis analysis curve. Therefore, the different between TOC and UV/vis analysis value depicts the existence of intermediates. The following section will discuss the patterns of both analyses for mixed dye and textile effluents.

Fig. 4 shows the depletion of TOC and dye degradation curves for mixed dye. The amounts of intermediates are almost constant throughout the experiment. Although UV/vis analysis shows the decrease of C/C_0 at 150 min, no significant decreases of C/C_0 in TOC analysis was observed. This probably due to some of the intermediates produced in the photodegradation process was non-degradable.

Fig. 5 shows the depletion in TOC and change in absorbance value as a function of irradiation time for raw effluent. The change in C/C_0 values for both TOC and UV/vis analyses were

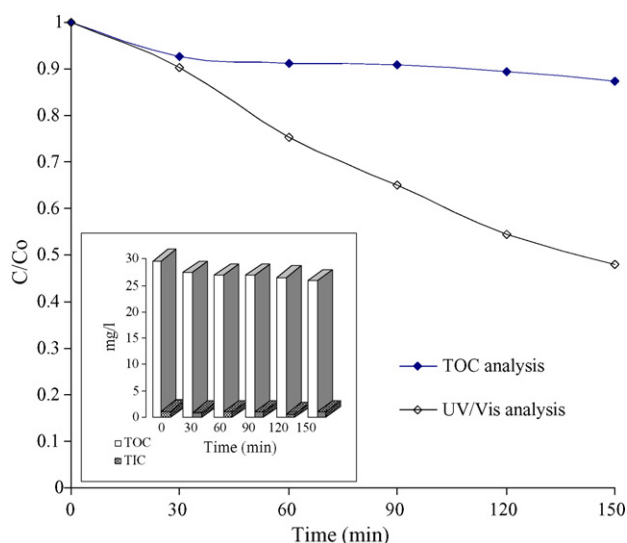


Fig. 6. Depletion in TOC and change in absorbance (UV/vis analysis) as a function of irradiation time for pre-treated effluent. Inset shows the changes of TOC and TIC contents.

rather small. For the first 60 min, constant TOC value was observed, depletion of TOC occurred thereafter. Meanwhile, UV/vis analysis shows degradation process started after 30 min irradiation. Both analyses show almost parallel patterns within that period. A drastic decrease of C/C_0 value was observed after 120 min. Huge amount of reaction intermediates accumulated successfully degraded at that time. This observation significantly marked the possibility of implementation of this method in the treatment of wastewater. As shown in Fig. 6 (inset), the textile effluent contained huge amount of TIC. The decrease of TIC was only observed for the first 30 min. Thereafter, it remained constant and increased at 120 min while TOC value decreased. This may due to some of the organic compounds were mineralised into inorganic carbons such as bicarbonates acid and mineral acids rather than into expected mineralisation products such as CO_2 and H_2O . Decreases of TOC occurred rapidly thereafter with almost constant TIC values.

Fig. 6 shows that TOC and UV/vis analyses as a function of irradiation time for pre-treated textile effluent. The depletion of TOC is slower than the decrease in UV absorbance. Only small depletion was observed for TOC along the experiment. The result indicated that the chemical and biological treatment at the factory treatment plant had mineralised most of the organic carbons. The organic carbons left are probably difficult to mineralise. Prolong experiment is needed to determine whether this

pre-treated textile effluent could be further mineralised. Inset in Fig. 6 shows that the amount of TIC after pre-treatment process is rather small compared to the raw textile effluent. No significant changes in TIC values were observed throughout the experiment.

3.3. Kinetics of the decolourisation and TOC disappearance

The kinetics for the photoelectrochemical degradation process using UV-vis spectrophotometer and TOC analyser were investigated. The Langmuir-Hinshelwood pseudo-first order kinetic model can be expressed by the following equation:

$$\ln\left(\frac{C}{C_0}\right) = -k_{\text{app}}t \quad (1)$$

where C is the concentration of the reactant at t time, C_0 the initial concentration of the reactant and k_{app} is the apparent rate constant.

A plot of $\ln(C/C_0)$ versus irradiation time should give a straight line whose slope represents the apparent pseudo-first order rate constant, k_{app} . Table 1 shows pseudo-first order kinetic apparent rate constant and half time, $t_{1/2}$ for the photoelectrochemical degradation of textile effluents. As seen from correlation factors, R^2 , the result shows that the TOC analysis for raw and pre-treated effluents did not follow the first order kinetic.

Therefore, pseudo-second order model was used to explain the kinetic involved. The pseudo-second order kinetic rate law can be expressed by the following equation:

$$\frac{dQ_t}{dt} = k_{\text{app}}(Q_0 - Q_t)^2 \quad (2)$$

$$\frac{dQ_t}{(Q_0 - Q_t)^2} = k_{\text{app}} dt \quad (3)$$

Integration of Eq. (3) will give

$$\frac{1}{Q_0 - Q_t} = \frac{1}{Q_0} + k_{\text{app}}t, \quad Q_t = \frac{t}{1/k_{\text{app}}Q_0^2 + t/Q_0},$$

$$\frac{t}{Q_t} = \frac{1}{k_{\text{app}}Q_0^2 + t/Q_0}, \quad \frac{t}{Q_t} = \frac{1}{k_{\text{app}}Q_0^2} + \left(\frac{t}{Q_0}\right) \quad (4)$$

where Q_0 is the total amount of degradable solute, Q_t the amount of degradable solute at time, t , and k_{app} is the apparent rate constant.

Table 1

The pseudo-first order kinetic apparent rate constant, half time and correlation factor values for the photoelectrochemical degradation of textile effluents and mixed dye by UV/vis and TOC analyses

Type of textile effluents	Apparent rate constant, k_{app} ($\times 10^{-3} \text{ min}^{-1}$)	Half time, $t_{1/2}$ (min)	Correlation factor, R^2
Mixed dye (UV/vis)	10.3	67.28	0.947
Mixed dye (TOC)	4.3	161.16	0.918
Raw effluent (UV/vis)	1.4	495	0.857
Raw effluent (TOC)	1.1	630	0.674
Pre-treated effluent (UV/vis)	5.1	135.9	0.996
Pre-treated effluent (TOC)	0.7	990	0.821

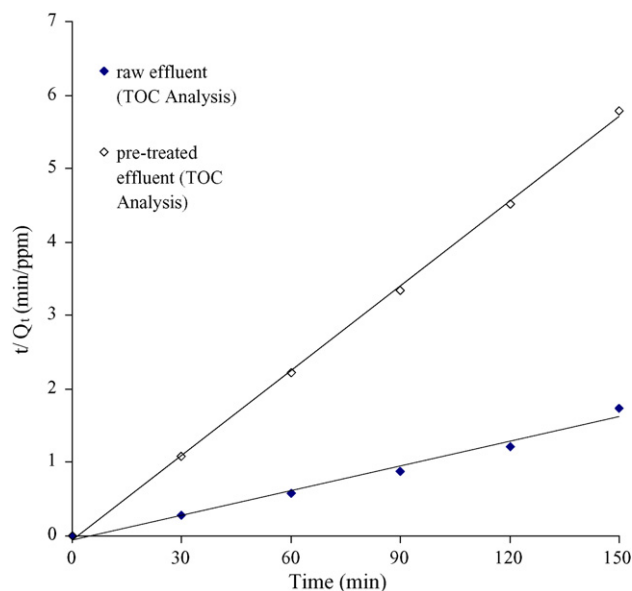


Fig. 7. Graph t/Q_t (min/ppm) vs. time, t (min) for the photoelectrochemical degradation of textile effluents.

Table 2

The pseudo-second order kinetic apparent rate constant and correlation factor values for the photoelectrochemical degradation of textile effluents by TOC analysis

Type of textile effluents	Apparent rate constant, k_{app} ($\times 10^{-3} \text{ min}^{-1}$)	Correlation factor, R^2
Raw	2.1	0.985
Pre-treated	27.1	0.999

By plotting graph t/Q_t , min/ppm versus irradiation time, t /min a straight line should be obtained where the apparent rate constant could be obtained from the intercept, $1/k_{app}Q_0^2$. The pseudo-second order kinetic graph is shown in Fig. 7. The straight-line plot of t/Q_t versus time indicated that the reaction is found to follow pseudo-second order kinetic. Table 2 shows the apparent rate constant and correlation factor for pseudo-second order kinetic.

From the obtained results, the differences between the kinetic order involved in the mixed dye and textile effluents could be observed. Kinetics describes the reaction rates while the order for a reaction defines the dependence of the reaction rates on the concentrations of reacting species. The reaction order is determined experimentally and not necessarily related to the stoichiometry of the reaction. However, it is governed by the mechanism of the reaction, that is, by the number of species that must collide for the reaction to occur [31]. The reaction rate

for pseudo-first order kinetic depends on one species while the second order reaction depends on two species. Thus, the mechanisms involved in the photoelectrochemical degradation of both pollutants are different.

3.4. COD and BOD removal

Table 3 shows that the percentages of COD removal for mixed dye and raw effluent were 73.1% and 28.9%, respectively. COD removal efficiency for raw effluent is lower because of high initial concentration of organic and inorganic substances in the effluent. Beside that, the value of BOD_5/COD is an indicator for the biodegradability of wastewater. The BOD_5/COD ratio for the raw effluent was about 0.49, which indicates that the effluent shows medium biodegradability where still it may not much amenable after biological treatment. Comparatively, COD values are higher than BOD values. The reason is that BOD measures only the quantity of organic material capable of being oxidized, while the COD represents a more complete oxidation includes waste compounds that are difficult to breakdown with bacteria or compounds that are completely non-biodegradable. In this study, BOD_5 removal percentage for raw effluent is found to be 21.48%.

3.5. Electrochemical characteristic of methyl orange and textile effluents

Fig. 8 shows the cyclic voltammogram of mixed dye and textile effluent in dark and under illumination. Voltammogram which obtained in the condition of without illumination could provide reliable information to identify the potential value for direct electrochemical oxidation. It is obvious that direct electrochemical oxidation or electrolysis was negligible at 1.0 V (potential applied in this work), where the dark current value was almost zero. This is supported by our control experimental data which showed that degradation of the samples did not occur when potential of 1.0 V was applied to the TiO_2 electrode in dark.

Both curves show obvious photoresponse at anodic side which representing the typical oxidation behaviour of TiO_2 . Mixed dye shows slightly higher photocurrent response than raw effluent at 1.0 V eventhough, the latter show slightly stronger current at negative potential. The almost equal photosensitivity results obtained in both media indicated that the effect on light penetrations to the electrodes due to the colour of the solutions could be considered negligible. Thus, it could be inferred that the major factor in affecting the photoelectrochemical degradation performance of both samples was the solution's chemical compositions. The existence of several reduction waves at the cathodic side represents the complexity of the raw effluent which

Table 3

Percentages of COD and BOD removal for mixed dye and raw effluent

Type of pollutants	COD initial (mg/l)	COD final (mg/l)	COD removal (%)	BOD_5 initial (mg/l)	BOD_5 final (mg/l)	BOD_5 removal (%)
Mixed dye	65.0	17.5	73.1	Non-detectable	Non-detectable	Non-detectable
Raw effluent	302.5	215.0	28.9	148.95	117.12	21.48

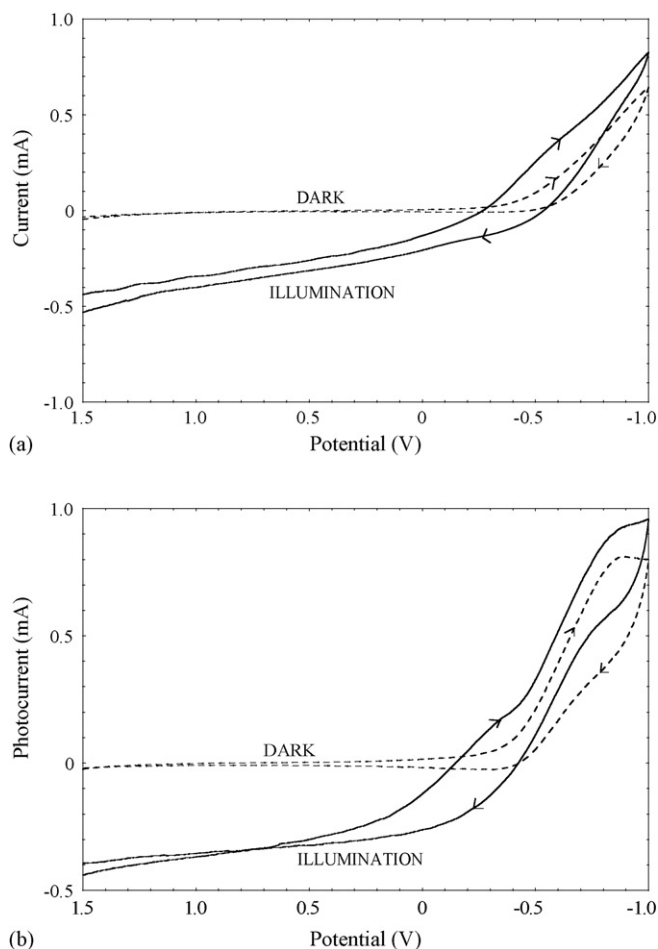


Fig. 8. Cyclic voltammograms for (a) mixed dye and (b) raw effluent with concentrations of 10 ppm and containing 0.1 M NaCl. The electrode was illuminated with a 300 W halogen lamp. The scan rate was 20 mV/s.

contains many active organic and inorganic species. The results obtained from COD and BOD analyses well supported this observation.

4. Conclusions and recommendations

The photoelectrochemical degradation of mixed dye and textile effluents indicate the possibility of implementing this technique in wastewater treatment with the following consideration. Results obtained clearly show that:

1. Real textile effluents seem rather difficult to be treated compared to mixed dye. This is due to textile effluents not only containing dyes but also other organic solvent and inorganic substances, which made the solution rather complicated.
2. Mixed dye behaves differently compared to real effluents in this electrochemical-assisted photodegradation studies. This is mainly due to the kinetic order involved in photodegradation of both pollutants are found to be different when analyses using TOC analyser. Therefore, the mechanism involved in photodegradation of these solutions would be different.
3. Pre-treated effluent shows higher TOC depletion rate compared to raw effluent (about 13 folds). This result suggests

that electrochemical-assisted photodegradation method is more suitable to be applied in final stage of wastewater treatment where effluents have undergone pre-treatment. Thus, photocatalytic process should be used to complement the conventional methods such as coagulation–flocculation and biological treatment to ensure complete mineralisation of the textile wastewater.

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