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Removal of dyes using immobilized titanium dioxide illuminated by fluorescent lamps

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Abstract

The photodegradation of various dyes in aqueous solution was studied. Experiments were carried out using glass coated titanium dioxide thin film as photocatalyst. Photodegradation processes of methylene blue (MB), methyl orange (MO), indigo carmine (IC), chicago sky blue 6B (CSB), and mixed dye (MD, mixture of the four mentioned single dye) were reported. As each photodegradation system is pH dependent, the photodegradation experiment was carried out in each dye photodegradation reactive pH range at $\approx 28\,^\circ$C. The dyes removal efficiency was studied and compared using UV–vis spectrophotometer analysis. The total removal of each dye was: methylene blue (90.3%), methyl orange (98.5%), indigo carmine (92.4%), chicago sky blue 6B (60.3%), and mixed dyes (70.1%), respectively. The characteristic of the photocatalyst was investigated using X-ray diffractometer (XRD). The amount of each dye intermediate produced in the photodegradation process was also determined with the help of total organic carbon (TOC) analysis.

1. Introduction

Large quantities of dyes are extensively used in the fundamental processing steps of textile industries. It is estimated that from 1% to 15% of the dye is lost during dyeing processes and is released in wastewater [1–3]. Hence, the wastewater discharge in rivers or public sewage treatment plants are highly contaminated. The existence of colour substances in dyeing effluents will affect its aesthetic view significantly besides causing potential toxicity. Moreover, environmental pollution by organic dyes also sets a severe ecological problem, which is increased by the fact that most of them are often toxic to microorganisms and have very long degradation time in the environment. Consequently, traditional wastewater treatment methods such as flocculation, adsorption, and biological degradation are increasingly ineffective [1–8]. Thus, a more effective method must be found and used to eliminate such recalcitrant pollutants.
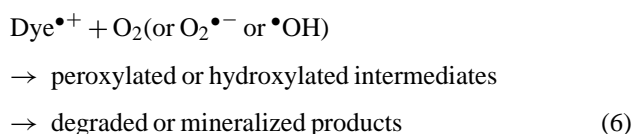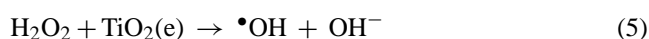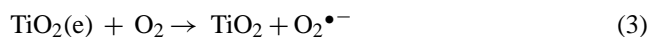
Lots of excellent studies have been published on the photocatalytic degradation of organic dyes in wastewater utilizing titanium dioxide (TiO_2). TiO_2 was chosen because it shows relatively high chemical stability and exhibits high activity for photocatalysis, which scientists are beginning to exploit. When TiO_2, an n-type semiconductor is irradiated with light of wavelength $\lambda \leq 390$ nm, electron (e^-)–hole (h^+) pairs are produced. The generated electron–hole pairs are capable of initiating oxidation and reduction reactions on the surface of TiO_2 particles. In aqueous solution, the holes are scavenged by surface hydroxyl groups to produce the very efficient oxidizing hydroxyl radicals ($^\bullet$OH). Subsequently, the reactive hydroxyl radicals will react rapidly with organic compounds leading to the total mineralization of the organic substrate [1,9–13].

Recently, there are a few groups of researcher examining the mechanism of degradation of several dyes under visible light or solar light irradiation. This process is inspired by the

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principle of photosensitization of wide band gap semiconductors [3,6,14]. A new method for the treatment or pre-treatment of dye-containing wastewater was suggested. When excited with visible light, the excited states of a sensitizing dye are capable of injecting an electron into the conduction band of semiconductor particles to form an oxidized radical. The oxidized form of the dye molecules will then undergo further degradation. Detail mechanism of dye degradation under visible light irradiation is described by Eqs. (1)–(6) [3,14]:

$$Dye + h\nu \rightarrow Dye^* \tag{1}$$

$$Dye^* + TiO_2 \rightarrow Dye^{\bullet+} + TiO_2(e) \tag{2}$$

$$TiO_2(e) + O_2 \rightarrow TiO_2 + O_2^{\bullet-} \tag{3}$$

$$O_2^{\bullet-} + TiO_2(e) + 2H^+ \rightarrow H_2O_2 \tag{4}$$

$$H_2O_2 + TiO_2(e) \rightarrow {}^{\bullet}OH + OH^- \tag{5}$$

$$Dye^{\bullet+} + O_2(or\ O_2^{\bullet-}\ or\ {}^{\bullet}OH)$$

$$\rightarrow peroxylated\ or\ hydroxylated\ intermediates$$

$$\rightarrow degraded\ or\ mineralized\ products \tag{6}$$

However, it is evident that in any wastewater purification process, filtration and resuspension of semiconductor powder should be avoided if possible. Matthews [15,16] and Zhao et al. [17] have reported the use of TiO2 thin film in photocatalytic degradation of organic impurities in water. They had attempted better technological conditions to improve the efficiency of the photocatalytic process as compared to using suspension method. The idea of using immobilized photocatalyst especially in the form of thin film is also beginning to be widely accepted as this would help to save unnecessary cost for catalyst separation and at the same time simplify the purification procedure. On the other hand, the use of immobilized photocatalyst also fulfills one of the important criteria to adsorb the dye on the TiO2 surface for an efficient photosensitization to take place. Photodegradation efficiency will be enhanced as photocatalytic reaction under illumination of visible light only takes place on the TiO2 surface [3]. In line with the research studies done thus far, it will be interesting to investigate the relationship between TiO2 thin film characteristic prepared in our laboratory and its photodegradation ability.

Another restriction which slowed down the photocatalytic system to be widely accepted by the general public is the costly and hazardous UV source. This may be overcome if acceptable photocatalytic system efficiency can be achieved using general light source capable of providing a photon of light which is more energetic than TiO2 band gap [1,18]. A few groups of researchers have achieved promising photodegradation results utilizing alternative light sources, namely San et al. applying black fluorescent light [10,11], Chen et al. [3], Bauer et al. [6] and Chatterjee and Mahata [19] applying visible light and Neppolian et al. [20] utilizing solar light. Thus, the use of fluorescent and visible light helps to

seek a safer and more economical light source besides using sunlight. It is in this regard that, we wish to report herein, the results of our studies of blue fluorescent light assisted photocatalytic decomposition of some commonly use model dye pollutants, such as methylene blue (MB), methyl orange (MO), indigo carmine (IC), chicago sky blue 6B (CSB), and mixed dye (MD, mixture of the four dyes).

2. Experimental details

2.1. Materials

Standard ethanol solution ($M = 46.07$ g/mol, purity $\approx 99.8\%$) was purchased from Fluka Chemical. Nitric acid ($M = 63.01$ g/mol, purity > 65%, 1 L ≈ 1.40 kg) was supplied by Hamburg Chemicals GmbH. Tetraisopropyl orthotitanate solution with more than 98% Ti ($M = 284.25$ g/mol) was obtained from Merck-Schuchardt. Hydrochloric acid and sodium hydroxide solution used for the pH adjustment of the model pollutants were of analytical grade. The model dyes powder used were purchased from two different suppliers. MB (basic blue 9), $M = 319.00$ g/mol, ~85% dye content and MO (4-[4-(dimethylamino)-phenylazo]benzenesulfonic acid, sodium salt), $M = 327.34$ g/mol, ~85% dye content were purchased from BDH Laboratory Supplies in England. IC (5,5′-indigodisulfonic acid, disodium salt), $M = 466.36$ g/mol, ~85% dye content and CSB (direct blue 1), $M = 992.8$ g/mol, ~50% dye content were purchased from Aldrich Chemical Company in USA. The structure of the four dyes molecule is illustrated in Fig. 1. All the reagents were used as received without further purification. The water used in the experiments was deionized using Millipore Alpha Q system.

2.2. Preparation of TiO2/glass photocatalyst

TiO2 sol–gel was synthesized using acid-catalyzed sol–gel formation method. Procedure for the preparation of TiO2 sol–gel was followed as described elsewhere [21]. Ten milliliters of standard ethanol solution, 1 ml of 18 M nitric acid, and 28.1 g (28.1 ml in equivalent) of tetraisopropyl orthotitanate solution were dissolved in 200 ml of deionized water in a 250 ml beaker. The produced slurry was peptized for 8 h. During the peptization process, concentrated light yellowish slurry was formed. The slurry was dried by evaporation at 50 °C for 2–3 h to get the desired sol–gel. The resulted sticky sol–gel was slightly transparent or clear white in colour.

Pieces of 50 mm × 100 mm × 3 mm glass plates were used as support for TiO2 sol–gel. The glass plates were first degreased, cleaned thoroughly and dried before deposition. Then, the glass plates were dipped in the viscous sol–gel with a uniform pulling rate manually. Dipping repetition was done as desired. The readily dipped photocatalysts were dried at 100 °C inside an oven or heat treated at 200–600 °C in Thermolyne Type 21100 furnace for 2 h. A thin film
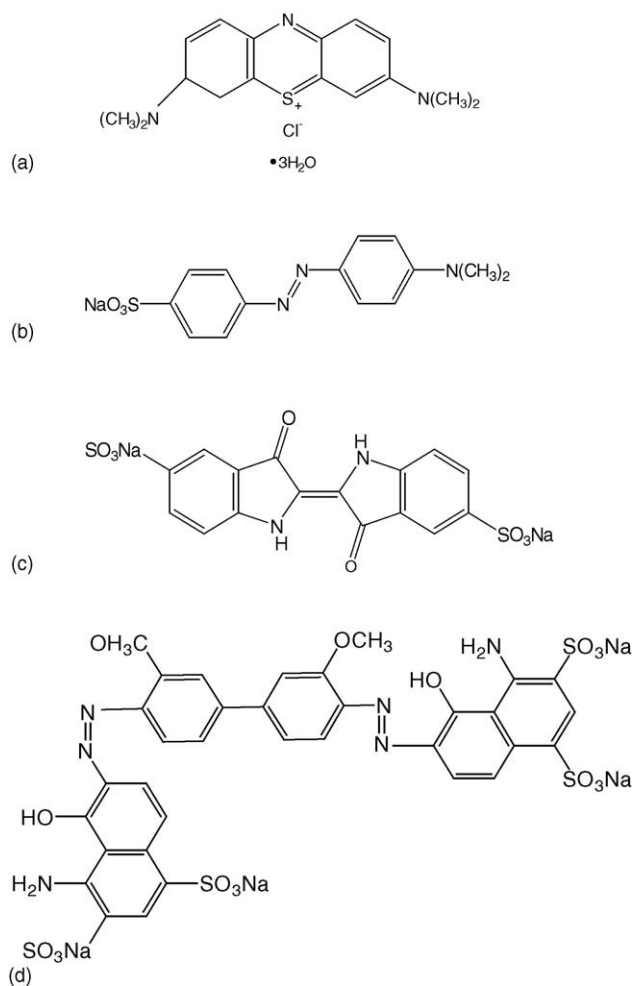
Fig. 1. The structure of (a) MB, (b) MO, (c) IC, and (d) CSB molecule.

of titanium dioxide was formed on the glass plates and they were used for photocatalytic reaction, otherwise the photocatalysts were stored in the dark to avoid pre-activation by room light or sunlight. The phase composition of photocatalyst was studied by the powder and plate XRD technique. The patterns were recorded on a Shimadzu X-ray Diffractometer XRD-6000 using Cu Kα radiation. Diffraction patterns were taken over the 2θ range 5–60°.

2.3. Photodegradation of model pollutants

The experiments were carried out in a custom made photocatalytic oxidation reactor measured by $15\,cm \times 12\,cm \times 15\,cm$. Five pieces of TiO$_2$/glass with five times of sol–gel dip-coating were used as photocatalyst and irradiated with four pieces of 20 W blue fluorescent lamps at a distance of 10 cm from the top of the model solution. Air was bubbled continuously into the solution reservoir using an aquarium pump to ensure constant supply of oxygen and to give agitation effect to the solution to achieve equilibrium state of model solution–TiO$_2$/glass surface. In typical experiment, 1000 ml of each dye solution

with initial concentration of 10 ppm was used as the model pollutant. A constant-temperature water bath was maintained at ≈28 °C. The experimental parameter used was followed from a reported previous work as it had been found out capable to photodegrade methylene blue solution efficiently [21]. The pH of the solution was adjusted to the desired values using dilute hydrochloric acid and sodium hydroxide solutions. Hydrochloric acid [1] and sodium hydroxide solutions were chosen because its effect on the adsorption surface properties of TiO$_2$ is negligible.

Ten milliliters of the samples were taken at regular interval time during irradiation and analyzed by a Perkin Elmer Lambda 20 UV–vis Spectrophotometer to measure the concentration of dye in the model pollutants. The determination wavelength is 661.0 nm for MB, 505.0 nm for MO, 466.4 nm for IC, and 618.0 for CSB, which is the maximum absorption wavelength. Lost of total organic carbon in the samples, before and after photodegradation process were determined using TOC 5000 A with ASI-5000 A auto sampler machine. For comparison purpose, the same experimental procedure was applied for all of the used model pollutants.

3. Results and discussion

3.1. XRD characterization of TiO$_2$ photocatalyst

The principal goal of carrying out XRD analysis was to identify the TiO$_2$ polymorphs and their crystalline phases. Fig. 2 shows the X-ray diffraction patterns of TiO$_2$/glass when heat treated at different temperature. The 2θ angle of the reflection corresponding to the basal spacing of the TiO$_2$/glass were 25.28°, 37.80°, 48.05°, and 55.06° for peaks 1, 2, 3, and 4, respectively. These corresponded to the d (Å) values for all of the peaks exist in TiO$_2$/glass from 100 to 600 °C with the standard JCPDS values 3.52, 2.38, 1.89, and 1.70 nm for peaks 1, 2, 3, and 4, respectively, showing existence of anatase phase TiO$_2$. The intensity of TiO$_2$ peak increases when the sample was heated at higher temperature. This shows that heating has a significant effect on the TiO$_2$/glass crystallinity. Higher intensity of TiO$_2$ peak indicates that the availability of TiO$_2$ compound increases as well, especially in the conversion of amorphous TiO$_2$ thin film into the active anatase TiO$_2$. Our result is in good agreement with the one reported by Harizanov and Harizanova [22]. They had observed that exothermic peaks of TiO$_2$ gel, localized between 250 and 550 °C show the process of oxidation of the organic residuals and crystallization of TiO$_2$–anatase structure. Similarly, Mazzarino et al. [23] and Facchin et al. [24] also found the conversion of amorphous titania thin film into the active crystallite structure of the catalyst (anatase) by a thermal treatment at 500 °C. Following that, removal efficiency of the organic waste should increase as well due to better crystallinity of the synthesized photocatalyst.

The average crystallite sizes of TiO$_2$ were calculated by Scherrer's equation using the full width at half maximum
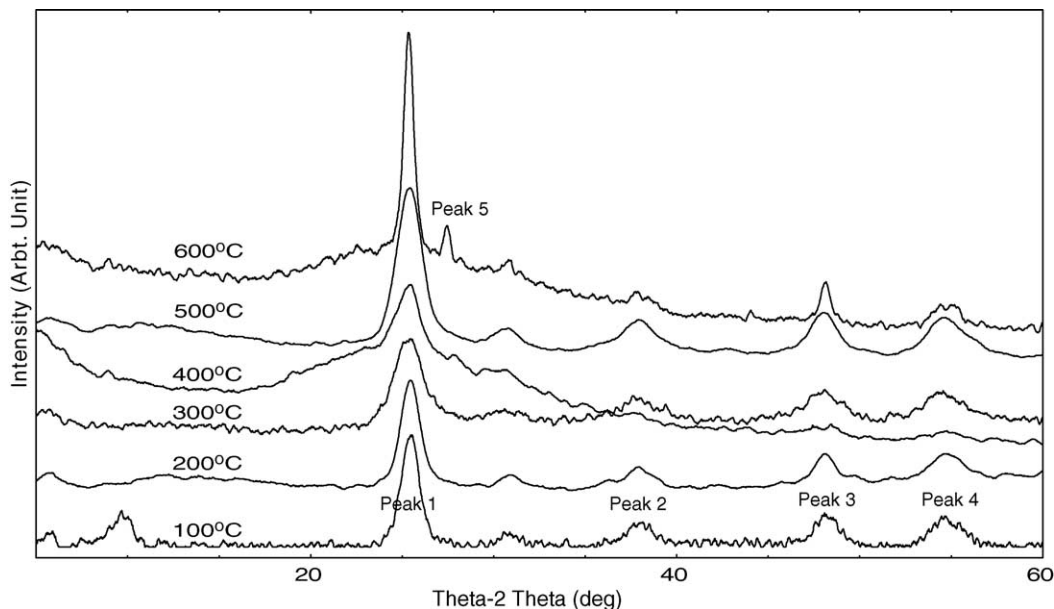
Fig. 2. XRD patterns for TiO$_2$/glass with five times of sol–gel dip-coating and heat treated at different temperature.

(FWHM) of the X-ray diffraction peaks at $2\theta = 25.3°$ for anatase. Typical values of anatase crystallite size have been calculated to be in the range of 4–11 nm for the synthesized TiO$_2$ particles on glass. Fig. 3 shows the change of the TiO$_2$ crystallite size with different thermal treatment temperature from 100 to 600 °C. The anatase crystallite size of TiO$_2$ increased with increasing heating temperature. It indicates that heat treatment enhanced the growth of anatase crystal of TiO$_2$.

Whereas, the TiO$_2$/glass heat treated at 600 °C shows another new peak (peak 5) at d (Å) value 3.25 nm corresponding to the existence of rutile phase TiO$_2$. The co-existence of both anatase and rutile phase in the sample heated at 600 °C was expected to be a characteristic trend of TiO$_2$ thin film. Tryba et al. [25] had also observed the same characteristic of TiO$_2$ thin films heat treated at 800 °C and above using activated carbon as support. The higher the calcination
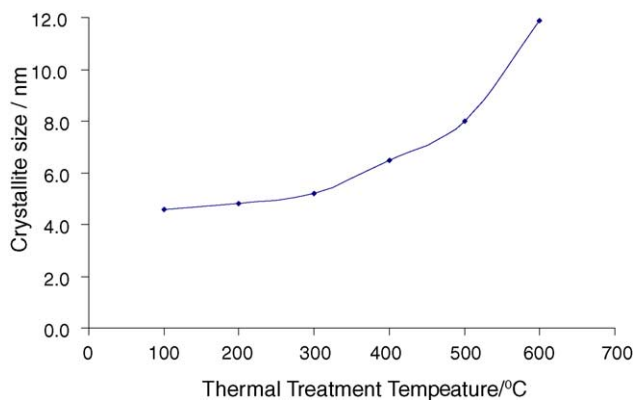
temperature, the amount of rutile formed was larger. Tryba et al. only observed such characteristic at a higher temperature (800 °C) as compared to our samples (600 °C), the reason may be the different support used for the TiO$_2$ thin film. However, co-existence of both anatase and rutile phase in the photocatalyst may be detrimental to the photoactivity as rutile is connected with its fast recombination rate of generated electrons and holes [25]. The study on heat treatment was limited as the prepared TiO$_2$/glass cannot be heat treated at temperature above 600 °C because it started to deform at higher temperature.

Fig. 4 shows XRD spectrum to compare TiO$_2$ existence in clean glass, dried TiO$_2$ powder, and TiO$_2$/glass with five times of dip-coating and dried at 100 °C. Dried TiO$_2$ powder sample shows very clear and intense peaks. All of its peaks from 1 to 7 corresponding to d (Å) values of 3.52, 2.43, 2.38, 2.33, 1.89, 1.70, and 1.67 nm, respectively indicate the existence of anatase form TiO$_2$. Comparatively, the XRD pattern for TiO$_2$/glass with five times of sol–gel dip-coating and heat treated at 100 °C is also quite significant. TiO$_2$/glass spectrum shows four humps at d (Å) = 3.52, 2.38, 1.89, and 1.70 nm attributable to the presence of anatase TiO$_2$. The peaks shown are relatively broad and low in intensity due to the co-existence of dried TiO$_2$ powder sample. The peaks for sample heat treated at 100 °C are the same in both Figs. 2 and 4. The intense peaks of dried TiO$_2$ powder sample had "over-shadowed" it, making it relatively broad and low in intensity. It may suggest that the content of TiO$_2$ in the prepared photocatalyst was not so significant analytically. The intensity of TiO$_2$ peaks should increase with increasing number of times of sol–gel dip-coating as more photocatalyst were loaded on the glass or with the increase in heating temperature as discussed earlier.
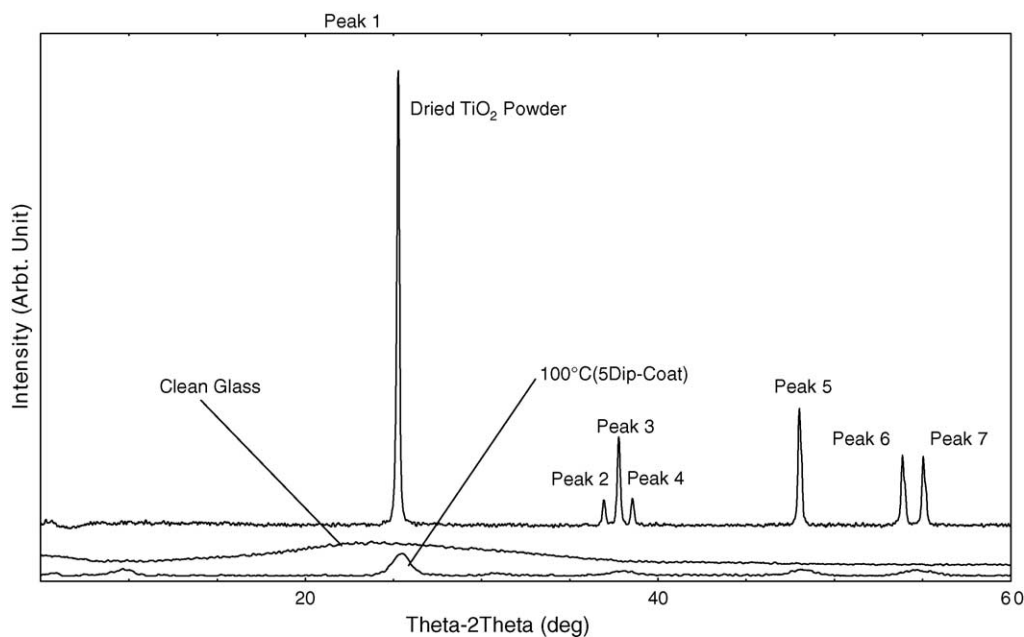

Fig. 3. Crystallite size of the anatase phase of TiO$_2$/glass particles with five times of sol–gel dip-coating as a function of different thermal treatment temperature.

Fig. 4. XRD spectrum for the comparison of clean glass, dried TiO$_2$ powder, and TiO$_2$/glass with five times of sol–gel dip-coating (dried at 100 °C).

Contrarily, clean glass did not show any intense peak. It only shows a big hump around d (Å) value of 3.50 nm indicating its amorphous nature and non-existence of TiO$_2$ as expected. By considering the facts that TiO$_2$ loading will increase with increasing times of dip-coating, the analyzed results may suggest that the number of dip-coating should have a significant effect on organic waste removal efficiency up to a certain extent. Nevertheless, other factors such as the effect of heat treatment and catalyst overlapping causing blockage of irradiating light source should also taken into consideration. By considering all the consequences, such as simplicity, efficiency and cost effectiveness, we had chosen TiO$_2$/glass with five times of sol–gel dip-coating and dried at 100 °C to be used as the photocatalyst in the photodegradation of the prepared model pollutant.

3.2. Photodegradation of various types of dye

A preliminary test was done to obtain a few sets of standard control data for each dye used in the photodegradation experiments. The preliminary test was carried out in the dark

using the prepared photocatalyst. The results reported in Table 1 confirmed that the removal of dyes was insignificant for the mentioned condition. It must be stressed that total removal of the model pollutants were not contributed by the effect of photodegradation alone. A small portion of the removal efficiency was attributable to the rapid attainment of adsorption equilibrium of the dyes onto TiO$_2$/glass with MO being the most significant (38.9%). However, when the photodegradation experiments were carried out under illumination of light, total removal of pollutant was enhanced significantly. Total removal of pollutant can be attributed to more than 50% of photodegradation capability in addition to the above-mentioned surface adsorption effect.

Optimum set of parameter was used for each of the experiment to investigate the effectiveness of photodegradation process using glass loaded TiO$_2$ on various types of organic dye. The investigation involves the comparison of removal efficiency among solution of MB (basic or cationic dye), MO (acid dye of the monoazo series), IC (acid dye of the indigoid series), CSB (direct dye of the diazo series), and MD thereof [26,27]. Photodegradation of mixed dye solution

Table 1
Preliminary test and experiments carried out applying optimum parameters

	Initial concentration (ppm)	Adsorption removal[a] (ppm/%)	Photodegradation removal[b] (ppm/%)	Total removal[c] (ppm/%)
Methylene blue	11.308	0.399/3.5	9.819/86.8	10.218/90.3
Methyl orange	10.350	4.027/38.9	6.165/59.6	10.192/98.5
Indigo carmine	10.423	2.796/26.8	6.842/65.6	9.638/92.4
Chicago sky blue 6B	9.883	2.601/26.3	3.368/34.0	5.969/60.3
Mixed dyes	10.058	1.553/15.5	5.493/54.6	7.046/70.1

Five pieces of TiO$_2$/glass, four pieces of blue fluorescent lamp, 1000 ml of each dye solution with initial concentration of 10 ppm and temperature (≈28 °C).

[a] Total removal in the dark using photocatalyst.

[b] Total removal − adsorption removal = photodegradation removal.

[c] Total removal under light illumination using photocatalyst applying optimum parameters.
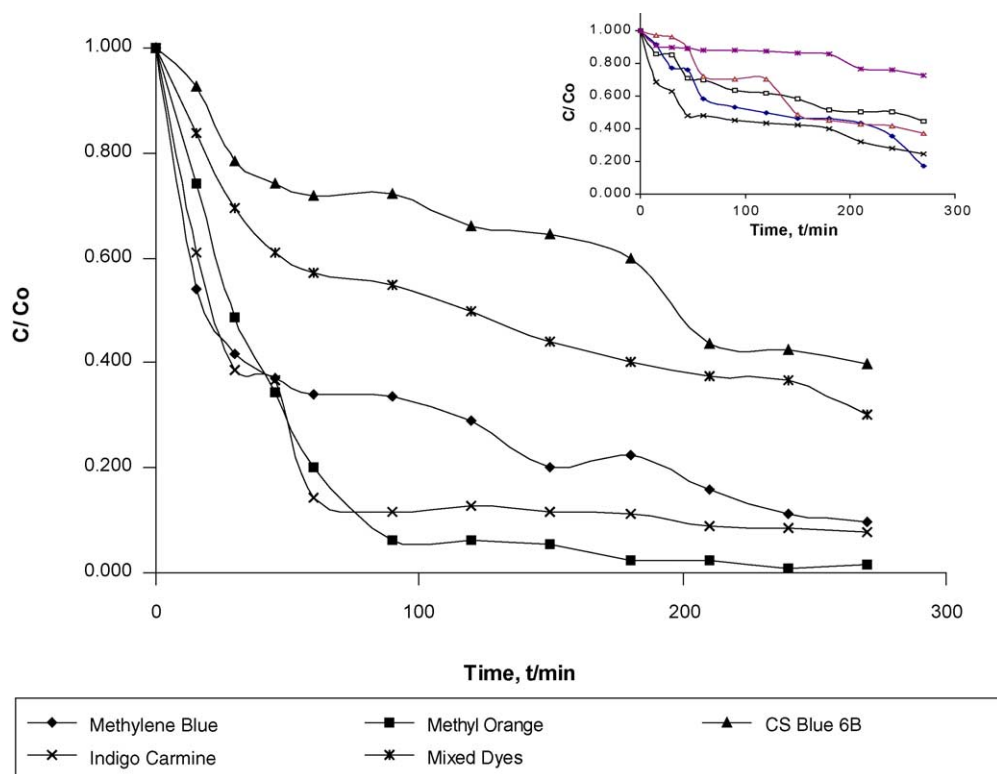
Fig. 5. Graph C/C_0 vs. time, t (min) for the removal efficiency of different type of dyes. Five pieces of TiO_2/glass, four pieces of blue fluorescent lamp, 1000 ml of each dye solution with initial concentration of 10 ppm and temperature (28 °C). Inset shows the temporal changes of TOC expressed as C/C_0 vs. time, t (min) from the same experiments.

involves the photodegradation of four dyes which were prepared in one mixed solution consist of MB, MO, IC, and CSB with the same concentration (10 ppm) each. This experiment was carried out to determine the effectiveness of photodegradation process on the four single dyes when they were mixed together into one aqueous solution imitating the actual complex nature of industrial wastewater pollutant.

Removal efficiency of different type of dye is reported in Fig. 5. It shows that the concentration of each type of dye decreased effectively with time. Temporal changes of TOC obtained from the same experiments also indicates the decrease in TOC is consistent with the observe results from the UV–vis absorbance. Evidence of TOC decrease confirms that each of the model dye pollutant can be photocatalytically degraded using TiO_2/glass under blue fluorescent light illumination. However, the decrease of the TOC content is significantly slower than the dyes conversion. This implies that a significant amount of intermediates are produced before the total mineralization of the dyes substrates.

Table 2 shows the percentage of total dyes removed and the intermediates content after 270 min of photodegradation. The results show that photodegradation process using titanium dioxide supported on glass is most effective in removing MO (98.5%). As higher removal efficiency will have a higher apparent rate constant, k_{app} value, shorter time was needed for the dye to be totally photodegraded as confirmed by the half time, $t_{1/2}$ value in Table 3. It is shown that the half time

needed to photodegrade MO is just 41.5 min. Although MO removal is very impressive, most of MO molecules were only degraded into intermediate compounds (42.9% as shown in Table 2) instantaneously rather than the expected non-toxic and safer H_2O, CO, CO_2, and mineral acids. It is possible also that complete mineralization of MO solute may not be

Table 2
Percentage for total removal of various dyes and the intermediates content after 270 min of photodegradation

Dyes	Cs_0 (ppm)	Cs_{270} (ppm)	% Removal	[Intermediates]$_{270}$ (%)
Methylene blue	9.6	0.9	90.3	7.5
Methyl orange	8.8	0.1	98.5	42.9
Indigo carmine	8.9	0.7	92.4	17.0
Chicago sky blue 6B	4.9	2.0	60.3	≈0.0
Mixed dyes	8.6	2.6	70.1	42.8

Table 3
The apparent rate constant, k_{app} and half time, $t_{1/2}$ for the of photodegradation various dyes

Dyes	Apparent rate constant, k_{app} ($\times 10^{-3}$ min^{-1})	Half time, $t_{1/2}$ (min)
Methylene blue	6.9	100.4
Methyl orange	16.7	41.5
Indigo carmine	8.1	85.6
Chicago sky blue 6B	3.1	223.5
Mixed dyes	3.7	187.4

achieved because the intermediates produced during the photodegradation process are quite stable. The results shown here were in agreement with the research findings of Baìocchì et al. [28]. Thus, more analysis should be done to confirm this phenomenon.

On the contrary, CSB is the most difficult to photodegrade with its removal efficiency of only 60.3%. As for IC (92.4%) and MB (90.3%), their removal is as effective as for MO with their half time value in the range of ≈ 100 min. It is suggested that photodegradation efficiency of each dye may be affected by their molecular size. A bigger molecular size of the dye may require prolong experimental time for it to be photodegraded completely. Since the molecular size of CSB is much bigger than the other three as shown in Fig. 1 ($M_{MB} = 319.00$ g/mol, $M_{MO} = 327.34$ g/mol, $M_{IC} = 466.36$ g/mol, $M_{CSB} = 992.80$ g/mol), lower removal efficiency of its dye content seems to be acceptable. Furthermore, total intermediates detected after 60 min of CSB photodegradation is almost nil, it may have been totally mineralized into the end products. It is also possible that CSB was directly mineralized into the end products without producing any intermediate. However, this suggestion will only indicate that total mineralization of CSB into the end products at a relatively slow rate, considering that both UV–vis spectrophotometer and TOC analysis produced an almost similar result ($\approx 60.3\%$ of removal efficiency). Photodegradation of CSB maybe rather slow comparatively, but direct mineralization of the intermediates produced in less than 60 min may prove to be a much more successful photodegradation process.

Photodegradation process of MD is the most difficult to predict among all of the model dyes pollutant, taking into consideration that it involves four types of dye with each dye having their own characteristics. The intermediates produced in the photodegradation process of MD solution increased with time almost through out the whole 270 min of experiment time. It shows that when the solute concentration decreased, the intermediates produced increased concurrently. This may due to the effect of the solution concentration, in which photodegradation efficiency is higher when the experiment was carried out with lower initial concentration.

As MD was the mixture of the other four single dyes with the same concentration, its initial concentration was four times higher than the others. The initial concentration dependence of the photodegradation rate of MD can be based on the fact that the degradation occurs on TiO_2 particles as well as in solution [11]. On the surface of TiO_2 particles, the reaction occurs between the $^\bullet OH$ radicals, generated at the active OH^- sites and a MD molecule from the solution. When the initial concentration is high, the number of these available active sites is decreased by MD molecules, because of their competitive adsorption on TiO_2 particles. In this case, rate of transfer of MD from the solution does not affect the degradation rate. However, the other model dyes pollutant have a lower initial concentration comparatively,

thus transfer rate plays an important role. Similar effect had also been discussed widely by many prominent researchers elsewhere [10,29]. They reported that photodegradation experiments run with lower initial concentration will give a higher removal percentage. Corresponding to initial concentration of MD, it is therefore the intermediates produced at the early stage of the experiment were also less. As MD concentration decreases with prolong experiment time, the photodegradation efficiency increased, thus producing more intermediates. This may also be the reason as why the intermediates produced in the photodegradation process was quite high and remained almost constant after 150 min. Another important point for this behaviour is that as the initial concentration of MD is higher compared to the other dyes, the path length of photon entering the solution will be less, and in low concentration the reverse effect is observed [20]. Thus, this proves that the rate of degradation will adversely affected with increase in the concentration of dye.

4. Conclusion

It is evident that the photocatalytic degradation of various organic dyes and mixed dye illuminated by blue fluorescent lamps give a promising result in the presence of titanium dioxide coated on glass plates. The research work done shows that other than a small portion of model pollutant removal attributed to adsorption process, photodegradation process using titanium dioxide supported on glass is most effective in removing methyl orange (98.5%). On the contrary, chicago sky blue 6B is the most stable against photodegradation process with total removal of only 60.3%. Relatively, the removal efficiency of indigo carmine (92.4%) and methylene blue (90.3%) is as effective as for methyl orange.

However, none of the organic solutes were instantaneously oxidized to the desired safer end products. It was shown by the presented results of TOC together with UV–vis spectrophotometer analysis that many intermediates may be produced during the course of photodegradation process. Some of the produced intermediates may be easily further oxidized to the non-toxic final products, while some of them may be quite stable and required prolong reaction time. The presented results in this study are in agreement with the reported results of Turchi and Ollis [30]. Photodegradation process will most probably degrade and oxidize various dyes and mixed dye to non-toxic and safer end products such as H_2O, CO, CO_2, and mineral acids proceeding via a number of intermediate compounds.

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