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# Decolorization and Mineralization of *Batik* Wastewater through Solar Photocatalytic Process

(Penyahwarnaan dan Penguraian Sisa Air Batik melalui Proses Fotopemangkinan Cahaya Matahari)

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ABSTRACT

*In this study, the photocatalytic degradation of* batik *wastewater in the presence of zinc oxide (ZnO) as photocatalyst was investigated. The effect of various operating parameters, such as pH of* batik *wastewater, catalyst dosage and aeration on the photocatalytic degradation process, was examined. The mineralization of* batik *wastewater was also evaluated through chemical oxygen demand analysis. The decolorization of* batik *wastewater was enhanced at acidic conditions (pH3) which was 88.2% after 10 h irradiated under solar light, meanwhile its mineralization was 286 mg/L after 12 h irradiation time. The data obtained for photocatalytic degradation of* batik *wastewater was well fitted with the Langmuir-Hinshelwood kinetic model. It can be concluded that* batik *wastewater could be decolorized and mineralized under solar light irradiation with presence of ZnO.*

*Keywords:* Batik *wastewater; decolorization; mineralization; photocatalytic; zinc oxide*

ABSTRAK

*Di dalam kertas ini, degradasi sisa air batik oleh fotopemangkinan dengan kehadiran zink oksida sebagai fotopemangkin telah dikaji. Kesan daripada pelbagai parameter operasi, contohnya, pH sisa air batik, dos fotopemangkin dan pengudaraan ke atas proses fotopemangkinan telah dikaji. Penguraian sisa air batik juga dinilai melalui analisis permintaan oksigen kimia. Penyahwarnaan sisa air batik meningkat dalam keadaan berasid (pH3) iaitu 88.2% selepas 10 jam diradiasi di bawah cahaya matahari, sementara itu, penguraiannya ialah 286 mg/L selepas 12 jam masa penyinaran. Data yang diperoleh untuk degradasi fotopemangkinan sisa air batik adalah mengikut model kinetik Langmuir-Hinshelwood. Dapat disimpulkan bahawa sisa air batik boleh dinyahwarnakan dan diuraikan di bawah penyinaran cahaya matahari dengan kehadiran zink oksida.*

*Kata kunci: Fotopemangkinan; penguraian; penyahwarnaan; sisa air batik; zink oksida*

## INTRODUCTION

The textile industry such as *batik* industry consumes large amounts of discharged effluents during dyeing and finishing operations. *Batik* industries used many other chemical substances such as sodium silicate, sodium salt and sodium alginate. The discharged wastewater from textile industry is one of the most polluting among all industrial sectors such as pharmaceuticals, pulp and paper mill and paints (Gümüş & Akbal 2011). Besides, the wastewater from textile industry also contains other chemical substances which are not biodegradable and difficult to be removed by conventional treatment methods (Arslan & Balcioglou 1999; Sun & Yang 2003; Tsang et al. 2007). An acute exposure to the untreated wastewater containing dyes may cause severe problems such as jaundice, vomiting and increasing the heart rate (Hameed & Ahmad 2009; Kitture et al. 2011).

Solar photocatalytic is one of the treatment methods under advanced oxidation processes (AOPs) which is low cost, environmental friendly and effective in treating wastewater. When solar light irradiation is equal or greater than the band gap energy of photocatalyst, an electron in the valence band will be excited out to the conduction band and leaves a hole in the valence band. The electron will combine with oxygen molecule to produce superoxide radical anions ($\bullet O_2^-$), meanwhile the hole in the valence band may react with water ($H_2O$) or hydroxyl ions ($OH^-$) to generate the hydroxyl radicals (•OH). The •OH and $\bullet O_2^-$ are the primary oxidizing species in the photocatalytic processes.

Photocatalyst also plays crucial part in photocatalytic process. Most of previous researchers (Badawy et al. 2009; Tang & Chen 2004) use $TiO_2$ as their photocatalyst, however, $TiO_2$ only show better performance under UV light irradiation. Other than that, $TiO_2$ also is uneconomical for large scale water treatment operations (Shinde et al. 2011). Due to that reason, ZnO is found to be a suitable alternative to $TiO_2$ since it has higher catalytic efficiency compared to $TiO_2$ (Chakrabarti & Dutta 2004; Daneshvar et al. 2004; Lin et al. 2011; Lizama et al. 2002). Moreover, ZnO also absorbs over a larger fraction of UV spectrum (Behnajady et al. 2006). Since Malaysia is one of the countries that

has ample amount of solar light, it is suitable to use ZnO as a photocatalyst.

The objective of this study was to investigate the influence of various operating parameters on the decolorization and mineralization of *batik* wastewater under solar light irradiation with ZnO as a photocatalyst.

## Materials and Methods

*Batik* wastewater was collected in early January 2014 from *batik* workshop in Beseri, Perlis, Malaysia, at discharged point. The collected wastewater was preserved in the refrigerator. The characteristics of wastewater such as biochemical oxygen demand (BOD), chemical oxygen demand (COD), pH, temperature, total suspended solid (TSS) and turbidity were analysed and the sample was then diluted by 1:1 using ultrapure water for further photocatalytic process. The photocatalyst used in this study was zinc oxide (ZnO) which supplied by HmBG and its molecular weight was 81.37 g/mol. Acid sulfuric ($H_2SO_4$) and sodium hydroxide (NaOH) was used for pH adjustment.

The photocatalytic degradation of *batik* wastewater was conducted in a batch study under solar light irradiation and various operating parameters were examined. A beaker contains 250 mL of sample and diluted with 250 mL of ultrapure water was prepared for each experiment and placed on a magnetic stirrer. 0.1 g of ZnO was added into the solution and the reaction started. To evaluate the effect of pH of *batik* wastewater, its pH was varied to pH3, 7 and 10. The dosage of ZnO also was differed to 0.05, 0.10 and 0.25 g for evaluating the effect of catalyst dosage on the degradation of *batik* wastewater. To evaluate the effect of aeration on the photocatalytic degradation of *batik* wastewater, air diffuser (Regent 9500) was used to supply aeration into the sample with 0.1 g of ZnO as a photocatalyst as shown in Figure 1. Experiments were conducted for 10 h and 15 mL of water samples were withdrawn with a syringe every 1 h of time interval (0, 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10 h). Then, it was filtered with 125 mm diameter of filter paper to remove the ZnO particles and the clear water was then analysed by UV-Vis spectrum. The DR2800 was used to analyse the concentration of BOD, COD and TSS of *batik* wastewater before and after the photocatalytic process.

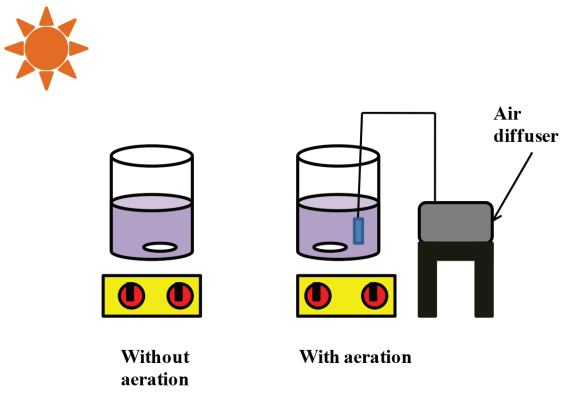


FIGURE 1. Experimental set up for study the effect of aeration on decolorization of *batik* wastewater

## Results and Discussion

The *batik* wastewater sample was characterized in terms of the biochemical oxygen demand ($BOD_5$), chemical oxygen demand (COD), pH, temperature, total suspended solid (TSS) and turbidity. The characteristics of *batik* effluent were shown in Table 1. The *batik* wastewater contained high value in all parameters especially COD concentration. This is in agreement with Şahinkaya (2013) who reported that most of the textile wastewater has high salinity, high COD and pH as well as strong color. Because of that, concentration of COD and color of *batik* or any textile wastewater need to be reduced before being discharged into water bodies.

TABLE 1. Characteristics of the *batik* effluent

| Parameters | Value |
|---|---|
| $BOD_5$ (mg/L) | 341.25 |
| COD (mg/L) | 4092 |
| pH | 10.77 |
| Temperature (°C) | 25.3 |
| Turbidity (NTU) | 217 |
| TSS (mg/L) | 303.03 |

The UV-Vis absorption spectra of raw *batik* wastewater showed absorption peaks at 232 nm and 516 nm as in Figure 2. The peak appeared in visible region (516 nm) indicated the existence of chromophore that is responsible in giving color to the *batik* wastewater meanwhile peak in UV region (232 nm) showed the aromatic ring that attached to the molecular structure of the *batik* wastewater.

*Batik* wastewater has a high pH value. *Batik* wastewater sample which collected had a pH of 10.77. pH played a crucial role in photocatalytic processes due to its influence towards the production of •OH. In order to study the influence of pH towards *batik* wastewater, pH was adjusted to pH3, 7 and 10 (unadjusted). The removal efficiency of *batik* wastewater at pH3, 7 and 10 was 88.2, 86.9 and 67.6%, respectively, after 10 h irradiation time as shown in Figure 3(a). The degradation rate of *batik* wastewater increased in acidic phase due to relation of acid base property of the metal oxide surface which can be explained by the basis of zero point charge (Kansal et al. 2007). The zero point charge (zpc) of ZnO was 9.00.3. The surface of ZnO was positively charged below pH9 and negatively charged above that pH. Therefore, acidic conditions such as in this case at pH3 would favor the electrostatic attraction between positively charged ZnO surface and the dye, which then increased the decolorization of *batik* wastewater (Gümüş & Akbal 2011).

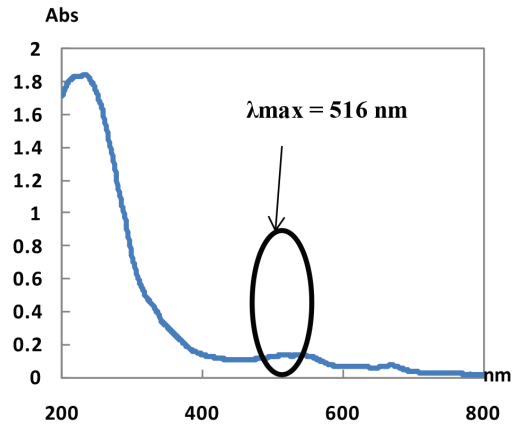


FIGURE 2. UV-Vis spectrum analysis of raw *batik* wastewater

Most of authors have used the modified Langmuir-Hinshelwood kinetic expression to analyse the heterogeneous photocatalytic reaction (Velmurugan & Swaminathan 2011; Vineetha et al. 2013; Zhu et al. 2009). Figure 3(b) depicts plots of ln $C_o/C$ against solar light irradiation time at three pHs of *batik* wastewater. The decolorization of *batik* wastewater at different pH followed Langmuir-Hinshelwood kinetic model. The rate constant decreased as the pH of *batik* wastewater increased. The pseudo-first-order rate constant of pH3, 7 and 10 was 0.304, 0.239 and 0.118 $h^{-1}$, respectively. At low pH or in acidic phase, these positive holes can react with $OH^-$ or $H_2O$ and oxidized them to form •OH, thus increased the photocatalytic process. On the other hand, in alkaline phase, there was a Coulombic repulsion between the $OH^-$ and negative charged surface of ZnO which could prevent the formation of •OH and then resulted in decreased of decolorization rate of *batik* wastewater (Habibi & Askari 2011).

Catalyst dosage is another important parameter in the photocatalytic treatment of dye. Three different amount of ZnO (0.05, 0.1, 0.25 g) was added into the *batik* wastewater for the treatment. As shown in Figure 4, the maximum removal efficiency was 91.9% at ZnO dosage of 0.25 g after 10 h irradiation time. Meanwhile, the removal efficiency for ZnO dosage of 0.1 and 0.05 g was 88.2 and 75.3%, respectively, at the same irradiation time. There was a significant positive correlation between catalyst dose and color removal efficiency. The result showed that increasing amount of ZnO dosage will increase removal efficiency of wastewater. The differences of removal efficiency between ZnO dosage of 0.1 and 0.25 g was only 3.7% and because of this reason, for other parameters in this research, 0.1 g of ZnO dosage was used as an optimum catalyst dosage. It was well known that excess dosage of photocatalyst would reflect back the solar light irradiation by catalyst particles (Krishnakumar & Swaminathan 2011). At lower catalyst dosage, the total surface area of active site which was available for interaction between dye and catalyst would be limited, hence decreased the efficiency of color to be removed (Akyol & Bayramoğlu 2005). On the contrary, increasing the catalyst dosage will increase the available surface of the catalyst and which in turn increase the reactive sites for generation of active radicals such as $•O_2$ and •OH and then, enhanced the removal efficiency of *batik* wastewater.

The study of removal of Acid Orange 7 from aqueous solution by UV irradiation in the presence of ZnO nanopowder was carried out by Daneshvar et al. (2007) found that the photodegradation efficiency increased with an increase in ZnO nanopowder concentration. Akyol et al. (2004) examined the effect of ZnO loading in decolorization of Remazol Red RR and found that decolorization efficiency of Remazol Red RR increased by increasing the catalyst loading.

The photodegradation of *batik* wastewater was conducted under the condition of with and without aeration. The removal efficiency of *batik* wastewater with aeration after 10 h irradiated under solar light achieved 71.1% as shown in Figure 5. However, in the case of without aeration, only 50.8% of *batik* wastewater could be decolorized. The

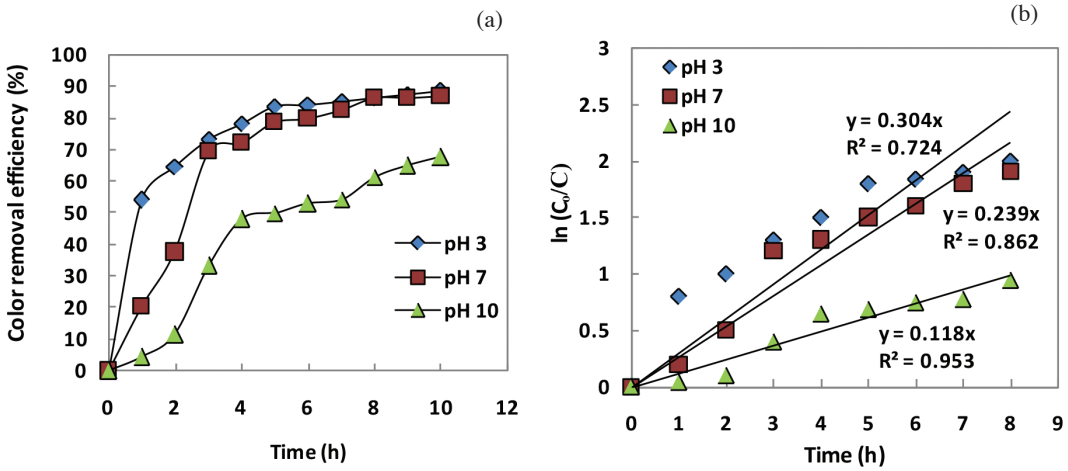


FIGURE 3. (a) Color removal efficiency and (b) plot of ln $C_0/C$ against irradiation time for different pH of *batik* wastewater

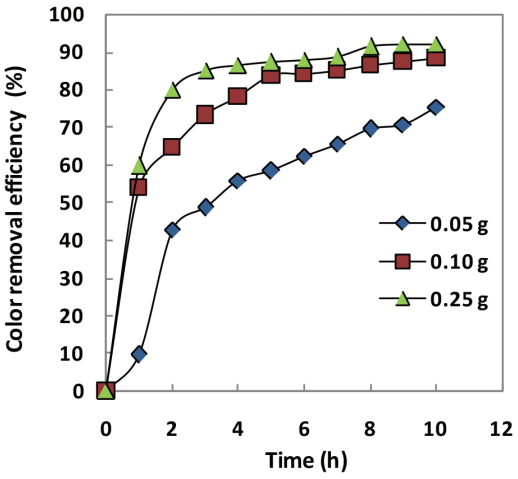


FIGURE 4. Removal efficiency of *batik* wastewater at different ZnO dosage

presence of oxygen enhanced photocatalytic degradation since it will react with conduction band electrons in order to form superoxide radical anions which eventually yield reactive •OH (Fotiadis et al. 2007). The oxygen supplied into the *batik* wastewater could prevent the recombination between electron and hole which would reduce the photocatalytic activity (Nishio et al. 2006). As the ZnO irradiated by solar light, an electron is excited out of its energy level to conduction band and leaves a positive hole in the valence band. The positive hole is a strong oxidant which can either react with electron donors like $OH^-$ or $H_2O$ to form •OH or oxidize the azo dye directly. Meanwhile, the excited electron can be trapped by oxygen molecules from air bubbling to form $•O_2^-$ on the surface of ZnO. Thus, the photocatalytic degradation can be enhanced due to the formation of more oxygen active species in the wastewater.

The complete decolorization of *batik* wastewater can be analyzed using UV-Vis spectrum. The reduction in absorption peak ($\lambda_{max}$) at 516 nm of *batik* wastewater was shown in Figure 6. Within 10 h of solar light irradiation, *batik* wastewater achieved almost 100% of color removal. The disappearance rate at maximum wavelength (516 nm) in visible region rapidly decreased compared to the maximum wavelength (232 nm) in the UV region. There was only slightly removal efficiency in aromatic compounds which is in UV region after 10 h irradiated under solar light. The generation of •OH from photocatalytic reaction attacked the azo bond linkage (-N=N-) which resulting in decolorization of *batik* wastewater. The broken down of azo bond linkage increased the generation of aromatic and naphthalene compounds. The solar photocatalytic process cannot completely mineralize the intermediate products due to the combination of *batik* wastewater with other substances such as sodium silicate in dyeing and washing processes.

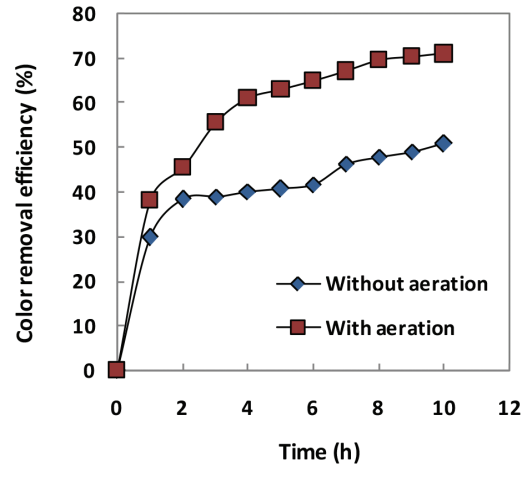


FIGURE 5. Removal efficiency of *batik* wastewater in with and without aeration

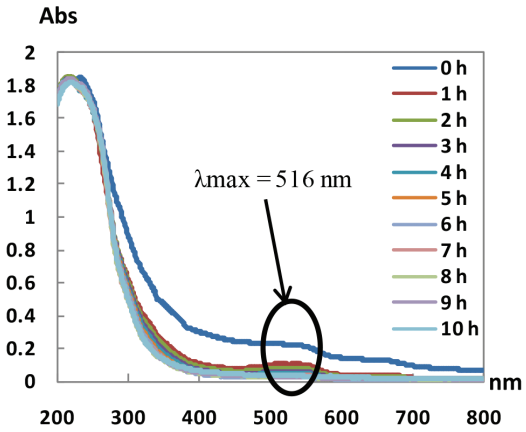


FIGURE 6. UV-Vis spectrum analysis of *batik* wastewater

The wastewater sample placed under direct solar light irradiation for 12 h to analyse its COD. The initial COD concentration of wastewater was 1332 mg/L and after 12 h irradiation time, its COD concentration decreased until 286 mg/L as shown in Figure 7. This result indicated that the degradation of *batik* wastewater occurred until 12 h solar irradiated. The decreased in COD concentration of *batik* wastewater was along with its removal efficiency. Although the COD concentration does not achieved the Seventh Schedule for Standard A and B as showed in Table 2, however, based on the results, the COD concentration could be reduced by extending the irradiation time up to 24 h. The •OH generated from interaction between ZnO and solar light irradiation will attack the azo bond linkage (-N=N-) of dye molecules and break down them to form nitrate and nitrite. The •OH then break down the benzene and naphthalene ring and formed intermediate products. The partially mineralization of *batik* wastewater after 12 h irradiated under solar light would produce $CO_2$, $NO_3^-$, $Na^+$, $SO_4^{2-}$, $H_2O$, $H^+$ and $Cl^-$. Krishnakumar and Swaminathan (2011) in their study reported that the COD value of dye decreased after 1 h irradiation time.

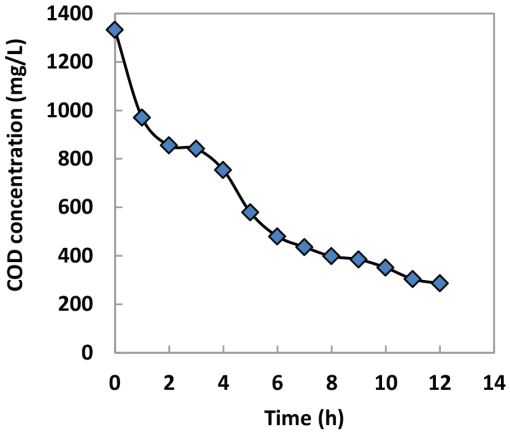


FIGURE 7. COD concentration of *batik* wastewater after 12 h irradiation time

TABLE 2. Seventh Schedule (Regulation 12) for COD in industry sector

| Trade/Industry | Unit | Standard A | Standard B |
|---|---|---|---|
| (1) | (2) | (3) | (4) |
| (a) Pulp and paper industry | | | 350 |
| (i) Pulp mill | mg/L | 80 | 250 |
| (ii) Paper mill (recycled) | mg/L | 80 | 300 |
| (iii) Pulp and paper mill | mg/L | 80 | |
| (b) Textile industry | mg/L | 80 | 250 |
| (c) Fermentation and distillery industry | mg/L | 400 | 400 |
| (d) Other industries | mg/L | 80 | 200 |

After the degradation of *batik* wastewater by solar photocatalytic process under optimized conditions (0.1 g of ZnO and operating pH of 3.00), the characterization of *batik* wastewater was evaluated. Table 3 shows the parameters which had been analyzed after 10 h irradiated by solar light. The results showed significant removal efficiency of the major parameters especially in COD. The removal efficiency of $BOD_5$, COD, turbidity and TSS was 52, 91, 54 and 74%, respectively. Other than decolorization of *batik* wastewater, its biodegradability also can be determined by the ratio of $BOD_5$/COD. The ratio of $BOD_5$/COD of *batik* wastewater within 10 h of solar light irradiation was 0.5, however, the ratio of $BOD_5$/COD of *batik* wastewater before treatment was 0.08. The *batik* wastewater has the ratio of $BOD_5$/COD higher than 0.3 where indicated that it has better biodegradability.

## CONCLUSION

Photocatalytic degradation using ZnO was successfully applied for the decolorization and mineralization of *batik* wastewater under solar light irradiation. The results indicated that the removal efficiency of *batik* wastewater was obviously affected by the photocatalyst dosage, pH and aeration. The decolorization of *batik* wastewater was increased significantly by increasing the amount of ZnO. The results also indicated that the decolorization of *batik* wastewater was faster than its mineralization. The removal efficiency of *batik* wastewater at optimum condition (pH3 and 0.1 g of ZnO) was 88.2% during 10 h irradiation time. The decolorization of *batik* wastewater followed pseudo-first-order rate constant of Langmuir-Hinshelwood kinetic model. The mineralization of *batik*

TABLE 3. Characteristics of *batik* wastewater after photocatalytic activity

| Parameters | Value | Removal efficiency (%) |
|---|---|---|
| $BOD_5$ (mg/L) | 164.56 | 52 |
| COD (mg/L) | 351 | 91 |
| pH | 3.21 | - |
| Temperature (°C) | 25.3 | - |
| Turbidity (NTU) | 99 | 54 |
| TSS (mg/L) | 80 | 74 |

wastewater through COD analysis achieved 286 mg/L after 12 h irradiation time.

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