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Wastewater Treatment from Batik Industries Using TiO2 Nanoparticles

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Abstract. Batik is cultural patterned fabric, and the this industries produce wastewater that can pollute the aquatic environment. Besides dyes, batik wastewater also contains synthetic compounds that are hard degraded, such as heavy metals, suspended solids, or organic compounds. In this study, photocatalitic membrane TiO_2 coated plastic sheets have been used to degrade batik wastewater under solar exposure. A total of 8 pieces of catalyst sheets are added on 1000 ml of the waste, and managed to degrade 50.41% of the initial concentration during 5-days irradiation. In this study, several parameters of the water quality such as chemical oxygen demand (COD), biological oxygen demand (BOD), and total suspensed solids (TSS) of the wastewater were observed to be decreased during photodegradation process. The catalyst sheet also is stable to be used repeatedly in wastewater treatment.

Keywords: Batik wastewater; COD, BOD, TiO_2 nanoparticles,TSS.

1. Introduction

Batik has been recognized by UNESCO as the world cultural heritage from Indonesia. Batik and textile industries are producers of wastewater originating from the dyeing process. Besides dyes, batik wastewater also contains synthetic ingredients which are recalcitrant to be degraded. Wastewater generated from batik or textile industries is generally a non-biodegradable organic compound, which can cause the environmental pollution, especially of the aquatic environment.

Some of the most commonly used in textile industry are remazol black, red and golden yellow. In the dyeing process these compounds can only be used about 5% while the remaining 95% will be discarded as a liquid waste. Because they are stable enough, their presence in nature are very difficult to be degraded, and in high concentrations these compounds are harmful to the environment because they can raise the COD and BOD levels of water.

Advanced oxidation processes (AOPs) with TiO_2 as a photocatalyst has been widely used in wastewater treatment. This method has several benefits include: the process is simple, environmentally friendly, can operate in the environmental conditions, as well as low costs. In addition, the TiO_2 catalyst is photostable, non-toxic, low cost, and stable in the water for a various of experimental conditions [1, 2, 3].

The implementation of TiO_2 in wastewater treatment can be classified in two ways: slurry suspension (TiO_2 nanoparticles directly dispersed in the wastewater) and immobilized system (TiO_2 nanoparticles being fixed to a carrier)[4]. Slurry suspension, although it is simple in technique and high surface area to adsorption and reaction, its application is limited by the low-efficient utilization of light coming and difficult to separate nanoparticles after reaction [5]. In this case, it is necessary to immobilize

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TiO2 nanoparticles on a support to overcome the deficiency of the slurry system for the practical application. In addition, the immobilized TiO2 can be used repeatedly and it can be regenerated.

Some simple methods have been developed to coat TiO2 nanoparticles on a transparent substrate. As performed by Isnaini *et al.* who coated the surface of the plastic fiber with TiO2 particles using the vibration method. TiO2-coated fibers were then applied to treat organic pollutants in wastewater [6]. Meanwhile, Aliah *et al.* using the thermal milling method, have managed to coat the surface of plastic granule with TiO2 nanoparticles [7]. Sutisna *et al.* using a combined method of the electrostatic and thermal treatment, have succeeded in superimposing TiO2 on the surface of the plastic sheet [8].

In this study, TiO2-coated plastic sheets were applied in photodegradation of batik wastewater. Parameters of the water quality such as color, COD, BOD, and TSS have been evaluated to see the performance of catalyst sheets.

2. Material and Methods

2.1. Reagent and materials

A technical grade of TiO2 (Bratachem, Indonesia) was used as a photocatalyst (density: 4.3[illegible] g cm-3, average particle size: 166 nm, BET surface area: 7.005 m2 g-1, total pore volume: 9.69x10[illegible] cc g-1, average pore diameter: 55.31 nm, crystalline structure: anatase). Compared with pure [illegible], this material is much less expensive and it has a fairly wide absorption band [9]. TiO2 particles were coated on plastic sheets of polypropylene (purchased from the local supplier) with a thickness of [illegible] mm and a melting point of 130-170 °C. As a treated solution, we used batik wastewater obtained from a batik industry in Jember, East Java, Indonesia.

2.2. Catalyst preparation

Before TiO2 catalyst is applied, first it was immobilized on surface of plastic sheets using a simple and cheap method. This coating method is a combination of electrostatic and thermal treatment [8]. The coating process was initiated by generating electrical charge on the plastic sheet by rubbing it with a wool cloth. The friction between surfaces of the plastic and wool cloth causes electrons to move from fabric to plastic. TiO2 particles were then sown on the surface of charged plastic and because of the electrostatic induction, they adhere to the plastic surface. To bind strongly TiO2 on the plastic, heating under pressure was done by using a modified lamination machine. Based on the amount of TiO2 in spite of the plastic surface during the washing process after coating, we identified that the optimum coating quality are obtained when it was heated at temperatures of 110 ° C for 4 minutes per sheet [8]. A SEM (scanning electron microscope) image of the sample proved that the TiO2 nanoparticles have been attached properly on the surface of the plastic.

2.3. Photocatalysis experiments

A total of [illegible] ml batik wastewater was placed in a container with dimension 13x19x9 cm3. Degradation of batik wastewater was performed under different experimental conditions: (i) control solution without catalyst under solar irradiation (photolysis reaction), and (ii) solution with catalyst sheets under solar irradiation (photocatalytic reaction).

All experiments were carried out in Bandung city, Indonesia with geographical coordinates latitude = [illegible] and longitude =107.6o on August - September 2015. Different locations will have different solar intensity. Experiments conducted during 8 hours (from 08:00 o'clock to 16:00 o'clock) on each day. The intensity of the sun light during experiment was measured using a TM 206 Solar Power Meter (TENMARS, Taiwan). During photocatalytic process, the solar illumination changed with time with the average intensity of about 622 W/m2. Photodegradation of wastewater has been analyzed by measuring absorbance spectrum, COD, BOD, and TSS.

2.4. Analytic Methods,

Brunauer-Emmett-Teller (BET) specific surface area analyzer (Nova Quantachrome 1200e) was used to determine the specific surface area and pore size distribution of TiO2 nanoparticles. A SEM (JSM-651OLA, JEOL, Japan) was used to analyze morphological feature of the TiO2 coated plastic sheet. Decolorization of dye compounds have been analyzed by absorbance measurement during

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photodegradation process using a UV-Vis spectrometer (Mikropack Brands, NanoCalc 2000, Florida, USA). The measurement of COD, BOD, and TSS are based on the Standard Methods for the Examination of Water and Wastewater 22nd edition 2012 (SMEWW).

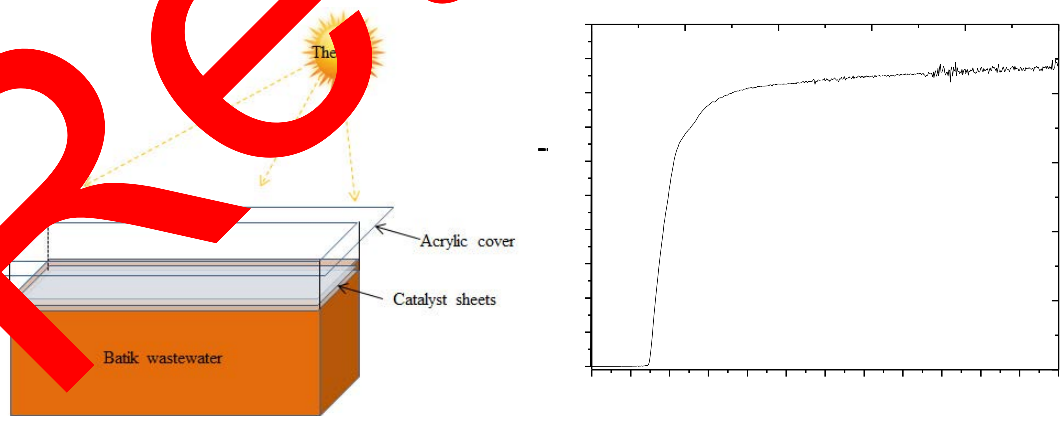
3. Results and Discussion

3.1. Decolorization of batik wastewater by photolysis and photocatalysis reactions

Photodegradation test of batik wastewater was done by placing 1000 ml wastewater in a con[illegible] this experiment, effect of number of catalyst sheets on degradation efficiency has been investigated by varying the number of catalyst from 5-10 pieces. Each sheet has a cross-sectional area of [illegible]x18 cm2. Batik wastewater without catalyst has been used as a control experiment. During the experiment, the container was covered by acrylic transparent (thickness of 2 mm) in order to avoid the effect of evaporation on the photodegradation reaction. Acrylic was selected for its transparency property [illegible] pass solar light spectra in the wavelength range from UV-B until visible light. Photons [illegible] this spectra range are needed to stimulate the photocatalytic reaction. The experimental setup and transmission spectra of acrylic can be seen in Fig. 1.

Decolorization process of dye compounds contained in batik wastewater was investigated by measuring the absorbance of the solution. According to Lambert-Beer law, the concentration of a solution is directly proportional to the amplitude of the absorption spectra. Therefore, a decrease in absorption spectra peaks of a solution during degradation process indicates a decrease in the concentration of the dye in the wastewater. UV-Vis absorption spectra of batik wastewater without and with a catalyst can be seen in Fig. 2.

The decomposition of dye in batik wastewater during photodegradation process for different variations of the number of catalyst is shown in [illegible] 2. It can be seen that the addition of catalyst sheets from 5 to 8 pieces have increased the photodegradation rate of batik wastewater. Nonetheless, this does not apply to the addition of the next catalyst sheet. The use of 9 to 10 pieces of catalyst sheets can no longer increase the photodegradation ability of the [illegible]. This phenomenon can be explained as follows: an increase in the amount of the catalyst will provide an increase in active sites of the catalyst that contact with contaminants in the wastewater and role in the photocatalytic reaction. On the other hand, the increase in the number of catalyst sheets [illegible] reduce the intensity of sunlight that penetrates and activate the catalyst. [illegible] number of catalyst sheets that can be penetrated by sunlight depends on the transparency of the catalyst sheet and the concentration of batik wastewater. In this case, the optimum number of catalyst sheets is 8 pieces.



(a) (b)

Figure 1. Experiment setup, (b) transmission spectra of acryl

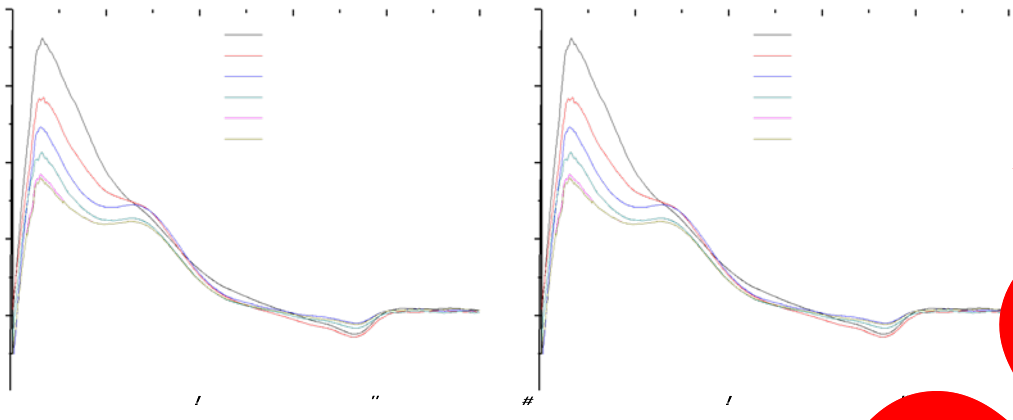


Figure 2. Absorption spectra of batik wastewater during degradation process, (a) no catalyst, (b) using 8 catalyst sheets.

The decomposition of dye in batik wastewater during photodegradation process for different variations of the number of catalyst is shown in Fig. 3. It can be seen that the addition of catalyst sheets from 5 to 8 pieces have increased the photodegradation rate of batik wastewater. Nonetheless, this does not apply to the addition of the next catalyst sheet. The use of 9 to 10 pieces of catalyst sheets can no longer increase the photodegradation ability of the system. This phenomenon can be explained as follows: an increase in the amount of the catalyst will provide an increase in active sites of the catalyst that contact with contaminants in the wastewater that play role in photocatalytic reaction. On the other hand, the increase in the number of catalyst sheets will reduce the intensity of sunlight that penetrates and activate the catalyst. The number of catalyst sheets that can be penetrated by sunlight depends on the transparency of the catalyst sheet and the concentration of batik wastewater. In this case, the optimum number of catalyst sheets is 8 pieces.

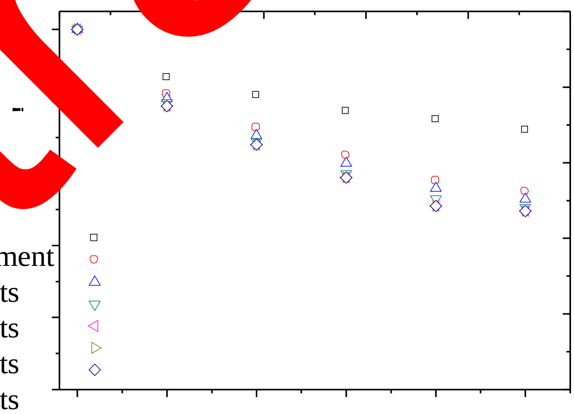


Figure. 3. Decomposition of batik wastewater during 5 days of irradiation for different variations of the number of catalyst sheets.

In the same figure is also shown that, very low degradation rate is observed in the control experiment that without catalyst. Photolysis mechanism was able to degrade the dye in batik wastewater at a rate that is much smaller than the photocatalytic mechanism. One other interesting thing is that not all the dye in batik wastewater can be decomposed. From the experimental data by using 8 pieces of the catalyst, it is observed that the mechanism of photodegradation as if suspended after the 4th day of irradiation. On the 5th day of irradiation, the dye concentration is almost unchanged compared to the 4^{th} day. We suspect that the remaining dye after the 4^{th} day of irradiation is inorganic compounds that can't be decomposed by the photocatalytic reaction.

3.2. COD, BOD, and TSS reductions of the treated batik wastewater

In addition to dye, water quality is also determined by parameters of COD, BOD, and TSS [1, 10]. Fig. 4 shows the level of parameters for batik wastewater before and after treatment. It is seen that after 5 days under solar exposure, the photocatalyst has been able to reduce the levels of parameters of water quality. COD, BOD, and TSS levels were decreased by 97, 23 and 71 points, respectively. A decrease in the level of COD, BOD, and TSS indicates an increase in the water quality.

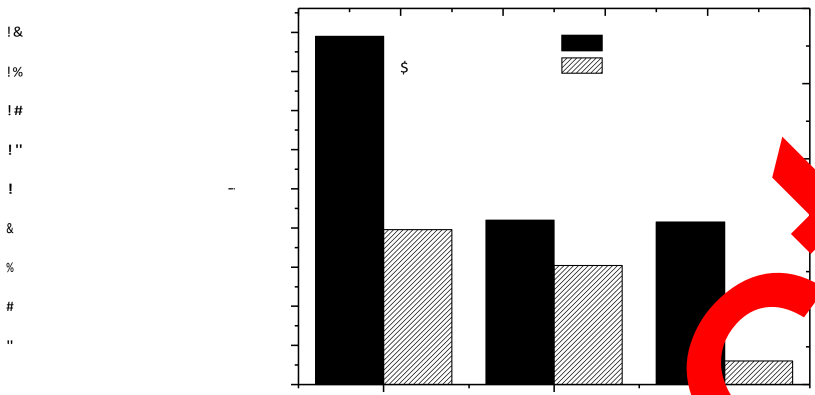


Figure 4. Reduction of parameters of water quality of the treated batik wastewater.

3.3. Repetitive operation performance

One of the benefits of the immobilized TiO_2 is that it can be used repeatedly. To evaluate the stability of the catalyst sheet to decompose batik wastewater, photodegradation experiment of 1000 ml batik wastewater was repeated up to 4 cycles. In each cycle of experiments we used 8 layers of TiO_2 coated plastic sheets. After each operation, catalyst sheets were washed using distilled water. The figure shows that over 4[illegible] dye is already decomposed after 5 days of photocatalysis in each operation. The four repetitive operations have a standard deviation of 0.57%, indicating that the stability of the catalyst sheets is almost constant. **Fig. 5** shows SEM images of the catalyst sheet before and after four times used. Based on the figure, it is clear that almost no differences in the morphology of the catalyst sheet before and after four times used. This fact shows that the TiO_2 nanoparticles are stably attached on the surface of the plastic. The stability of the catalyst sheets ca[illegible] its performance to degrade organic compound are also very stable when it is used repeatedly.

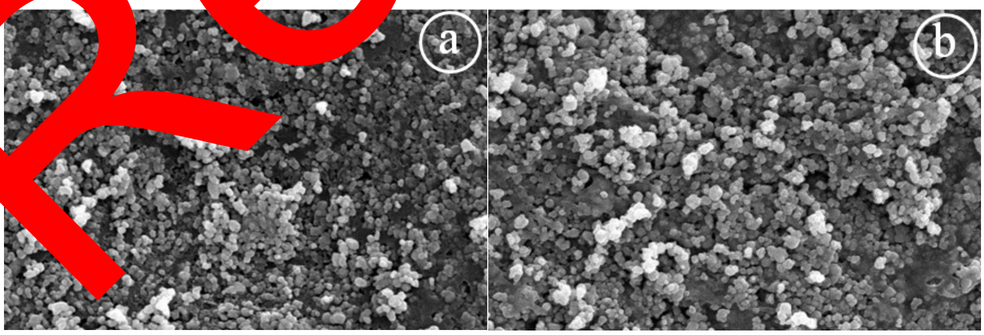


Figure 5. SEM images of the catalyst sheet, before (a) and after (b) four times used in the photodegradation of batik wastewater.

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4. Conclusion

TiO2-coated plastic sheets were used to degrade wastewater produced in the dyeing process of batik. A total of 1000 ml batik wastewater was placed in a container and a number of catalyst sheets were the added to the solution. Optimization of the catalyst number was carried out by varying the number of catalyst sheets of 5 to 10 sheets. As a result, eight pieces of the catalyst are the optimum number of catalyst sheets with its ability to degrade batik wastewater upto 50.41% for 5 days irradiation. The decline in COD, BOD, and TSS were also observed during photodegradation which decreased by [illegible]7, 23 and 71 points, respectively. In this study also found that the catalyst sheet is stable to [illegible] repeatedly in wastewater treatment.

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