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To cite this article: Dessy Ariyanti *et al* 2021 *IOP Conf. Ser.: Mater. Sci. Eng.* **1053** 012057

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Performance of free standing TiO₂ nanostructures (FSTNS) photocatalysis for batik industry wastewater treatment

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Abstract. In this work, the effectiveness and reusability of free standing TiO₂ nanostructures (FSTNS) for batik industry wastewater treatment were investigated. The FSTNS photocatalyst were prepared via hydrothermal process at 180°C for 18 hours in the presence of acetone (5% v/v) as oxidation agent. Batik industry wastewater used in this study were analysed prior the photocatalysis, thus contained organic pollutants including dyes and phenolic compound with chemical oxygen demand (COD) 303.7 mg/L; total phenol 0.8 mg/L and measured pH 5.84. The results show FSTNS is able to degrade the majority of dyes which leads to the reduction of COD value up to 56,7 mg/L, total phenol to 0.3 mg/L and acidity level to 7.15. It is also found out that the effectiveness of FSTNS reduce less than 20% after it is reuse in three times cycles, confirming its fair reusability as photocatalyst for batik wastewater treatment.

1. Introduction

Indonesian batik industry is considered to have dominated the global market since it recognized by UNESCO as one of world heritage and thus linearly support the national economy with the export value in 2017 around US\$ 58.46 million¹. The implication to the environment is also massive as about 10–20% of total dye products use in batik coloring is commonly lost in the wastewater and released as effluents into the water body². Organic dyes and other organic compounds are one of the leading groups of pollutants released into wastewaters from textile and other industrial processes³⁻⁵.

The existing methods such as aerobic and anaerobic processes have succeed to degrade organic pollutants with a very long processing time^{4,6}. The chemical and physical separation methods such as coagulation, flocculation and adsorption were able to separate the dyes and other organic pollutants from the water body with very good performance⁷, however it creates new challenges such as new contaminant presents in the water body or desorption of the concentrated dyes and other organic pollutants from the adsorbents. Other physical method is separation through nanofiltration membrane⁸ which claimed to performed 80% efficiency on dye removal. However, dyes are soluble in water which have higher chances to penetrate through membrane during the processing time.

Many potential emerging methods were developed to be an alternative way for batik industry wastewater treatment. A relatively new destructive methods that can be applied in batik industry wastewater is advanced oxidation processes (AOPs). It basically a process that involves the generation of hydroxyl radicals (\bullet OH) which can be used to degrade dyes or any other organic pollutants. AOP methods are varies depend on the use of chemicals or hydroxyl radicals (\bullet OH) source and whether it



is using photon as energy sources. Namely, ozonolysis, UV/ozone, UV/H₂O₂, photocatalysis with semiconductor and combinations of the above are categorized as AOP⁹.

Photocatalysis with TiO₂ has been investigated as one of the visible methods to be applied in the wastewater treatment field as it has high photoreactive properties and chemical stability in comparison to other materials¹⁰. The hydroxyl radicals (\bullet OH) are generated when a catalyst (TiO₂) is dissolved in the water and illuminated by ultraviolet (UV) light. As a result, organic compounds can be demineralized to CO₂, H₂O and other inorganic constituents^{9, 11}. Studies have conclude the effectiveness of TiO₂ nanoparticles as a photocatalyst for various organic degradation¹²⁻¹⁵. However, from the technical application point of view the immobilized TiO₂ is preferable because it does not need additional post-treatment for the catalyst recovery after the degradation process as employing nanoparticle requires additional separation system to prevent new pollution in the treated water¹⁶⁻¹⁸. In this paper the immobilized TiO₂ has been developed referring to the method described in the previous study¹⁹ and its visibility in treating batik industry wastewater including the reusability is reported.

2. Materials and Methods

2.1. Batik Industry Wastewater

The wastewater was collected from Pekalongan Batik Industry in Central Java, Indonesia. Prior the use, it was filtered to remove fat and grease. Initial analysis was also performed to determine the chemical oxygen demand (COD), pH and total phenol.

2.2. Preparation of FSTNS as photocatalyst

Titanium foil 99% as a substrate for FSTNS were purchased from BTMM Co. Ltd. It was cut into 20 mm x 20 mm x 0.25mm. The synthesis process was following the process described elsewhere¹⁹. The foil was treated in ultrasonic bath for 10 min and washed with DI water prior FSTNS synthesis. The foil then placed in Teflon hydrothermal autoclave (volume 50 mL) which contained 30 mL of acetone solution (5% v/v) as oxygen source. The Teflon hydrothermal autoclave were then heated inside the oven for 18 hours with temperatures 180°C. After hydrothermal process, the sample were cleaned with DI water and dried in oven at 110°C for 2 h followed by calcination in the furnace for 2 h at 500°C. Characterization of the sample were conducted by SEM and XRD to find out its crystal structures and surface morphology.

2.3. Photocatalytic degradation of batik industry wastewater

The performance of FSTNS photocatalysis in treating Batik industry wastewater were investigated by conducting the photocatalysis in batch mode with black light 20 W irradiation as a photon source. Filtered batik industry wastewater (50mL) were placed in the reactor and the FSTNS were immersed in the half level of the wastewater solution for 4 hours with continues stirring. Prior the photocatalysis, the process was conducted in the dark mode for 1 hour to make sure no adsorption activity interfering the photocatalysis. Sample of wastewater were withdrawn every 1 hour and immediately analyzed by UV Vis Spectrophotometer in the wavelength 400-800 nm. The recyclability study was conducted by repeating the same photocatalysis for three times. The FSTNS photocatalyst were recovered by drying process in the oven at 110°C for 1 hour before it was used in the following cycle process. Other measurement such as COD, pH and total phenol analysis were conducted at the end of photocatalysis.

3. Results and Discussion

3.1. Characterization of FSTNS photocatalyst

The hydrothermal process under mild condition 180°C in 18 hours in the present of acetone (5% v/v) has created a new layer on titanium surface. The new layer appeared as nanorods morphology that grew from the titanium foil base with diameter 30-50 nm. It was evenly distributed throughout the surface with the thickness ranges from 3.3-4.4 μ m as confirmed by the SEM image in Figure 1. As

previously reported, high pressure environment that theoretically can go up to 9.9753 bar at 180°C inside the hydrothermal reactor and the present of acetone as an oxygen source will force titanium to be oxidized and form rods type of structure^{19, 20}. In addition, the acetone carboxyl groups assist the vertical growth of the nanorods following the oxidation of titanium^{21, 22}.

Figure 2 shows the XRD pattern of as produced and annealed FSTNS. In both pattern, titanium metal peak is dominating the pattern which it is understandable as titanium foil is the substrate of the sample and its initial thickness is around 250 microns. But the TiO₂ anatase peaks were also visible especially at the angle position of 2 theta 20-28°. Some of the small peaks in both of XRD pattern at the angle position of 25,367°, 37,053°, 48,158°, 54,051°, 55,204°, 62,867°, which define the crystal structure 101, 004, 200, 105, and 204 (Anatase XRD JCPDS Card no. 78-2486)²³. The annealed sample appeared to have more obvious peaks compared to the as produced FSTNS which can be addressed as having higher crystallinity. The annealing process at 500°C for 2 hours drives the atoms to do rearrangement and ordering themselves to form more stable anatase phase^{24, 25}.

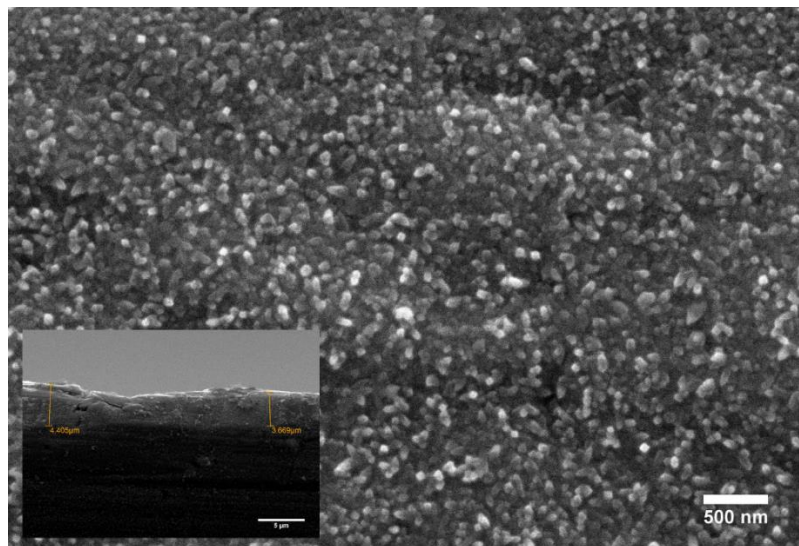


Fig. 1 SEM images of FSTNS synthesized at 180°C 18 hours (surface and cross section)

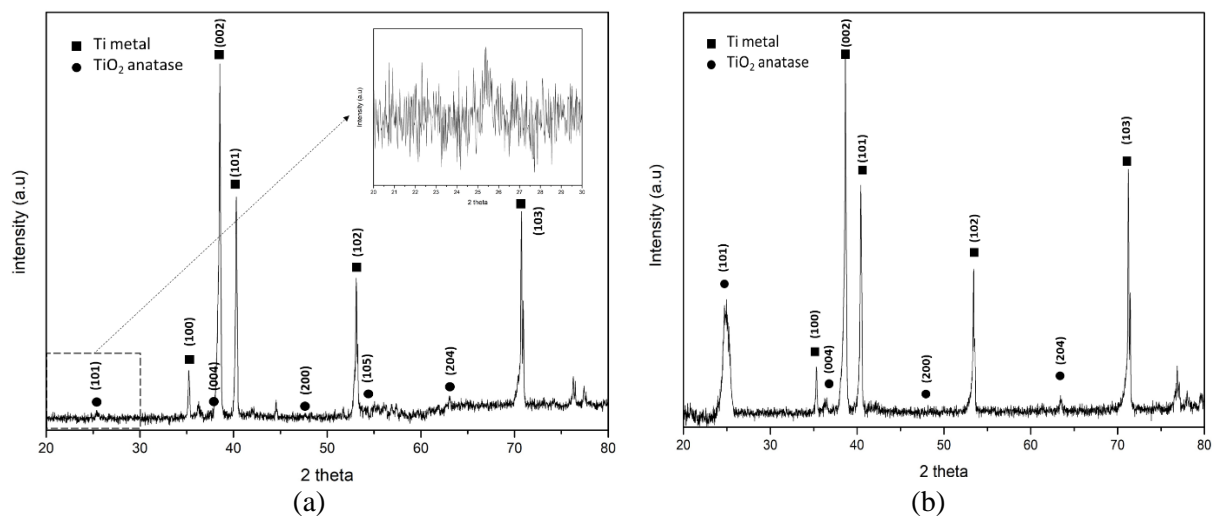


Fig. 2 XRD Pattern of FSTNS synthesized at 180°C for 18 hours (a) as produced (b) annealed 500°C for 2 hours

3.2. FSTNS photocatalyst performance in Batik wastewater treatment

The photocatalytic performances of FSTNS were evaluated in the dyes degradation contained in batik industry wastewater solution at atmospheric condition. Direct degradation of dyes in the absence of photocatalyst was not detected under black light irradiation. Figures 3 shows the dyes degradation profiles via photocatalysis using FSTNS synthesized at 180°C with and without annealing. The degradation ability of FSTNS with annealing is higher than the one without with 34% and 51% respectively. Referring to the XRD results, the annealing treatment after hydrothermal process resulted higher crystallinity of the TiO₂ in the form of free-standing nanostructures.

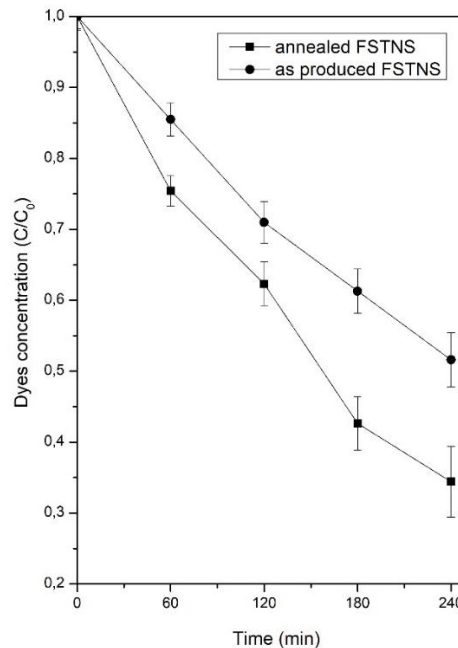
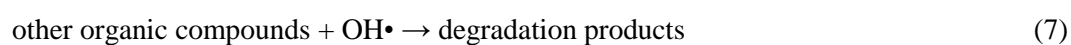


Fig. 3 Batik wastewater degradation profiles via photocatalysis using as produced and annealed FSTNS

Crystallinity of TiO₂ as photocatalyst plays an important role during photocatalysis. Well-ordered TiO₂, upon excitation of photon with energy higher than its bandgap (3.2 eV) will generate charges shown in Eq. (1). Thus, charges in the present of water is triggering another reaction of hydroxyl and oxygen radical's production that leads to the generation of more radicals (Eq.2-5) to perform degradation of organic pollutants (Eq.6-7) ^{11, 17}.



The migration of the electron and a positive hole can perform better in the larger crystal than in a smaller crystal and the evidence from previous studies shows that the photocatalytic activity increased with the increasing of crystallinity and crystal size ²⁶⁻²⁸.

The performance of FSTNS in the application of batik industry wastewater treatment can be measured by predicting the reaction rate of the degradation process. The degradation via photocatalysis generally follows pseudo first-order reaction kinetics as the common photocatalyst plays role as a reactant in the catalytic system which its concentration remains unchanged²⁹. The reaction kinetics can be described as Langmuir-Hinshelwood model to accommodate the fact that the concentration of adsorption in the dark condition is very small and negligible. According to the law of mass-action, photocatalytic rate can be expressed as Eq.8 and simplified as Eq.9^{29,30}:

$$r = -\frac{dC_0}{dt} = kC_t \quad (8)$$

$$\ln \frac{C_0}{C_t} = kt \quad (9)$$

where C_0 is initial concentration of organic substances before photocatalysis, and C_t is the reactive concentration at time t during the photocatalytic reaction. k is rate constant.

The rate constant of dyes contained in batik wastewater degradation via photocatalysis using FSTNS synthesized at 180°C with and without annealing are illustrated in Fig 4. The rate constant of photocatalytic activity with annealed FSTNS is higher compared to the as produced FSTNS with 0.045/min and 0.028/min respectively. The rate constant for film or layered type of TiO₂ photocatalyst typically around 11-13 min⁻¹ m⁻²^{31, 32}. These rate constants are low compared to the use of nanoparticles to 2-3 magnitude.

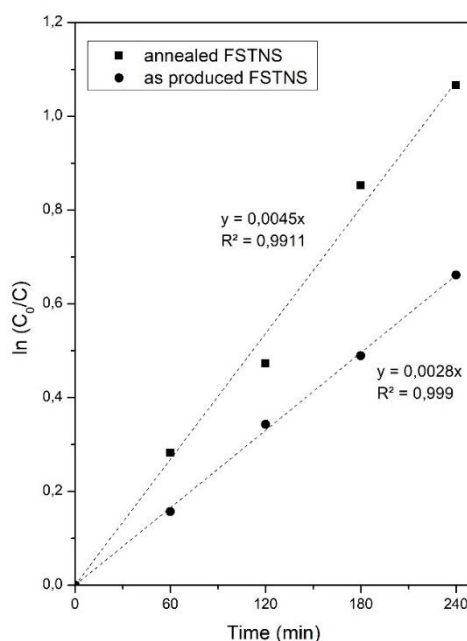


Fig. 4 Kinetic constant of dyes contained in batik wastewater degradation via photocatalysis using as produced and annealed FSTNS

In order to analyse the chemical stability and reusability of FSTNS photocatalyst, three cycles of degradation were carried out with the same sample with annealing and under same conditions. The recyclability was conducted up to 3 cycles and the results are presented in Figure 5. The results show that FSTNS photocatalyst was able to degrade up to 54% even after three cycles of repeated usage. This experiment supports the practical applicability of FSTNS in batik industry wastewater treatment for repeated usage and minimalization of the nanoparticle contamination to the environment.

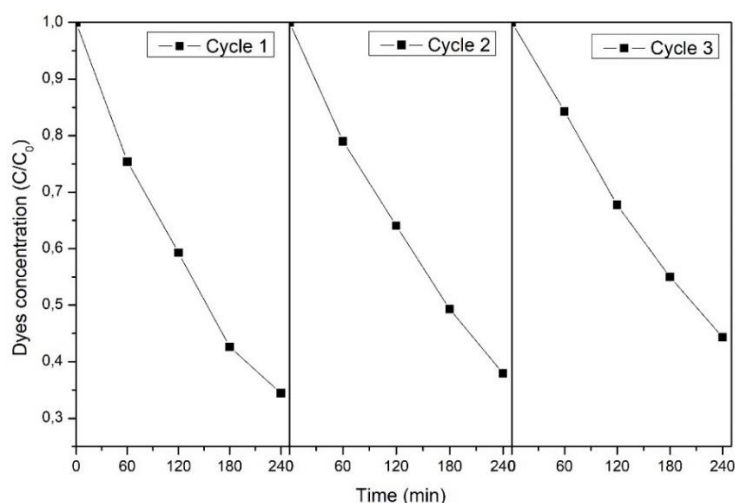


Fig. 5 Recyclability study of FSTNS photocatalyst for three cycles

Table 1. Comparison of batik wastewater parameters before and after the photocatalysis

Parameters	Batik wastewater (mg/L)		Standard for discharged textile wastewater (mg/L)
	before treatment	after treatment	
COD	303,7	56.7	150
Total Phenol	0.8	0.3	0.5
pH	5.74	7.15	6.0-9.0

The final analysis to validate the effectiveness of FSTNS photocatalysis in batik wastewater treatment is presented in Table 1. Photocatalysis using annealed FSTNS were able to reduce COD value to 56.7 mg/L that represent organics component in wastewater. In addition, phenolic compound also reduces to 0.3 mg/L with the reduction of the solution acidity. The organic degradation performs by the photocatalytic activity of annealed FSTNS proven to minimize the wastewater parameter values less than the standard discharged value of textile wastewater mandate by the Indonesian government.

4. Conclusion

The effectiveness of FSTNS photocatalyst synthesized via hydrothermal routes under mild condition in the application of batik wastewater treatment is successfully investigated. By the addition of annealing process at 500°C for 2 hours, it can improve the degradation ability up to 20% and rate constant up to 1.5 times. It is observed that by the ability of FSTNS degrade particularly dyes in the wastewater leads to the reduction of COD value up to 56,7 mg/L, total phenol to 0.3 mg/L and acidity level to 7.15. The reusability studies suggest that the effectiveness of FSTNS reduce less than 20% after it is reuse in three times cycles, confirming its fair reusability as photocatalyst for batik wastewater treatment.

5. Acknowledgements

Dessy Ariyanti would like to acknowledge Directorate of Research and Community Service, Deputy for Research Strengthening and Development, Ministry of Research and Technology / National Research and Innovation Agency of Indonesia, Indonesia for the financial support No: 257-24/UN7.6.1/PP/2020.

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