

## Heterogeneous Fenton Degradation of Batik Wastewater using Natural Pyrite

Wenny Irawaty<sup>1,2,\*</sup>, Maria Yuliana<sup>2,3</sup>, Christian J. Wijaya<sup>1,2</sup>, Ery S. Retnoningtyas<sup>3</sup>,  
Suratno Lourentius<sup>4</sup>, Nathania Puspitasari<sup>1,2</sup>, and Umi Hamidah<sup>2,5</sup>

<sup>1</sup>Department of Chemical Engineering, Faculty of Engineering, Widya Mandala Surabaya Catholic University  
Jl. Kalijudan 37 Surabaya

<sup>2</sup>Collaborative Research Center for Zero Waste and Sustainability  
Jl. Kalijudan 37 Surabaya

<sup>3</sup>Chemical Engineering Master Program, Faculty of Engineering, Widya Mandala Surabaya Catholic University  
Jl. Kalijudan 37 Surabaya

<sup>4</sup>Professional Engineer Study Program, Faculty of Engineering, Widya Mandala Surabaya Catholic University  
Jl. Kalijudan 37 Surabaya

<sup>5</sup>Research Center for Environmental and Clean Technology, National Research and Innovation Agency, Samaun  
Samadikun Science and Technology Center, Jl. Sangkuriang, Bandung

\*) Corresponding author: wenny\_i\_s@ukwms.ac.id

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### Abstract

*Heterogeneous Fenton processes with solid natural pyrite catalyst have gained attention for wastewater treatment. The improvement of degradation efficiency of natural pyrite is specific and therefore, it is still a challenging issue. This study was aimed to investigate the performance of Indonesian natural pyrite, without any purification, to treat the real wastewater obtained from batik home industry. To address this issue, several experimental variables such as pre-reaction between pyrite and hydrogen peroxide, hydrogen peroxide concentration, and pH were investigated. COD removal has been found to increase in a slightly acid condition (4.5 to 5.65) and inhibited at pHs of 8 and above 10. The results showed the presence of hydrogen peroxide was indeed greatly influence the wastewater degradation and the solution pH did not significantly change the wastewater degradation in the range of 3 and less than 8. Moreover, the pre-reaction period was found as the important part to initiate the degradation process. The optimum degradation efficiency was obtained by providing the pre-reaction time of 20 min with the addition of 326 mmol/L of H<sub>2</sub>O<sub>2</sub> in the system and the mixture was reacted for 30 min at room temperature and real wastewater pH. Based on results observed in this study, it can be concluded that batik wastewater can be degraded by natural pyrite up to 84% under reaction conditions studied. This finding offers great opportunity to further investigate and develop the heterogeneous Fenton process for real applications in industry.*

**Keywords:** batik; fenton; heterogeneous; pyrite; wastewater

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## INTRODUCTION

Textile is one of the promising business areas in most developing countries with large population, such as Indonesia. Therefore, textile-based businesses have developed well ranging from small to large companies. Indonesian government has played an important role in developing the textile-based small business/industries in every subdistrict of big cities, including Surabaya. There are numerous numbers of small textile-based industries developed by the local government that allowed local society to design, print, wash, and conduct other processes to produce batik fabric.

There are several steps to produce batik fabric, such as sizing, de-sizing, scouring, bleaching, dyeing, washing, etc. Different chemicals will be released from each step. For example, size reduction process will discharge enzymes, starch, and waxes, whilst the effluent from the scouring process will release sodium hydroxide, surfactants, soaps, fats, and waxes. Dyes, metals, formaldehyde and solvents will be present in water discharged from printing area (Yaseen and Scholz, 2019). Therefore, textile industries is one of the biggest global polluters to water bodies.

The presence of dyes in water bodies not only causes aesthetic problem, but also retards sun light penetration into the water. The latter will create serious problems, especially related to reduction of ultraviolet supply that is required for photosynthesis. Consequently, the dissolved oxygen concentration will be decreased and thus, affecting the entire aquatic biota by altering their food chains. Most of dyes used in textile industries are aromatic rings containing synthetic dyes that make them or their intermediates are less degradable (Lellis et al., 2019). Therefore, the wastewater discharged from textile industries usually contains high concentration of chemical oxygen demand (COD), biological oxygen demand (BOD), alkalinity, and color. Moreover, these dyes exhibit high solubility in water and this property causes more difficulties during their conventional removal process (Hasan and Carr, 2018).

Advanced oxidation processes (AOPs) offer efficient treatment processes to remove dyes from wastewater such as Fenton, photo-Fenton, ozone treatment, photocatalytic degradation, electrochemical oxidation, UV photolysis, wet air oxidation, and their combinations (Anil et al., 2022). Among those, Fenton-based treatment is an option with many advantages that involves easily accessible and low cost reagents as well as their process conditions are widely reported in the literature (Wang et al., 2021; Fayazi, 2021; Levy and Radian, 2023). In addition, Fenton-based processes can degrade dyes and their intermediate products unselectively due to the high redox potential of hydroxyl radical ( $E = 2.80$  V). Hydroxyl radicals are resulted from catalytic reaction between catalyst  $Fe^{2+}$  and hydrogen peroxide ( $H_2O_2$ ) in acidic conditions. Based on the catalyst used in the system, the Fenton reaction is classified to homogeneous and heterogeneous processes.

Conventional homogeneous Fenton reactions involve the reaction between dissolved iron catalyst and  $H_2O_2$  in pollutants-containing acidic solution. Several drawbacks of homogeneous Fenton are narrow operation pH, catalyst consumption, massive sludge production, and the need to adjust pH due to strict acidic environments (Shokri and Fard, 2022). These problems lead to a greater attention to develop heterogeneous Fenton system.

Heterogeneous Fenton process through iron ions replacement by solid catalyst have gained much attention as a strategy to enhance the degradation performance. The activation of  $H_2O_2$  to produce hydroxyl radicals occurs on the catalyst surface. Therefore, different kinds of iron-based catalysts, such  $Fe_3O_4$  (Quynh et al., 2023),  $FeS_2$  (Zhang et al., 2021),  $FeO$  (Jiang et al., 2020),  $Fe_2O_4$  (Gupta et al., 2020), and their combination (Ghasemi et al., 2021; Xu et al., 2020) have been tested in laboratory scale. In addition, different catalyst supports, such as clays (Levy and Radian, 2023), carbons (Wang et al., 2022), zeolites (Quynh et al., 2023), aluminas (Mahamallik and Pal, 2020), alginates (Ayed et al., 2023), nanoparticles (Yang et al., 2015) and metal-organic frameworks (Yang et al., 2021) have been well reported.

Natural minerals receive great attention due to their abundant sources, low cost, and are environmentally friendly. One of iron minerals investigated in heterogeneous Fenton reaction is pyrite (Wang et al., 2021; Khataee et al., 2016). Pyrite has been reported to exhibit high performance toward degradation of textile dyes, i.e. rhodamine B (Diao et al., 2017), reactive orange (Khataee et al., 2016), AHPS (Labiadh et al., 2015), methylene blue (Fayazi, 2021). By using simulated dye-containing wastewater as the target, those studies have shown the ability of the natural pyrite to degrade dyes. Further development of the process requires a system that is more complex by introducing real industry wastewater to replace the synthetic dye. Testing the ability of pyrite to treat real dyes-containing wastewater has also been reported in literature (Chen et al., 2021). The study reveals the capability of natural pyrite to be used to degrade various pollutants in the wastewater. However, improving catalytic efficiency is still a challenging issue since different pyrite source may result in different compositions that in turn affecting the degradation rate of the target wastewater. Moreover, the wastewater sample generated by each industry would be specific and therefore, the results cannot be generalized and compared with studies mentioned previously.

The present study focused on COD removal from real batik wastewater using heterogeneous Fenton reaction. The effect of reaction conditions such as pre-reaction time to produce hydroxyl radicals,  $H_2O_2$  dosage, and solution pH were investigated. The experimental results further highlight the potential of using natural pyrite to achieve high degradation rate of contaminants in wastewater of the target local batik fabric home industry in Surabaya.

## RESEARCH METHOD

### Materials

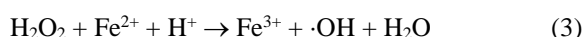
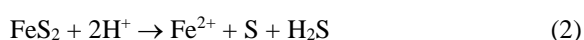
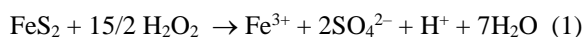
Wastewater sample was obtained local batik fabric, located at Tambak Rejo Subdistrict, Simokerto District, Surabaya City, East Java Province, Indonesia. It was effluent from the wash-off process. Chemical used were hydrogen peroxide ( $\text{H}_2\text{O}_2$ , 30%, CAS 7722-84-1), sulfuric acid ( $\text{H}_2\text{SO}_4$ , Fluka, 97%, CAS 7664-93-9), silver sulfate ( $\text{Ag}_2\text{SO}_4$ , Merck, CAS 10294-26-5), potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ , Merck, CAS 7778-50-9), mercury(II) sulfate ( $\text{HgSO}_4$ , Merck, CAS 7783-35-9), 1,10-phenanthroline ( $\text{C}_{12}\text{H}_8\text{N}_2$ , Merck, CAS 66-71-7), ferrous sulfate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , Merck, CAS 7782-63-0), ammonium iron(II) sulfate ( $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$ , Merck, CAS 7783-85-9), sodium hydroxide ( $\text{NaOH}$ , Merck, CAS 1310-73-2), and iron disulfide ( $\text{FeS}_2$ , Sigma-Aldrich, CAS 12068-85-8). All chemicals were analytical grade and used as received. Natural pyrite was obtained from Bali, Indonesia. The pyrite was crushed into particles less than 0.105 mm and was used as catalyst without purification.

### Method

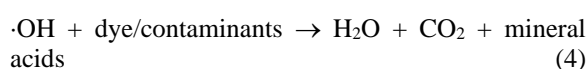
Prior to the treatment, the wastewater was passing through the filter paper to remove precipitates. Pyrite (2.5 mg) was put in a series of reaction tube and a certain amount of  $\text{H}_2\text{O}_2$  solution was added. The mixture was allowed to stand at specific time for pre-reaction stage. After that, wastewater sample was introduced and the mixture was reacted for a specific reaction time (10-120 min) before COD measurement (Lovibond, RD125). The concentration of pyrite used in experiment was 0.8 g/L. All reaction were performed at room temperature, except the COD analysis ( $150^\circ\text{C}$ , SNI 6989.73:2009).

## RESULTS AND DISCUSSION

Hydroxyl radicals play a substantial role in Fenton-based degradation system since this species is responsible in attacking contaminants to form less-harmful intermediate products and finally release the end products. Hydroxyl radicals are formed as the result of reaction between iron and hydrogen peroxide according to the following reactions:



Then, hydroxyl radicals attack any organic and/or inorganic compounds and their intermediates present in the wastewater until complete mineralization is achieved.



Reaction scheme of dye degradation by involving pre-reaction step is shown in Figure 1.

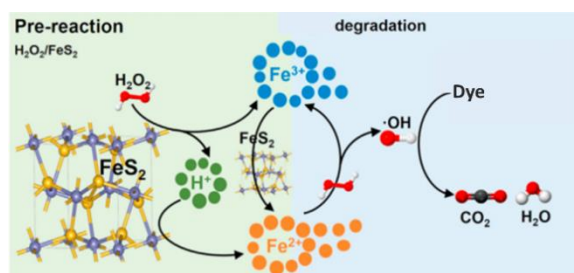


Figure 1. Reaction scheme of dye degradation by pyrite/  $\text{H}_2\text{O}_2$  system, modified from Wang et al. (2021)

### Effect of Pre-Reaction Time

In this study, pre-reaction time refers to the period when pyrite ( $\text{FeS}_2$ ) and hydrogen peroxide are allowed to react at certain time to produce hydroxyl radicals. Then the hydroxyl radicals attack contaminants, including dyes, in the wastewater to release end products. Dye degradation can be expressed in term of  $C/\text{Co}$  that final COD value and initial COD value is represented to  $C$  and  $\text{Co}$ , respectively. Accordingly, lower  $C/\text{Co}$  value means higher degradation rate. The effect of pre-reaction on wastewater degradation is shown in Figure 2.

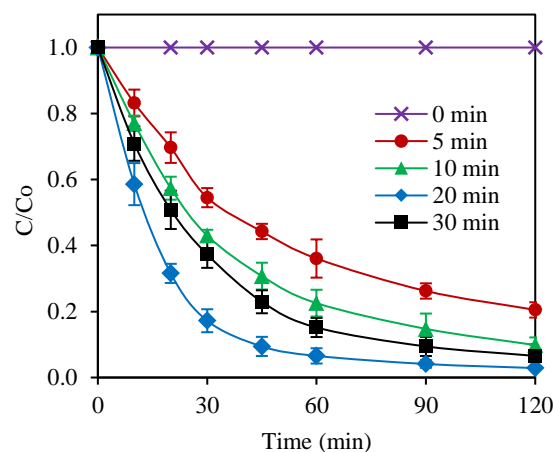


Figure 2. Effect of pre-reaction time (0-30 min) on degradation. Experiment conditions:  $\text{H}_2\text{O}_2$  concentration: 326 mmol/L, initial pH: 5.65 (real wastewater pH)

As seen in Figure 2, the degradation rate increased with reaction time up to 120 min. This can be explained by increasing the reaction time, more contact between hydroxyl radicals and the wastewater contaminants as well as their intermediates which in turn reduce the content of chemicals (low  $C/\text{Co}$ ) in the wastewater. Moreover, it can also be seen from Figure 1 that pre-reaction influences the degradation rate to certain extent. The degradation rate has been found to increase with pre-reaction up to 20 min. This could be explained by the increase of hydroxyl radicals produced by extending the contact time between pyrite and hydrogen peroxide up to 20 min. As a result, more contaminants can be degraded and led to the accelerated contaminants-degradation rate as observed in this study. However, prolonging the period of pre-

reaction up to 30 min led to decrease the degradation rate by a factor up to 1.4 (reaction time of 45 min). Extending the pre-reaction time means more free hydroxyl radicals in the solution that increase their possibility of the radicals to recombine (Mouele et al., 2020). Consequently, the addition of wastewater into the system did not improve the degradation rate due to a fewer number of hydroxyl radicals available to attack the contaminants. Further investigation on this topic will strengthen the findings. The increase of degradation rate with pre-reaction time was also reported by others (Wang et al., 2021) who observed the optimum pre-reaction time in their system is 10 min. The control experiment without pre-reaction treatment demonstrated no observable changes in COD value.

The Indonesian government regulation has stipulated the maximum COD limit for textile industry wastewater is 150 mg/L (PermenLHK No. 16/MENLHK/SETJEN/KUM.1/4/2019, 2019), which is equivalent to the ratio of  $C/C_0$  is 0.18. Based on this requirement, the optimum reaction conditions for the pre-reaction and reaction time are 20 and 30 min, respectively.

### Effect of $H_2O_2$ Concentration

As seen in Equation (3),  $H_2O_2$  and ferrous ions are responsible to the generation of hydroxyl radicals. Therefore, this study investigated the effect of  $H_2O_2$  concentration on degradation rate, and the results are shown in Figure 3.

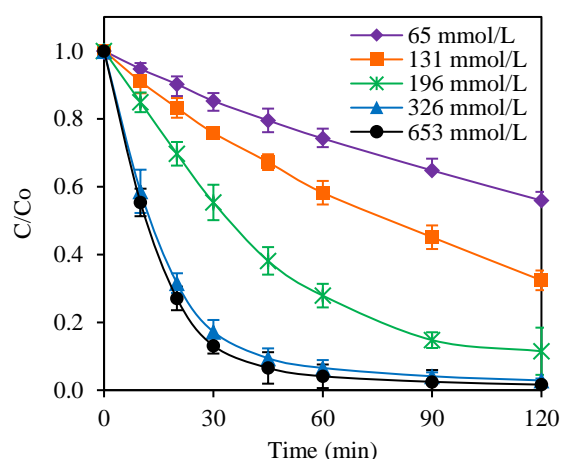


Figure 3. Effect of  $H_2O_2$  concentration (65-653 mmol/L) on degradation. Experiment conditions: pre-reaction time: 20 min, initial pH: 5.65

Figure 3 demonstrates the addition of  $H_2O_2$  at different concentrations has affected the degradation rates at certain factor. The presence of  $H_2O_2$  with a concentration of 65 mmol/L resulted approximately half of the wastewater contaminants has been degraded after the system was reacted for 120 min. Doubling the amount of  $H_2O_2$  in the system has improved the degradation by a factor of 1.75 for the same reaction time.  $H_2O_2$  enrichment up to 326 mmol/L has significantly improved the degradation

that is equivalent to the COD value of 24 mg/L. More addition of  $H_2O_2$  to 653 mmol/L did not much improve degradation since they have comparable degradation rates. Thus, the optimum  $H_2O_2$  concentration for the degradation of sample wastewater studied here is 326 mmol/L. The degradation rate of wastewater influenced by  $H_2O_2$  added into the system was also reported by others (Chen et al., 2021; Wang, 2021). This supports the results observed in this study.

### Effect of Solution pH

The degradation of batik fabric wastewater by using natural pyrite was investigated in the pH range of 3-10 while maintaining the experimental variables of  $H_2O_2$  concentration and pre-reaction time. The effect of solution pH on the degradation rate of the wastewater is presented in Figure 4.

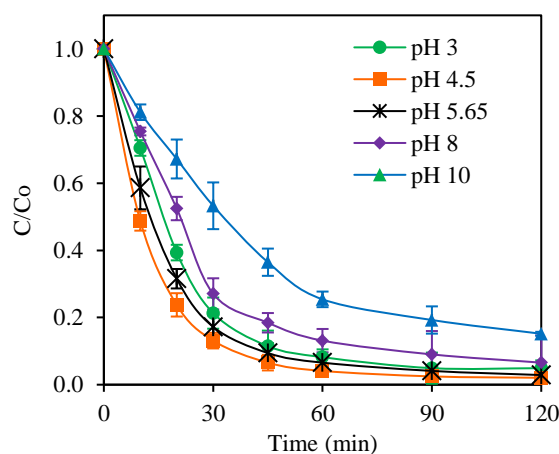


Figure 4. Effect of solution pH on degradation. Experiment conditions: pre-reaction time: 20 min,  $H_2O_2$  concentration: 326 mmol/L

It can be seen from Figure 4 that the degradation rate is affected by solution pH. At natural wastewater pH, i.e. 5.65, the degradation time required to meet the regulation (PermenLHK No. 16/MENLHK/SETJEN/KUM.1/4/2019) is 45 min. At this condition, the COD value is 61.4 mg/L. When the initial solution pH was set at 4.5, the degradation rate was comparable with the previous one. A similar trend was observed when the initial solution pH was adjusted to 3. Generally, the degradation of contaminants by classic heterogeneous Fenton reaction is favored at acidic conditions. However, the use of natural pyrite as the iron source has exhibited its ability to degrade wastewater contaminants at wider pH range (Sun et al., 2015). Our study confirmed that the wastewater degradation is comparable in the initial pH range between 3 and 5.65. When the initial solution pH was adjusted to 8, the degradation rate is slower by a factor up to 0.3. Further increasing the pH up to 10 results in a much slower degradation in all reaction times. The decrease of degradation at this condition up to 4 times compared to the real wastewater pH (5.65).

One of important parameters that determines the possibility of particular technique to be applied in

the wastewater degradation in real industry is economic factor. Since the degradation rates were comparable at pH range of 3-5.65 as described previously, thus the degradation process performed at real wastewater pH would be the most economical, and hence, the pH adjustment is not required.

Based on the results described above, the optimum operating conditions to fulfill the Indonesian government regulation (maximum COD value of 150 mg/L) are pre-reaction of 20 min, H<sub>2</sub>O<sub>2</sub> concentration of 326 mmol/L, and the reaction time of 30 min at real wastewater pH. To assess the performance of natural pyrite to degrade the wastewater sample studied here, a similar experiment was performed by using commercial FeS<sub>2</sub> instead of pyrite. Table 1 shows the comparison of degradation rate between catalysts of pyrite and commercial FeS<sub>2</sub>.

Table 1. Degradation rate of wastewater using pyrite and commercial FeS<sub>2</sub>

Catalyst	C/Co
Pyrite	0.16
Commercial FeS <sub>2</sub>	0.02

As seen in Table 1, pyrite and commercial FeS<sub>2</sub> were successful to degrade contaminants in wastewater to a certain extent. Natural pyrite can degrade the wastewater up to 84% which is equivalent to a COD value of at the end treatment is 136.67 mg/L. When commercial FeS<sub>2</sub> was used as the iron catalyst, approximately 98% of contaminants in the wastewater can be degraded. Higher degradation efficiency exhibited by commercial FeS<sub>2</sub> could be contributed by its much lower impurity content than natural pyrite. Based on the results above, it can be concluded that the wastewater of a local batik fabric can be degraded well by natural pyrite under reaction conditions investigated in this study. This offer great opportunity for further development for industry scale.

## CONCLUSION

Study on COD removal from batik wastewater was carried out by heterogeneous Fenton process using natural pyrite. Pre-reaction period to produce hydroxyl radicals is an important initial step to accelerate the degradation reaction. The optimum pre-reaction time achieved in this study is 20 min. COD removal has been found to increase in a slightly acid condition (4.5 to 5.65) and inhibited at pHs of 8 and above (10). The optimum operating conditions are pre-reaction of 20 min, H<sub>2</sub>O<sub>2</sub> concentration of 326 mmol/L, and the reaction time of 30 min at real wastewater pH.

Despite the wastewater contaminants have been successfully degraded by natural pyrite up to 84%, complete mineralization of contaminants still need to be further investigated. The degradation process may result the formation of new toxic by-products which means that the end product(s) remains toxic. Therefore, further biological tests will required both in laboratory and outdoor. Carbonates,

bicarbonates, and NOM (natural organic matters) are common compounds present in water. Those compounds may act as radical scavenger for hydroxyl radicals. Further investigation on the effect of the scavengers on the degradation rate of batik wastewater will give insight for the possibility of heterogeneous Fenton applications in industries. Stability and reusability of used catalyst is also important to evaluate the economy value of the heterogeneous Fenton process.

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