Batik Waste Degradation Using Heterogeneous Fenton Method Using Catalysts To Reduce Environmental Pollution

Pita Adis Hernanda[1], *Ida* Sriyana[1], *Sandhy Auliya* Ma'arief[2], and *Shinta* Amelia[1,*]

[1] Department of Chemical Engineering, Ahmad Dahlan University Jl. Ringroad Selatan, Kragilan, Tamanan, Banguntapan, Bantul, Yogyakarta, Indonesia
[2] Department of Electrical Engineering, Ahmad Dahlan University Jl. Ringroad Selatan, Kragilan, Tamanan, Banguntapan, Bantul, Yogyakarta, Indonesia.

Abstract. The batik industry is one of the industries that develops from time to time. Among the problems that are still a concern today is industrial waste, especially the content of dyes. Reactive dyes found in batik wastewater are very harmful in the environment, and so far only a few industries process the batik waste before disposing of it into the environment. AOPs technology is a combination of several processes such as ozone (O_3), hydrogen peroxide, UV light, titanium oxide, photocatalyst, electrolysis, electron beam, electrical discharge, and several others to produce hydroxyl radicals. One method of AOPs is the process of using fenton reagents. This study aims to identify the impact of variations that occur on the active components of batik color waste. The results showed that the use of zeolite catalysts tends to be more effective in absorbing polar components and less effective in absorbing organic matter. This statement is supported by a higher percentage of removal from natural zeolite than activated carbon which is 100%.

1 Introduction

Water is a resource produced from nature that is needed by humans to meet the needs of life. However, currently the existence of clean water is scarce due to the amount of water pollution [1]. There are several causes of clean water pollution, one of which is batik waste. The batik industry is one of various industries that continue to grow from time to time. In the process of making batik through the dyeing stage using textile dyes where the waste produced contains reactive dyes that can harm the environment. As a result of the dyeing process, the batik and textile industry has become one of the producers of liquid waste that contains dyes in the high category and contains synthetic materials that are difficult to dissolve [2]. Lately many batik industries have disposed of batik waste into the environment with no procedure for processing the waste before. Batik waste containing reactive dyes is difficult to degrade by microorganisms, thus the reactive dyes are still present in the waste in the form of search which is disposed of directly into the environment.

*Corresponding author: shinta.amelia@che.uad.ac.id

The waste produced from the batik making process also contains heavy metals in the form of Pb and Cr. The source of the heavy metals lead (Pb) and chrome (Cr) which are categorized as having properties namely toxins, the origin is coloring. Heavy metals contained in batik waste when discharged into the river body will pose a danger to human health. Chrome can cause kidney disease, liver damage and lungs. If you come into contact with the skin, it can cause irritation and if swallowed cause vomiting and abdominal pain. While lead can enter the body from humans through breathing, digestive tract or exposure. In general, water from batik processed waste has a high organic content in the category and its characteristics are alkaline. Due to its characteristics that can hold damage in the oxidative context produced by light from the sun, dyes in water from batik processed waste are difficult to degredate [3]. There are various methods that can be used to make dyes disappear, including decolorization, ozonization, electrochemical techniques, filtration with membranes, adsorption, precipitation, coagulation, and flocculation [4]. This research used a method in the form of adsorption combined against heterogeneous fenton to degrade dyes in waste with the help of activated carbon catalysts and natural zeolite.

Adsorption is a purification method that is predominantly used in various industries, one of which is to handle waste containing dyes and impurities. However, the adsorption method only removes impurities or pollutants to other media, so it is feared that saturated adsorbent waste can cause new problems related to solid waste in waters. Other methods can be used as advanced oxidation processes (AOPs). The advantages contained in this method are able to degrade harmful compounds in waste through oxidative degradation [5]. However, the reaction of fenton whose context is homogeneous has a weakness in the aspect of separation of catalysts carried out from the mixture. This resulted in a high operating budget. To overcome this, a system in the form of heterogeneous catalytic reactions can be used, namely through developing active catalysts from iron in materials that have pores, for example zeolite and activated carbon.

The impregnation method is a way to make a catalyst in the form of filling metal into the cavity from the pore through bringing the dissolved solids in the solvent into the cavity of the pore so that it can be bonded to the supporting surface such as zeolite, carbon, silica gel etc. There are several models of impregnation methods, including the wet impregnation method. This method is a stage of making catalysts where the volume of the solution used is more than the volume of the pore buffer [6]. The first step is to make contact between the solution of the salt in the metal and the surface of the carbon. The stage continues with calcination and drying to evaporate from volatile components so that metals at the active site level can be bound to metals on their supporting surfaces. Metal oxides are catalysts that can be used at the degradation stage of color waste. The metal oxidation that can be used is Fe_2O_3. In its use, metal oxides can be used in forms such as nanoparticles or realized in supporting materials. In terms of the level of ease of separation of metal oxides embedded in materials that have pores, there are advantages. Porous carbon is a very good candidate in carrier contexts due to its relatively high surface area and excellent chemical stability [7].

This study has the novelty, namely degrading color waste using heterogeneous fenton simultaneously with the adsorption process. The development substances used are activated carbon and natural zeolite. Before use, activated carbon and natural zeolite are treated first with iron oside. The iron oxide produced acts as a catalyst which can help the decomposition process of hydrogen peroxide (H_2O_2) to produce a hydroxyl group (*OH) which will degrade the reactive dye. While activated carbon and zeolite as carriers provide surface area to absorb dyes to degrade. So that there is a simultaneous system between the adsorption of activated carbon and zeolite with degradation of color waste through heterogeneous fenton reactions.

2 Methods

2.1 Tools and Materials

The tools used in this study were measuring pipettes, beakers, magnetic stiredants and stirers, stopwatches, ovens, furnaces, ultrasonicators, vial bottles for samples, and UV/Vis spectrophotometry used to analyze the concentration of surfactant waste per unit time. Meanwhile, the materials used in this study are activated carbon, natural zeolite, $Fe(NO_3)_3.9H_2O$ and isopropyl which are respectively used as catalyst carriers, iron precursors and solvents as well as batik color waste in the form of Methyl Orange, Remazol Yellow, Fast Green, Acid Red, and Methilen Blue. While hydrogen peroxide is used as the initiator hydroxyl ion.

2.2 Method

2.2.1 Preparation of Carrying Substances

Mashing the carrying agent (zeolite and activated carbon) then screening with a mesh size of <100 micrometers. Oven 50 grams of zeolite and activated carbon that has been homogenized to remove impurities for 1 hour with a temperature of 60 ºC.

2.2.2 Catalyst Preparation

Dissolving $Fe(NO_3)_3.9H_2O$ with 10 ml 0.09 M isopropyl, then made a mixture of impregnation of $Fe(NO_3)_3.9H_2O$ catalyst and its developing substances (zeolite and activated carbon) by mixing 10 ml of iron nitrate solution into 5 grams of activated carbon and 5 grams of zeolite and. Then stirred with ultrasonicator for 1 h. The homogeneous catalyst mixture is air dried naturally for 24 hours. Then calcined to remove NO_3, at a temperature of 300 ºC using a furnace for 3 hours.

2.2.3 Degradation Process in Waste

Make a synthetic color solution (Methyl Orange, Remazol Yellow, Fast Green, Acid Red, and Methilen Blue) with a concentration of 20 ppm using aquades as much as 200 ml. Then add 10 ml of H_2O_2. Then put a catalyst with a variation of development as much as 50 mg into the solution. Stirring with a magnetic stirer at a medium speed of 450 rpm, then taking samples per time with a variation in the time span of 30 minutes ranging from minutes to 0-150. Then the sample is analyzed to determine the percent removal by adsorbantion test measured by UV-Vis spectrophotometry, with aquadest blank solution.

2.2.4 UV-Vis Spectrophotometry Analysis

Determine the optimum wavelength through the use of a UV-Vis spectrophotometer. Samples at 0, 30, 60, 90, 120, and 150 minutes were measured by UV-Vis spectrophotometry with a wavelength of 571 nm. Next, a curve is made between adsorbantion and operational time. Making raw solutions for color waste (Methyl Orange, Remazol Yellow, Fast Green, Acid Red, and Methilen Blue) with a concentration of 20 ppm. Then the adsorbantion of each solution was measured at a wavelength of 571 nm using UV-Vis spectrophotometry. Furthermore, the preparation of a standard curve that gives a statement of the relationship of adsorbantion and concentration, thus obtaining the equation in the form of y = ax + b.

3 Results And Discussion

In this study, 2 types of development were used in the form of activated carbon and zeolite which had been impregnated with iron nitrate and then stirred using an ultrasonicator for 1 hour. This catalyst impregnation is done in addition to making a homogeneous mixture is also used to remove iron in the mixture. The homogeneous mixture is dried for 24 hours indoors before being advertised in a furnace for 3 hours to remove the NO_3 content. Then used activated carbon catalyst and zeolite weighing 50 mg which has been activated with 4% Fe dissolved with batik color waste solution that has been made with a concentration of 20 ppm with the addition of H_2O_2 as much as 10 ml stirred with a magnetic stirr which ranges from 0-150 minutes.

Analysis using UV-Vis Spectrophotometry is used to determine the effect of stirring time with the adsorbantion value. Before performing analysis with UV-Vis spectrophotometry, determine the standard solution that will be used to determine the wavelength. According to Khopkar quoted Yoga, The determination of calibration or standard curves in tests from spectrophotometry is based on the Lambert-Beer law where the graph of concentration to absorbance will produce a straight line. The calibration curve makes it easy to calculate the concentration of a compound in a sample that can be calculated through the use of the regression equation, y = ax + b, where y is absorbance, a is interception, x is concentration, and b is slope [8].

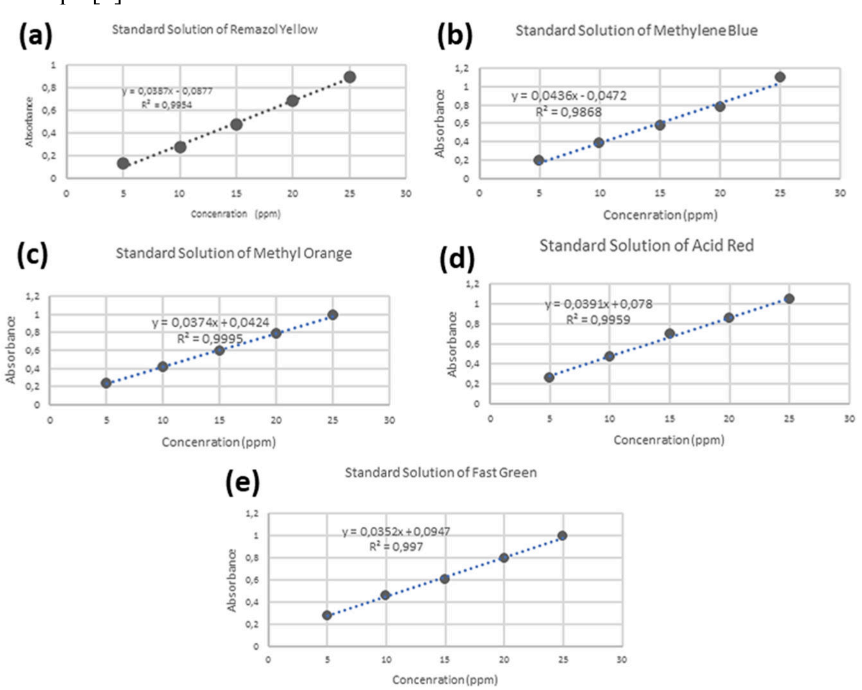

Fig. 1. Color Standard Solution Curve (a) Remazol Yellow, (b) Metylene Blue, (c) Methyl Orange, (d) Acid Red, (e) Fast Green.

Based on Figure 1. Above obtained the coefficient score of the correlation (R2) on average is close to number 1. The determination of this standard curve is determined through a standard solution in the form of a standard solution that has understood its concentration with certainty, then a linear absorbance measurement is carried out through a standard solution using Uv-Vis spectrophotometry which has a wavelength of 571 nm. The price of the correlation coefficient close to number 1 gives a linear correlation statement between the absorption that becomes the result and the concentration also has the meaning of the escalation of the value at the analyte absorption level between concentrations directly proportional to the escalation of the concentration in accordance with the coefficient of the collation R2 obtained 0.999 [9]. It can be said that the wavelength used to determine the absorbance value for batik color waste analysis is in accordance with the calibration standard, which is 571 nm.

The absorbance value produced in the analysis can be affected by the length of stirring time during degradation of batik color waste. Based on research on color waste treatment using heterogeneous fenton reagents that have been carried out, data were obtained in the form of absorbance values of each color with activated carbon catalysts and natural zeolite. From the study, the concentration value was calculated by the regression equation to obtain the percent removal of each dye according to the following graph.

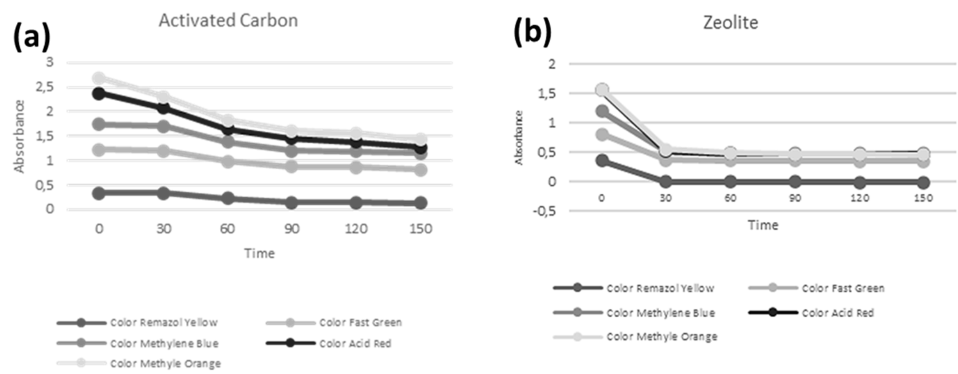

Fig. 2. The relationship between degradation time and concentration in catalysts (a) Activated Carbon, (b) Zeolite.

Based on figure 2 above, it can be seen that the longer the time used in degrading the dye, the smaller the absorbance value produced. The smaller the absorbance value, the more faded the color of the waste that has been degraded. To determine the influence of the type of catalyst used in degrading color waste can be seen based on the figure below.

From figure 3. It can be seen that the degradation process of batik waste with Fe-impregnated activated carbon and the addition of Hydrogen Peroxide shows that the use of Fe_2O_3 Activated Carbon development is more effectively applied to Red dye (Acid red) compared to other dyes such as remazol yellow, fast green, methylen blue, and methyl orange with a percentage of 100%. This is because activated carbon tends to absorb organic matter and has a more porous structure and the presence of very strong oxidative characteristics through hydroxyl radicals (OH*) which are the result of hydrogen peroxide. The hydroxyl radical will react to Fe ions to decompose the dye, thus the capacity of adsorption can increase [10].

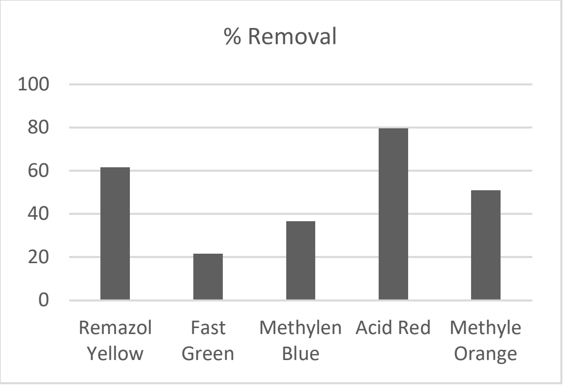

Fig. 3. Percentage of Batik Color Waste Removal with Activated Carbon / Fe_2O_3 Catalyst.

While the results of degradation of batik waste with Zeolite / Fe2O3 development substances are shown in figure 4. The results showed that the use of Zeolite / Fe2O3 development agents and the addition of Hydrogen Peroxide to zeolite catalysts were effectively applied to Acid Red, Remazol Yellow and Methyl Orange dyes. This is because zeolite has an effective tendency to absorb polar components and is not so effective in absorbing organic materials. This statement is supported by the high percent removal from natural zeolite compared to activated carbon.

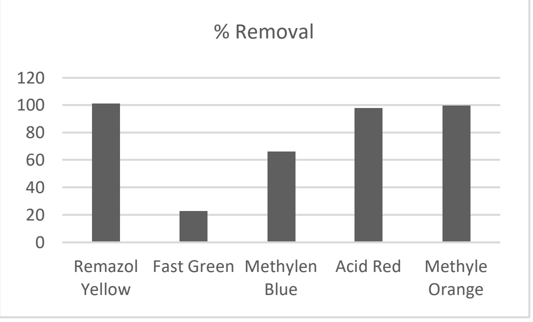

Fig. 4. Percentage of Batik Color Waste Removal with Natural Zeolite Catalyst / Fe_2O_3

4 Conclusion

Guided by the resultant research that has been discussed above, it can be concluded that degradation using activated carbon development substances is more effectively applied to acid red dyes compared to other dyes with a 100% removal percentage. While zeolite development agents are more effectively applied to methyle orange, remazol yellow and acid red dyes, this is because zeolite tends to absorb pillar components and is less effective in absorbing organic matter. In addition, the length of stirring time used to degrade waste affects the color produced during degradation and can affect its absorbance value.

References

1. S. Amelia, W. Rahmadani, L. R. Amalia, & Z. Mufrodi, Majalah Kulit, Karet, Dan Plastik, 35, 2 (2020)
2. R. Hermawan, & M. Syafila, Jurnal Teknik Lingkungan, 23, 1 (2016).
3. Apriyani, Nani. Media Ilmiah Teknik Lingkungan. (2018).

4. B. H. Hameed, A.A., Ahmad, N. Aziz, Chemical Engineering Science, 133, (2007).
5. S. Malato, J. Blanco, A. Campos, J. Caceres, C. Guillard, J. M. Herrmann, & A. R. Fernandez-Alba, Appl. Catal. B: environ. 42, 4 (2003).
6. J. Haber, J. H. Block, J. H., & Delmon, Pure and Appl. Chem., 67 (1995).
7. S. Amelia,W. B. Sediawan, Z. Mufrodi, & T. Ariyanto, Jurnal Bahan Alam Terbarukan, 7, 2 (2019).
8. I. K. W. Yoga, *Proceedings SeminarNasional FMIPA UNDIKSHA V*, (2015).
9. J. N. Miller, J. C. Miller, *Statistics and Chemometries for Analytical Chemistry Sixth Edition*. (2010).
10. N. I. Oktavitri, E. Kuncoro, M. Hayati, H. Purnobasuki, Ecol. Environ. Conserv., 25 (2019)