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Eggshell Waste as a Potential Catalyst Support for Fe203/CaCO3 in Methylene Blue Degradation Process

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Abstract. Advanced Oxidation Processes (AOPs) are a promising advanced oxidation process to degrade waste containing aromatic compounds, pesticides, and oil. In this study, the AOP process with the phantom method was used which used hydrogen peroxide as an oxidizing agent and iron salt as a catalyst. This method has been widely proven as a method for treating various types of water pollutants, one of which is methylene blue. In this study, a heterogeneous catalyst in the form of a CaCO3 composite derived from chicken eggshell waste and Fe2O3 from Fe (NO3)3. 9H2O with a variation of 1%, 2%, and 3% Fe loading using the wet impregnation method. The wet impregnation method was carried out by mixing CaCO3 and Fe (NO3)3. 9H2O using a magnetic stirrer for 8 hours at room temperature. After that the sample is filtered and oven for 1 hour at a temperature of 1200C. Then the sample that has been in the oven is calcined at a temperature of 5000C for 3 hours. Testing of the catalyst was carried out by FTIR, XRD, visual test, and UV-Vis. Each test uses a catalyst mass of 0.1 grams in the FTIR and XRD tests. Meanwhile, 0.25 grams of catalyst are needed for each variable of Fe loading and 20 ppm of methylene blue is needed with a volume of 100 ml visual and UV-Vis testing, visual and UV-Vis testing is carried out in dark conditions. In this study, the catalyst sample with a concentration of 3% Fe loading showed the most optimum results with 24% degradation of methylene blue in the 60th minute and 38% at the 120th minute.

Keywords: *AOP; degradation; eggshell; fenton; methylene.*

1 Introduction

The textile industry in Indonesia is growing rapidly, causing a lot of waste from the coloring process. The Dyes were disposed of without treatment into the waters which cause environmental effects, health, and reduced light neutralization in polluted water [1]. One of the dyes that are often used in the textile industry is methylene blue (Methylene Blue).

Methylene blue is a synthetic dye that is carcinogenic and non-biodegradable so that it cannot be decomposed by microorganisms and has an impact on health in the form of irritation to the skin, respiratory tract and the danger of liver cancer if the concentration of the dye is relatively large [2]. According to the Decree of the Minister of Environment and Forestry of the Republic of Indonesia number P.68/MENLHK/Setjen/Kum, the permissible levels of methylene blue are 5.0-10.0 ppm. So there needs to be a method to overcome this problem. One promising way is using Advanced Oxidation Process (AOPs) technology.

AOPs is a method that has been widely developed and has succeeded in degrading dyes in liquid waste. AOPs are a combination of several materials including Ozone, Hydrogen Peroxide (H2O2), Ultraviolet Light, Titanium Dioxide, Photocatalyst, Sonolysis, Fenton, and several other processes, to produce Hydroxyl Radical (•OH). OH is an active compound that has a high oxidation potential of 2.8 V, exceeding ozone which has an oxidation potential of 2.07 V [3]. Fenton is one of the AOPs methods that is often used to degrade organic compounds by the formation of free radicals OH• obtained from the reaction of H2O2 with Fe ions from Fe2O3 under irradiation conditions or without Ultra Violet (UV) radiation from the sun. In the Fenton method, hydrogen peroxide (H2O2) functions as an oxidizing agent and Fe ions as a catalyst [4]. However, based on experiments conducted by Theis et al, 1992, Fe2O3 has a weakness, namely the hydraulic conductivity of Fe2O3 is low, so additional material is needed. One way to increase conductivity is to add catalyst support from porous materials [5]. CaCO3 is one candidate for good catalyst support because of its high surface area, excellent chemical stability, high thermal stability, and low cost [6].

The chicken eggshell is one of the abundant sources of CaCO3 in Indonesia as waste. Based on data from the Directorate General of Livestock in 2013, egg production for laying and free-range chickens in Indonesia in 2012 was 1,337,030 tons per year. The composition of the shell in eggs is approximately 10% so that approximately 133,703 tons of eggshells are produced per year. The eggshell contains about 98% CaCO3 (calcium carbonate) and has 10,000 - 20,000 pores so that it has a high surface area and can absorb a solute. So that eggshell waste can be used as catalyst support to increase and balance the degradation ability of Fe2O3. The method used for the synthesis of CaCO3 impregnated Fe2O3 is the wet impregnation method [6].

Wet impregnation is a method for inserting metal into the support by immersion. The concentration of precursor ions is adjusted to the pores of the buffer used so that there is an interaction between the precursor ion solution and the buffer. Then with the capillary motion caused by the difference between the surface layers, the Fe ion solution will enter the pores of the CaCO3 buffer. This process is relatively fast but will be slow if there is air trapped in the pores of the support. Generally, the pores will be filled with a solution containing metal for about 10 seconds [7]. So in this study, the wet impregnation method was used to synthesize Fe2O3 into the pores on the surface of CaCO3 and become a catalyst for Fe2O3/CaCO3 so as to improve the properties of Fe2O3 to degrade waste dyes, especially methylene blue.

2 Material and Method

2.1 Material

Chicken eggshells waste as the CaCO3 source was collected from merchants in Balikpapan. Fe(NO3)3.9H2O (99%, CDH) was used as a source of Fe2O3. The hydrogen peroxide (30%, Sigma Aldrich) is an oxidizing agent. The dyes are from methylene blue (95% analytical grade, Sigma Aldrich). The tools used in this research are Fourier transform infrared (FTIR), x-ray diffraction (XRD), and UV-Vis spectrophotometer.

2.2 Preparation of CaCO3 Powder from Chicken Egg Shells

Preparation of CaCO3 powder from chicken eggshells was based on research conducted by Oko et al (2019). The eggshell was weighed as much as 500 grams and then washed, and the membrane and dirt attached to the eggshell were removed. The chicken eggshells were then oven for 24 hours at a temperature of 1100C then the shells were mashed using a blender and sieved on a 200 mesh sieve.

2.3 Wet Impregnation CaCO3 Powder with Fe(NO3)3.9H2O

The manufacture of Fe2O3/CaCO3 using the wet impregnation method was based on research by Buckley et al (2010). The Fe(NO3)3.9H2O salt solution with varying concentrations of 1%, 2%, 3% w/v was put into a bottle that contained 2 grams of CaCO3 from chicken eggshells. The mixture of CaCO3 and Fe(NO3)3.9H2O salt solution was then stirred with a stirring speed of 350 rpm at a temperature of 300C for 8 hours, then filtered and in an oven at a temperature of 1200C for 1 hour and continued with the calcination process at a temperature of 5000C for 3 hours.

2.4 Sample Characterization

Fe2O3/CaCO3 catalyst was analyzed by function using FTIR (Fourier Transform Infrared Spectroscopy), crystal structure analysis using XRD (X-Ray Diffraction), and morphological analysis using SEM

2.5 Methylene Blue Degradation

Methylene Blue degradation was carried out in the dark. 5 ml of H2O2 and CaCo3/Fe2O3 catalyst were added to 100 ml of Methylene Blue (10 ppm). After that, the samples were observed using UV-Vis at a wavelength of = 670 nm in each time interval for 2 hours.

3 Results and Discussion

3.1 Fourier Transform Infrared Spectroscopy (FTIR) Test Results

The FTIR test was carried out to determine the functional groups of each sample on chicken egg shell samples, CaCO3/Fe2O3 catalyst with Fe loading 1%, 2%, and 3%. Figure 1. and Table 1 are graphs of the results of the FTIR test.

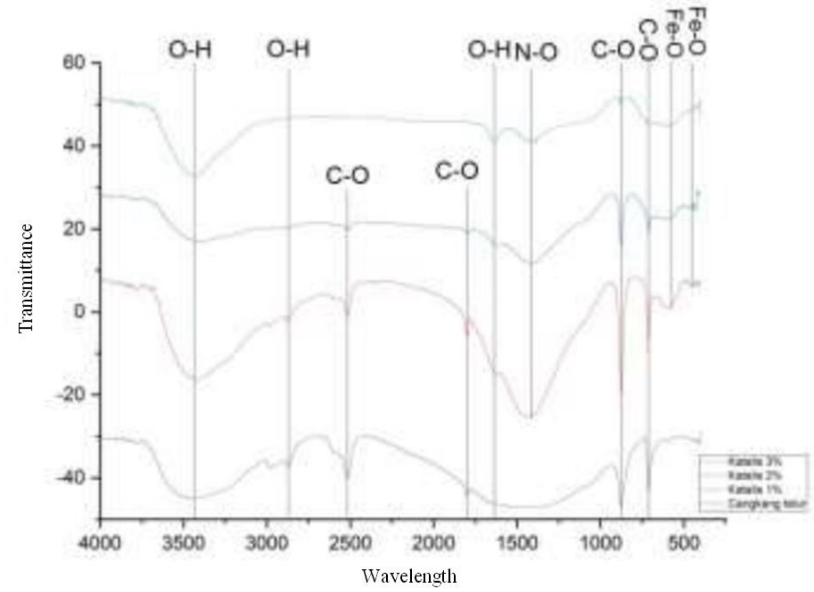

Figure 1 Graph of FTIR Test Results.

Table 1 Functional group of catalyst.

No	Chicken Eggshell	1% Fe_2O_3	2% Fe_2O_3	3% Fe_2O_3	Functional Groups
1	3432	3432	3432	3432	*Stretching* O-H
2	2921	2921	2921	-	*Stretching* O-H
3	2518	2518	2518	-	*Stretching* C-O
4	1798	1798	1798	-	*Stretching* C-O
5	1637	1637	1637	1637	*Stretching* O-H
6	-	1423	1423	1423	*Stretching* N-O
7	875	875	875	875	*Stretching* C-O
8	730	730	730	730	*Stretching* C-O
9	-	576	576	576	*Stretching* Fe-O

Figure 1 and table 1 shows that the wavelengths 3432, 2921, and 1637 are O-H Stretching vibrations. At wavelengths 2518, 1798, 875, and 730 are vibrations of C-O stretching [8]. While at 1350 wavelength is the vibration of N-O [9]. At wavelengths 450 and 576 are vibrations of Fe-O stretching [10]. This indicates that the Fe-O group has been successfully impregnated into CaCO3 as evidenced by the presence of Fe-O groups.

3.2 X-Ray Diffraction (XRD) Test Results

Figure 2 (a) shows that there is CaCO3 in the sample of chicken eggshells shown at peak 2Ө with angles of 23.240, 29.60, 35.860, 39.50, 42.850, 47.220, and 57.20. This is in accordance with research conducted by Angboriboon (2012). Based on the results of the analysis of Figure 2 (b) on the CaCO3/Fe2O3 catalyst sample with a 2% Fe loading variable, it shows that the CaCO3 compound derived from chicken eggshells has peak accumulation with Fe2O3 compounds this is due to the addition of Fe loading in the catalyst sample [9]. This can be seen at peak 2Ө with an angle of 23,240, 47,220, 48,700, and at an angle of 57,20. Figure 2 (c) is a sample of CaCO3/Fe2O3 catalyst with a 2% Fe loading variable, there is a reduction in CaCO3 compounds due to the addition of 2% Fe compounds. The results of XRD analysis can be seen in the graph, the amount of Fe2O3 and CaCO3 compounds formed is almost the same, this can be observed at peak 2Ө with angles of 23.240, 35.70, 39.50, 43.60, 47,220, 48,700, and at angles of 57.20. Where at that angle occurs peak accumulation between Fe2O3 and CaCO3 compounds. Figure 3 (d) which is a CaCO3/Fe2O3 catalyst with a

3% Fe loading variable shows the amorphous crystal structure results. The reduction in the number of CaCO3 compounds in the 3% Fe loading variable is in accordance with the results of the FTIR test where the FTIR test results for the catalyst with a 3% Fe loading variable indicate a termination of the CO fungi group from the CaCO3 compound due to the addition of 3% Fe to the catalyst so that the XRD graph results show the concentration Fe2O3 appears more than in the other XRD graph results.

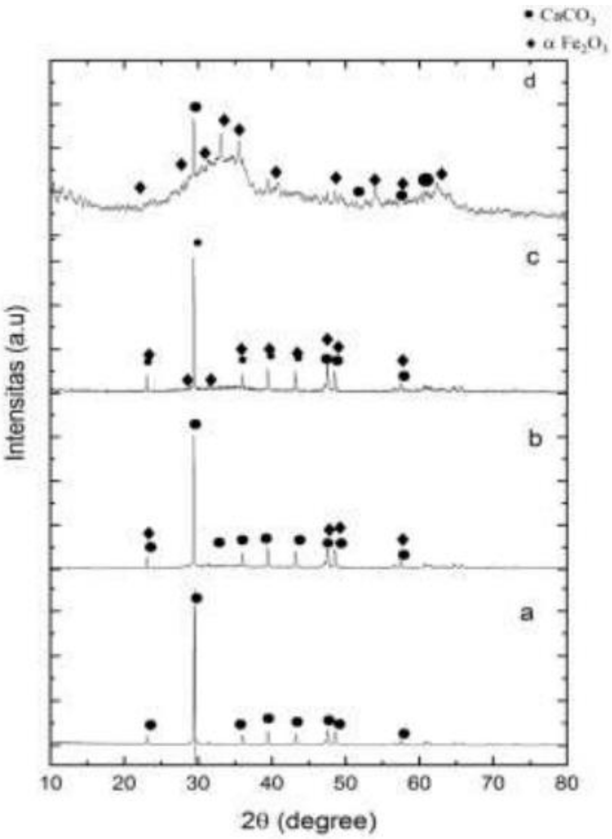

Figure 2 XRD Analysis of 3% Fe2O3/CaCO3 Catalyst with Egg Shell.

3.3 UV-Vis Result

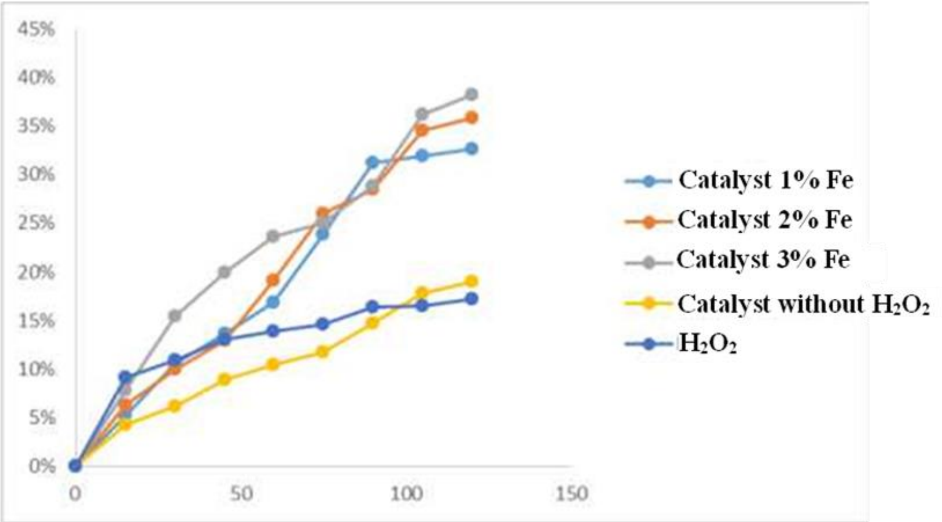

Figure 3 Methylene Blue Degradation Chart.

Table 2 Methylene Blue Degradation Results.

No	Variable	Time at 60	Time at 120
1	Catalyst without H_2O_2	11%	19%
2	Catalyst 1%	17%	33%
3	Catalyst 2%	19%	36%
4	Catalyst 3%	24%	38%
5.	H_2O_2 without catalyst	14%	17%

UV-Vis Spectrophotometer testing was carried out for 2 hours at a wavelength of 670 to see the degradation that would occur in the methylene blue solution. From figure 3 and table 2, it was found that the CaCO3/Fe2O3 catalyst without the addition of H2O2 was able to degrade 11% of methylene blue at the 60th minute and 19% at the 120th minute. The UV-vis test results with methylene blue samples with H2O2 without the addition of a catalyst, it was able to degrade the solution. as much as 14% at the 60th minute and 17% at the 120th minute. The Fe2O3/CaCO3 catalyst with a variable loading of Fe as much as 1% was able to degrade 17% methylene blue solution at 60 minutes and was able to degrade 33% methylene blue solution in minutes on the 120th Fe2O3/CaCO3 catalyst with a

Fe loading variable of 2% able to degrade 19% methylene blue solution at 60 minutes and able to degrade 36% methylene blue solution at 120 minutes. And on the Fe2O3/CaCO3 catalyst with variable loading Fe as much as 3% was able to degrade 24% methylene blue solution at 60 minutes and was able to degrade 38% methylene blue solution at 1 minute 20. Based on the results of this test, it was found that the best degradation results of methylene blue solution were 3% catalyst.

4 Conclusions

CaCO3/Fe2O3 catalyst was successfully made by the wet impregnation method. The addition of loading Fe is able to remove some of the compounds contained in eggshells thereby increasing the surface absorption process and the addition of loading Fe on the CaCO3/Fe2O3 catalyst can increase the degradation of methylene blue so that the most optimum CaCO3/Fe2O3 catalyst is a catalyst with a variable loading of 3% Fe.

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References

[1] Karthic, S., Murugesan. S., Suresh. S. & Raj S.P., *Nanostructured CuO Thin Films Prepared Through Sputtering for Solar Selective Absorbers*, Journal of Solar Energy. **1**(6), 2013.

[2] Wijayanto, A.T., *Fotodegradasi Metilen Biru Menggunakan Komposit TiO2- SiO2*, Skripsi. Fakultas Sains dan Teknologi Universitas Islam Negeri Sunan Kalijaga, YogyakartA, 2013.

[3] Wardiyati Siti, Sari Hasnah Dewi, Adel Fisli., *Deklorinasi Limbah Industri Batik Menggunakan Proses Fenton dan Foto Fenton*, Jurnal Sains Meteri Indonesia, **14**(2), pp. 131-135, 2012.

[4] Castro, C.S., Guerreiro, M.C., Oliveira, L.C.A., Goncalves, M. & Anastacio, A.S., *Iron Oxide Dispersed Over Activated Carbon: Support Influence on The Oxidation of the Model Molecule Methylene Blue*, Applied Catalysis A: General, **367**, pp. 53-58, 2009.

[5] Amelia, S. & Mufrodi, Z., *Uji Aktivitas Adsorben Karbon Aktif Tempurung Kelapa Termodifikasi dengan Active Site Fe2O3*., **5**(2), pp. 51-55, 2018.

[6] Ahmed, S. & Ahsan, M., *Synthesis of Ca-hydroxiapatite Bioceramic from Egg Shell and its Characterization*, Bangladesh Journal of Scientific and Industrial Research, **43**(4), pp. 501-512, 2008.

[7] Lusi Ernawati., Ruri Agung Wahyuono., Inggit Kresna Maharsih., Ade Wahyu Yusariarta., Andromeda Dwi Laksono., Christina Wahyu Kartikowati. & Asep Bayu Dani Nandiyanto, *Fotodegradasi Zat Pewarna Tekstil (Rhodamin B) Menggunakan Adsorben berbasis Material Komposit Kalsium Titanate (CaTiO3),* Jurnal Teknik Kimia, 2020.

[8] Petcharoen, K. & Sirivat, Anuvat., *Synthesis and characterization of magnetite nanoparticles via the chemical co-precipitation method*. Materials Science and Engineering: B. **177**. Pp. 421–427, 2012. 10.1016/j.mseb.2012.01.003.

[9] Oulego P, Laca A, Calvo S. & Díaz M., *Eggshell-supported Catalysts for the Advanced Oxidation Treatment of Humic Acid Polluted Wastewaters*. Water. 2020; 12(1):100. https://doi.org/10.3390/w12010100

[10] Aragaw, B.A., Pan, C.J., Su, W.N., Chen, H.M., Rick, J. & Hwang, B.J., *Facile one-pot controlled synthesis of Sn and C codoped single crystal TiO2 nanowire arrays for highly efficient photoelectrochemical water splitting*. Appl. Catal. B Environ. **163**, pp. 478–486, 2015.

[11] Angboriboon, K. R. & Unanuruksapong, S. A., Irivat., *reparation and properties of calcium oxide from eggshells via calcination*. Scorpus ID: 201835201