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Reducing COD Levels of Batik Waste Using Chicken Egg Shells and Tea Dregs

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Abstract *– In the last ten years, the batik industry has experienced very rapid growth. This provides benefits but also has adverse effects on humans and the environment because the sector generates waste. Batik liquid waste contains chemical compounds that can increase the COD value. Alternative treatment of liquid waste from batik factories is the biosorption process using biosorbent from chicken egg shells and tea dregs. This study aimed to investigate the effect of variations in the biosorbent ratio, contact time, and initial pH of the sample on changes in COD. In this study, the acid activation method was used to increase the ability of the biosorbent to absorb the COD content in the batik industry wastewater. This research method uses the Response Surface Methodology (RSM) method, where the biosorbent made is then contacted with batik wastewater to determine the decrease in COD levels contained in it. The critical value was achieved when the material ratio was 12.3270 grams of eggshell : 2.6730 grams of tea dregs, with a contact time of 47.1281 minutes at a pH of 1.71281. The best results were obtained in sample 5 with a biosorbent ratio of 11.25:3.75, contact time of 50 minutes, and initial pH 2 with a decrease in COD levels of 77%.*

Keywords: *acid activation; chicken egg shells; COD rate; tea dregs.*

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INTRODUCTION

The batik industry's proliferation impacts increasing sources of environmental pollutants, especially air pollution. Batik industrial wastewater generally contains heavy metals (Zn, Cu, Cr, Cd, Ni, Pb, Fe, and Ag), free NH_3, sulfides, organic materials such as phenol, and chemicals such as NaOH, oils, and fats. The presence of these substances causes batik liquid waste to have levels of BOD, COD, TSS, and turbidity (Saputri, 2016). The high level of COD in batik liquid waste will reduce the quality of water sources polluted by this waste, so there needs to be a processing step before batik liquid waste is discharged into the environment (Nurlela, 2018).

One technique that can be used in wastewater treatment is adsorption. In the adsorption process, there are several influencing factors, including the adsorbent's characteristics, particle size, surface area, adsorption properties, temperature, system pH, and contact time (Azzahra and Taufik, 2020). Some raw materials used as adsorbents include sawdust, light coal, coconut shells, oil palm shells, coffee, tea dregs, rice husks, rubber seed shells, castor bean shells, and candlenut shells (Sudarja and Caroko, 2012). In addition to the materials previously mentioned, currently, one of the popular adsorption media to study is the use of organic waste (Ilmi, 2018).

Chicken egg shells and tea dregs are solid wastes from households, restaurants, and industries produced in large quantities but have not been utilized optimally. Calcium carbonate ($CaCO_3$) is the most considerable content in egg shells, where calcium carbonate is an adsorbent (Purwaningsih *et al*., 2021). The research conducted by Purwaningsih

(2021) showed that chicken egg shells could reduce COD levels with a yield of 87% at 60 minutes. In addition to chicken egg shells, tea dregs can be used as an alternative raw material in the manufacture of biosorbents, as in Retnowati's research (2005) which has an efficiency of up to 98% against the removal of COD levels. In this study, the tea dregs used contained cellulose, hemicellulose, and lignin.

The research that has been carried out in this paper is the manufacture of biosorbents made from chicken egg shells and tea dregs which are then activated using sulfuric acid. Previous studies underlie this research to further develop previous research by combining two raw materials highly effective in reducing COD levels from batik industrial wastewater.

METHODOLOGY

The materials used in this study were chicken eggshell waste, tea dregs, H_2SO_4, CH_3COOH, NaOH, aquadest, pH indicator paper, and batik industry waste samples. In addition, chicken eggshell waste was obtained from bakery shop waste, tea dregs were obtained from food stalls, and waste samples were obtained from water left over from batik production in Kampung Batik Laweyan, Surakarta City. Meanwhile, other chemicals were obtained from the Indrasari Chemical Store, Semarang.

The tools used in this research are measuring cup, beaker, erlenmeyer, watch glass, analytical balance, dropper, magnetic stirrer, funnel, spoon, thermometer, grinder, oven, sieve, desiccator, and UV-Vis Spectrophotometer.

Material Preparation

The manufacture of biosorbents begins with the preparation of materials carried out separately between chicken egg shells and tea dregs. First, wash the chicken egg shells and tea dregs using aquadest. Then it was ground using a grinder and sieved using a 40 mesh sieve. After being sifted, the egg shells and tea dregs were dried at 105°C for 1 hour and 30 minutes. After drying, the egg shells and tea dregs are stored separately in a desiccator (Purwaningsih *et al*., 2021).

Activation Process

Chicken eggshell powder and tea dregs which were the result of the preparation, were then activated separately using sulfuric acid. The first step is to weigh each powder as much as 300 grams. The powder was immersed in a 0.05 N H2SO4 solution and stirred for 90 minutes. After that, the powder was filtered and washed using distilled water until a neutral pH was obtained. After obtaining a neutral pH, the eggshell powder and tea dregs were filtered again to separate the powder from the water. The powder was dried using an oven at the same temperature of 105°C for 1 hour 30 minutes. The activated powder is then stored in a desiccator and can be used as a biosorbent (Purwaningsih *et al*., 2021).

Adsorption Process

The activated biosorbent is then used as an adsorbent in the batik industry wastewater.

Table 1. Independent Variabels

Run	Eggshell : Tea dregs (g/g)	Contact Time (minutes)	Initial pH (-)
1	1 : 3	50.00000	2.00000
2	1 : 3	50.00000	4.00000
3	1 : 3	70.00000	2.00000
4	1 : 3	70.00000	4.00000
5	3 : 1	50.00000	2.00000
6	3 : 1	50.00000	4.00000
7	3 : 1	70.00000	2.00000
8	3 : 1	70.00000	4.00000
9	0,71 : 3,29	60.00000	3.00000
10	3,29 : 0,71	60.00000	3.00000
11	1 : 1	47.12811	3.00000
12	1 : 1	72.87189	3.00000
13	1 : 1	60.00000	1.71281
14	1 : 1	60.00000	4.28719
15	1 : 1	60.00000	3.00000
16	1 : 1	60.00000	3.00000

*chicken eggshell: tea dregs with a total mass of 15 grams

First, prepare the sample and adjust the pH according to the variable. Then, weigh the biosorbent according to the variable as well. Then enter the biosorbent into 250 mL of the batik industry liquid waste sample and stir using a magnetic stirrer at a speed of 130 rpm with a time according to the predetermined variable. Furthermore, COD levels were analyzed (Pratama, 2017).

RESULTS AND DISCUSSION

Biosorbent Moisture Content

The quality of the adsorbent in the water content test is determined based on SNI 06-3730-1995.

Table 2. Results of Analysis of Water Content Biosorbents of Tea Dregs and Chicken Egg Shells

No	Biosorbent	Parameter	SNI	Test Result
1.	Tea dregs	Water Content	Maks 4.4 %	0.88%
2.	Chicken			0.18%

eggshell

The results of testing the water content of the biosorbent can be seen in Table 2, which shows that the water content of the biosorbent produced has complied with SNI 06-3730-1995, with the water content of tea dregs and eggshells being 0.88% and 0.18%, respectively. Thus, it can be concluded that the resulting biosorbent has good quality.

Biosorbent Ash Content

The quality of the adsorbent in the ash content test is determined based on SNI 06-3730-1995.

Table 3. Results of Analysis of Ash Content of Tea Dregs and Egg Shell Biosorbents

No	Biosorbent	Parameter	SNI	Test Result (%)
1.	Tea dregs	Ash Content	Maks 2.5 %	28.57
2.	Chicken eggshell			6.15

The test results for the ash content of the biosorbent can be seen in Table 3, which shows that the ash content of the biosorbent produced does not meet SNI 06-3730-1995 with the ash content of tea dregs and eggshells of 28.57% and 6.15%, respectively. The high ash content is due to the formation of mineral salts during the activation process using an acid solution which then forms fine particles of the mineral salt. This can be due to the mineral content in the biosorbent at the activation time (Sa'diyah *et al.*, 2020).

Analysis of the pH of the Batik Industry Liquid Waste

From the observations obtained, the value of the batik industry wastewater is shown in Table 4:

Table 4. Results of measuring the pH of the Batik Industrial Liquid Waste

Sample	Initial pH (-)	Final pH (-)
1	2.000000	6.3
2	4.000000	6.5
3	2.000000	6.7
4	4.000000	7.2
5	2.000000	7.4
6	4.000000	7.6
7	2.000000	7.8
8	4.000000	7.9
9	3.000000	6.8
10	3.000000	7.8
11	3.000000	6.7
12	3.000000	7.4
13	1.712811	7.1
14	4.287189	7.2
15	3.000000	7.3
16	3.000000	7.3

From Table 4, can be seen that the pH level of the batik industry wastewater before and after treatment changed. The pH level before contact with the biosorbent ranges from 2-4, which is an acidic pH, and the pH after contact with the biosorbent can be said to be close to neutral because it ranges between pH 6-7. Egg shells contain calcium carbonate in about 87% - 97% (Lucio *et al.*, 2018). Calcium carbonate is alkaline which can raise the pH of the water. This is in line with research by (Novianti, Fitria and Kadaria, 2019), where the use of a filter column filled with eggshell filter media can increase the pH of peat water.

Analysis of Reduction of COD Levels in Batik Industry Liquid Waste Using *Response Surface Methodology* (RSM)

Response Surface Methodology (RSM) is a multiple regression analysis using empirical statistical techniques. In this study, the Central Composite Design was used, which is a practical design in providing a response, which in this study is in the form of a percentage reduction in COD levels that biosorbents can absorb. The dependent variable in this study was the decrease in COD levels of the batik industrial wastewater. The independent variables in this study were the ratio of materials, initial pH of the sample, and contact time. The data that has been obtained can be seen in Table 5.

Table 5. Tabulated Data on Decrease in COD Levels in Batik Industry Liquid Waste by Biosorbent

Eggshell : Tea dregs (-)*	Contact Time (minutes)	Initial pH (-)	Decrease in COD Levels (%)
1 : 3	50.00000	2.00000	38
1 : 3	50.00000	4.00000	40
1 : 3	70.00000	2.00000	38
1 : 3	70.00000	4.00000	39
3 : 1	50.00000	2.00000	77
3 : 1	50.00000	4.00000	75
3 : 1	70.00000	2.00000	69
3 : 1	70.00000	4.00000	67
0.71 : 3.29	60.00000	3.00000	24
3.29 : 0.71	60.00000	3.00000	74
1 : 1	47.12811	3.00000	59
1 : 1	72.87189	3.00000	49
1 : 1	60.00000	1.71281	49
1 : 1	60.00000	4.28719	41
1 : 1	60.00000	3.00000	51
1 : 1	60.00000	3.00000	51

*chicken eggshell: tea dregs with a total mass of 15 grams

A regression coefficient is generated from the % decrease in COD levels, which can be seen in Table 6.

Table 6. Model Summary Response Surface Regression Decrease in COD

S	R-sq	R-sq(adj)	R-sq(pred)
4.94126	92.34%	90.3%	86.03%

In Table 6, it can be seen that the R-Square adjust value is 0.9043 or 90% which means that 90% of the value of the dependent variable (% decrease in COD levels) is influenced by the independent variables contained in the study (material ratio, contact time and sample pH). In comparison, the remaining 10% is influenced by other factors. Then the regression equation can be written as:

Decrease in COD Level = 36.5 + 4.652 Biosorbent Ratio - 0.264 Contact Time - 1.00 initial pH

The results of the analysis of variance can be seen in Table 7.

Table 7. Analysis of Variance Response Regression Decrease in COD Levels

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Regression	3	3532.94	1177.65	48.23	0.000
Biosorbent Ratio	1	3442.79	3442.79	141.01	0.000
Contact Time	1	78.87	78.87	3.23	0.097
Initial pH	1	11.28	11.28	0.46	0.510
Error	12	292.99	24.42		
Lack-of-Fit	11	292.99	26.64	*	*
Pure Error	1	0.00	0.00		
Total	15	3825.94			

In the ANOVA table in the linear section, the P-values for the biosorbent ratio and contact time are 0.000 and 0.097, respectively, where this value is smaller than (α = 0.05), which means that the variable biosorbent ratio and contact time give a significant effect on the percentage of COD level reduction in batik industrial wastewater. In comparison, the P-value at the initial pH of the sample is 0.510, where this value is more significant than (α = 0.05) so that the initial pH of the sample does not significantly affect the percentage decrease in COD levels in batik industrial wastewater. In addition, this model shows a significant correlation in the F value of Fisher's test on the ratio of the biosorbent material of 141.01, the contact time of 3.23, and the initial pH of the sample of 0.46.

From the data obtained and analyzed, a Pareto diagram can be made to help identify the significant factors that affect the percentage reduction in COD levels of the batik industry wastewater resulting from the experiment. The Pareto diagram can be seen in Figure 1.

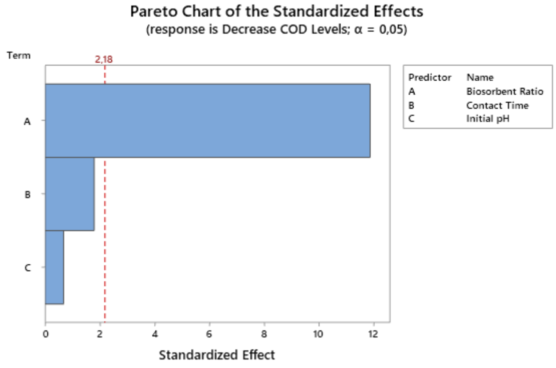


Figure 1. Pareto Diagram of the Effect of Independent Variables on the Percentage of Decrease in COD Levels

The Pareto diagram in Figure 1 shows that the biosorbent ratio factor has the most significant effect on the percentage reduction in the resulting COD levels. Then in the second order, there is a contact time variable that has an impact on the percentage of COD level reduction, and the variable that has a minor effect on the resulting COD level decrease is the initial pH variable of the sample.

After performing regression analysis on RSM, it is necessary to know the residual plot of the resulting water content. Residual is the difference between the dependent variable or Y with Y prediction. Y prediction itself is a Y value based on the regression equation results. The resulting plot residual can be seen in Figure 2.

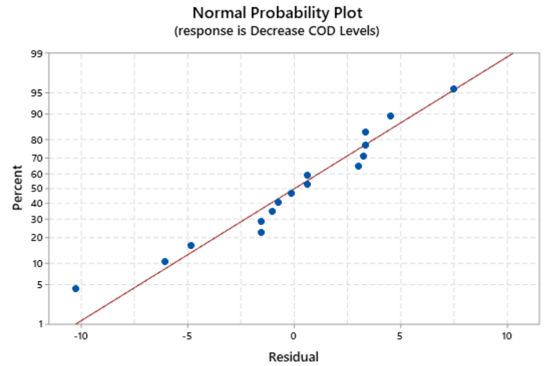
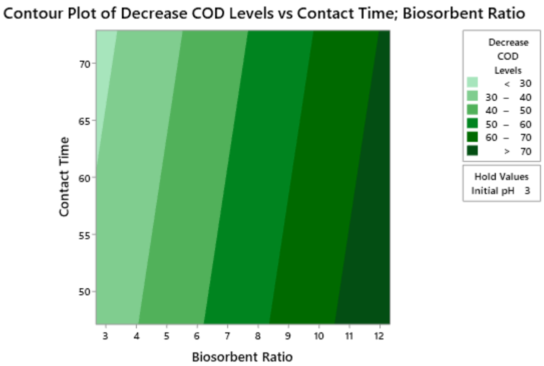
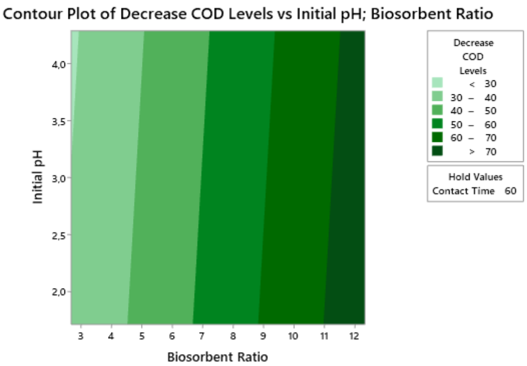


Figure 2. Comparison of Experimental Data with Estimated Percentage of Decrease in COD Levels

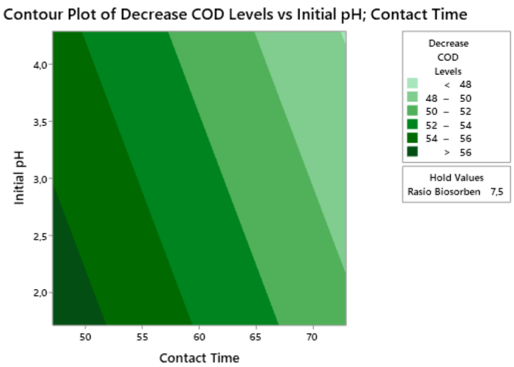
Figure 2 explains that the closeness of the estimated value to the model is close to the value obtained from the experimental results. Furthermore, the plot values on the graph show a pretty good correlation between the observed and estimated values because the deviations between these values approach a linear line that is not randomly distributed. From this, it can be concluded that the residuals are normally distributed.



(a)



(b)

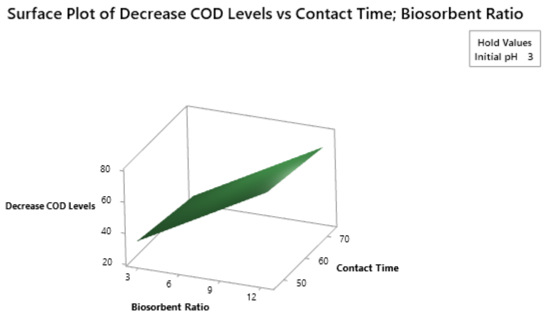


(c)

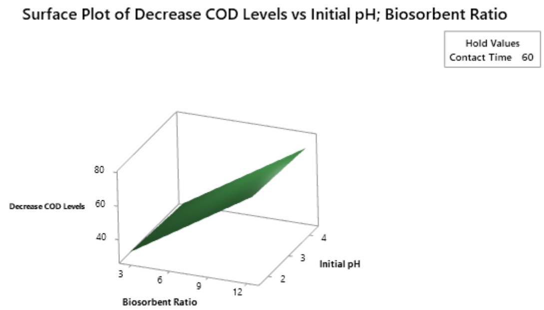
Figure 3. Contour Plots Effect of Independent Variables on Reduction of COD Levels in Batik Industry Liquid Waste

In Figure 3(a), the effect of the biosorbent ratio and contact time on the % reduction in COD, it can be seen that the most optimum part (the most significant decrease in COD content occurs) is marked with a dark green colour. This is because optimum conditions were obtained when the biosorbent ratio was 9-12 grams and contacted for 50-70 minutes. Then in Figure 3(b), the effect of the ratio of the material and the initial pH of the sample on the % reduction in COD, the optimum conditions are obtained at the ratio of 11-12 grams of material and the initial pH of the sample is 2-4. Meanwhile, for the effect of contact time and initial pH of the model on the % reduction in COD, the optimum conditions were obtained when contacted for 50-55 minutes at an initial pH of 2-3 samples.

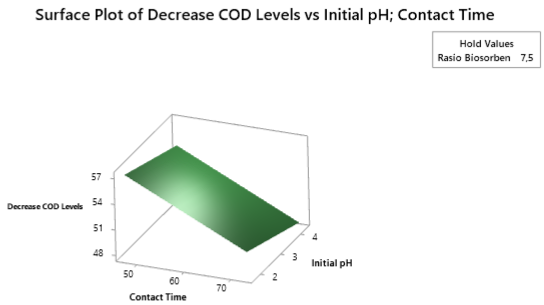
Furthermore, surface plots can be used to confirm the results of the contour plots, which can be seen in Figure 4.



(a)



(b)



(c)

Figure 4. Surface Plots for the Effect of Independent Variables on the Percentage of COD Levels in Batik Industry Liquid Waste

In Figure 4, in part (a), which is the effect of material ratio and contact time on decreasing COD levels, we can see that the most optimum part (the most significant % decrease in COD content) is marked at the right end of the highest curve sheet, and is at a material ratio of 9-12 grams and a contact time of 50-70 minutes. The greater the ratio of the biosorbent material, the lower the percentage of COD in the batik liquid waste produced. Then in part (b), the effect of sample pH and material ratio on decreasing COD levels, we can see that the most optimum amount (the most significant % decrease in COD levels) is marked by the highest end of the curve on the right. There is a material ratio of 9- 12 grams and a pH of 2-4. The greater the biosorbent proportion, the more significant the percentage reduction in COD levels, while the initial pH of the sample has no considerable effect. Then for part (c), the impact of sample pH and contact time on decreasing COD levels, we can see that the most optimum amount (% decrease in COD levels) is marked by the highest end of the curve, which is on the left at the contact time of 54-57 minutes and the pH of the sample. 2-4.

Table 8. Predicted Value of Optimal Decrease Percentage at Critical Values

Sol	Material Ratio (-)	Contact Time (minutes)	Initial pH (-)	Decrease COD Level Fit (%)	Comp. Desirability
1	3,29 : 0,71	47,1281	1,71281	79,7005	1

The critical value can be seen in Table 8. From the table, it can be concluded that the critical value for the optimization condition of the percentage reduction in COD levels of the batik industry wastewater is achieved when the material ratio is 12.3270, the contact time is 47.1281 minutes, and the initial pH of the sample is 1.7128 with a value of prediction of COD percentage of 79.7005%.

Adsorption Isotherm

From the experimental data obtained, the ability to reduce COD levels of the eggshell biosorbent and tea dregs was then plotted into a graph seen in Figure 5.

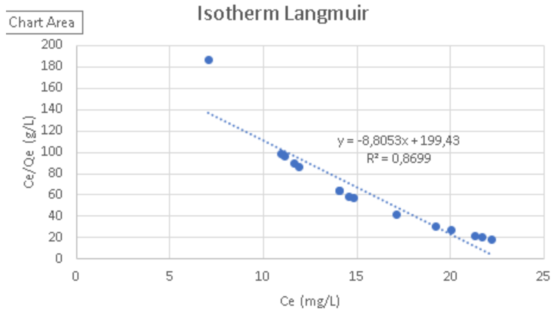


Figure 5. Graph of Langmuir Isotherm Pattern

Figure 5 shows the shape of the trend of the Langmuir isotherm so that it can be stated that the results of the adsorption isotherm for decreasing COD levels in liquid batik waste with eggshell and pulp biosorbent follow the Langmuir isotherm. Furthermore, from the results of the graph of the Ce/Qe and Ce relationship, it is obtained an equation in the form of a linear equation y = -8.8053x + 199.43 with a value of R^2 = 0.8699, which can be concluded that the graph of the results of the Ce/Qe and Ce relationship is modelling of Langmuir isothermal.

CONCLUSION

Biosorbent is a solid substance that can absorb (adsorption) from a fluid phase. This study focuses on utilizing chicken egg shells with the activation method using H_2SO_4 to reduce COD levels of batik industrial wastewater.

Based on the results obtained, the best percentage reduction in COD levels was achieved when the material ratio was 12.3270 grams of eggshell : 2.6730 grams of tea dregs, the contact time was 47.1281 minutes, and the initial pH of the sample was 1.7128 with a predictive value for COD presentation of 79.7005%.

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