Journal of Vocational Studies on Applied Research

Optimization of Biosorbent on Cd(II) Metal Biosorption Using Duck Eggshell Waste

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Abstract - *Every year the production of duck eggs in Indonesia increases, and this causes an increase in duck eggshell waste.. Duck eggshell waste has components that can be utilized into a biosorbent. Improve the quality of the biosorbent can be done with an activation method and immobilization method. This study aimed to determine the effectiveness of biosorbent made from duck eggshell waste in absorbing Cd(II) metal. . In this study, duck eggshells were activated with physical activation by heating in a furnace at a temperature of* 900^oC *for 2 hours. In addition, the adsorbent can be immobilized with alginate to improve the quality. The Independent variables of this study are biosorbent mass, contact time and concentration of cadmium solution. Critical values for Cd levels optimization condition were accomplished when the biosorbent mass 1.45 grams, contact time 100 minutes and Cd solution concentration 86 ppm with a percentage decrease in Cd levels in the amount of 89%.*

Keywords: *biosorbent, duck eggshell, immobilization.*

Received: June 06, 2022 Revised: September 17, 2022 Accepted: December 20, 2022

Doi: http://dx.doi.org/10.14710/jvsar.v4i2.14749
[How to cite this article: Tasmalia, R., Prameswari, N.H., and Paramita, V. (2022). Optimization of Biosorbent on Cd(II) Metal Biosorption Using Duck Eggshell Waste. *Journal of Vocational Studies on Applied Research, 4*(2), 61-65. doi: http://dx.doi.org/10.14710/jvsar.v4i2.14749]

INTRODUCTION

With increasing population and human activities, millions of tons of various wastes and pollutants are discharged into the environment along with a large number of other organic and inorganic pollutants. This problem could lead to a lack of sufficient water supply for about 2 billion people in 60 countries and more (Godwin et al., 2016). Highly toxic heavy metals such as lead, cadmium, chromium and others, are discharged into the water by industrial activities such as battery production, electronics, metal fabrication, paint production, petroleum refining and steel manufacturing. These heavy metals are not biodegradable and adversely affect the environment and human health. Therefore, an effective solution is needed to reduce these pollutants (Deng et al., 2018). Biosorbent is an adsorbents made from various biomass sources, such as agricultural waste, forestry waste and food waste by pyrolysis and chemical or thermal activation in the absence of oxygen (Kiggundu & Sittamukyoto, 2019). One of alternative adsorbent is duck eggshell waste. Based on data sourced from statistical data on Farm Statistics and Animal Health 2021, it shows that duck egg production in 2020 reached 316 thousand tons and figures while duck egg production in 2021 reached 329 thousand tons. The shell of duck eggs has the main component calcium carbonate by 94%, 4% organic matter and other minerals. Therefore, eggshell waste has the potential to be an efficient adsorbent. CaCO3 content in duck egg shells can be converted into calcite (CaO) (Mittal et al., 2016). The adsorption capacity of the adsorbent can be increased by the activation process to provide the desired properties. In addition, to improve the quality of biosorbent, immobilization with alginate can be done. Biosorbent immobilization with alginates can have mechanical strength, forming strong aggregates, rigidity, size and characteristics. These advantages increase absorption capacity, facilitate the separation of biosorbent from solutions, are resistant to chemical environments and can be desorbed (Pharma et al., 2016).

METHODOLOGY

The main material used in this study was duck eggshell waste. While the auxiliary materials are sodium alginate, $Cd(NO_3)_2$, $CaCl_2$, and aquadest. The tools used are oven, furnace, 50 mesh sieve, desiccator, UV-Vis spectrophotometer, magnetic stirrer, grinder, measuring cup, beaker glass, analytical balance, drip pipette, volume pipette, glass funnel and filter paper. This study uses the principle of adsorption, with duck eggshell as adsorbent and Cd metal as adsorbate. The independent variables used were biosorbent mass (1 ; 1.5 ; 2 grams) contact time (60 ; 90 ; 120 minutes) and Cd solution concentration (60 ; 80 ; 100 ppm). While fixed variables used are drying temperature (105ºC), drying time (24 hours), adsorbent size (50 mesh), furnace temperature (900ºC), immobilization temperature (55ºC), $CaCl_2$ (0.2 M) and wavelength (320 nm). This study, using surface response methodology (RSM) which is the design and model that works with various continuous treatments when finding optimal value or describe the response in accordance with the objectives. The main goal of RSM is to find the optimal response.

Table 1. Responses Surface Methodology (RSM)

Run	Biosorbent mass (gr)	Contact Time (minutes)	Cd Concentration (ppm)
1	1	60	60
2	1	60	100
3	1	120	60
4	1	120	100
5	2	60	60
6	2	60	100
7	2	120	60
8	2	120	100
9	0.66	90	80
10	2.34	90	80
11	1,5	39.54	80
12	1,5	140.45	80
13	1,5	90	46.36
14	1,5	90	113.63
15 (C)	1,5	90	80
16 (C)	1,5	90	80

RESULTS AND DISCUSSION

Water Content and Ash Content Test Results

Water content test for biosorbent quality is determined based on SNI 06-3730-1995. Water content testing is used as one of the indicators of biosorbent quality requirements because it can affect the absorption of liquids and gases (Larasati et al., 2016). The quality of biosorbent can be seen from the low and high value of water content where the lower the value of water content, the more adsorbate that can occupy the pores of biosorbent.

Biosorbent ash content testing is determined based on SNI 06-3730-1995. Ash content testing was conducted to determine the content of metal oxides in biosorbent. The lower the ash content, it will make be better the biosorbent.

Table 2. Test Results of Water Content and Ash Content of Biosorbent

Parameters	Units	SNI	Results
Water Content	%	Maks 4.4	5.6
Ash Content	%	Maks 2.5	3.4

Table 2 shows the water content of duck eggshell biosorbent at 5.6%. The value of the water level has yet to meet SNI.This is because there are any water content that is still attached to biosorbent (Parawitasari Pardede et al., 2020). The higher purity of the alginate will be trapped the more water in the matrix during the process stages of immobilization drying. Alginate has the ability to hold water excellent (Sinurat et al., 2017).

In Table 2, it can be seen that the ash content of duck eggshell biosorbent is 3.4%. The resulting ash content still does not fulfilled SNI. The formation of salts minerals can cause the high ash content during the immobilization process with sodium alginate which forms fine particles of the mineral salts. The levels high also can be caused by its lack of the process of leaching immobilization and causing blockage of biosorbentt pore and the surface area of biosorbent is reduced (Sa'diyah et al., 2020).

Optimization of Duck Eggshell Biosorbent using Response Surface Methodology (RSM)

In this study using central composite design, central composite design is an effective design in providing a response. The RSM method is also used to show the effect of the ratio of biosorbent mass, contact time and Cd concentration to the percentage decrease in Cd levels that can be absorbed by the biosorbent. The data obtained can be seen in Table 3.

Table 3. Percentage Decrease Cd Levels

Biosorbent mass (gr)	Contact Time (minutes)	Cd Concentration (ppm)	Decreased Cd Levels (%)
1	60	60	59%
1	60	100	99%
1	120	60	60%
1	120	100	98%
2	60	60	58%
2	60	100	97%
2	120	60	63%
2	120	100	98%
0.66	90	80	80%
2.34	90	80	79%
1,5	39.54	80	78%

1,5	140.45	80	79%
1,5	90	46.36	50%
1,5	90	113.63	98%
1,5	90	80	80%
1,5	90	80	78%

Based on table 3, obtained the regression coefficient of decreased Cd levels from biosorbent duck eggshell, which can be seen in Table 4. The effect of the variable on the response can be determined by a first-order polynomial regression equation.

Table 4. Regression Coefficient

Factor	Effect	Standard Error
Mean/Interc.	-0.194394	0.610469
(1)Biosorbent Mass (gr)(L)	0.143404	0.301427
Biosorbent Mass (gr)(Q)	-0.086021	0.074416
(2)Contact Time (minutes)(L)	-0.009006	0.005024
Contact Time (minutes)(Q)	0.000033	0.000021
(3)Cd Concentration (ppm)(L)	0.014555	0.008602
Cd Concentration (ppm)(Q)	-0.000077	0.000047
1L by 2L	0.001750	0.001335
1L by 3L	-0.000775	0.002002
2L by 3L	-0.000002	0.000033

From the table, obtained the value of R-square adjust is 0.72182 or 72% which can be interpreted that 72% of the value of the dependent variable (Cd levels) is influenced by the independent variables contained in the study (biosorbent mass, contact time and solution concentration). While the remaining 38% is influenced by other factors. The regression equation can be written as follows :

$$y = -0.194394 - 0.086021x_1^2 + 0.143404x_1 + 0.000033x_2^2 - 0.009006x_2 - 0.000077x_3^2 + 0.014555x_3 - 0.001750x_1x_2 - 0.000775\, x_1x_3 - 0.000002x_2x_3$$

Where in this equation the value of X_1 is the mass of the biosorbent, X_2 is the contact time and X_3 is the concentration of the solution and y is the percentage decrease in Cd levels. From the data that has been obtained and analyzed can then be made Pareto diagram to help identify significant factors that have an effect on the percentage of Cd levels produced from the experiment. The Pareto Diagram can be seen in Figure 1.

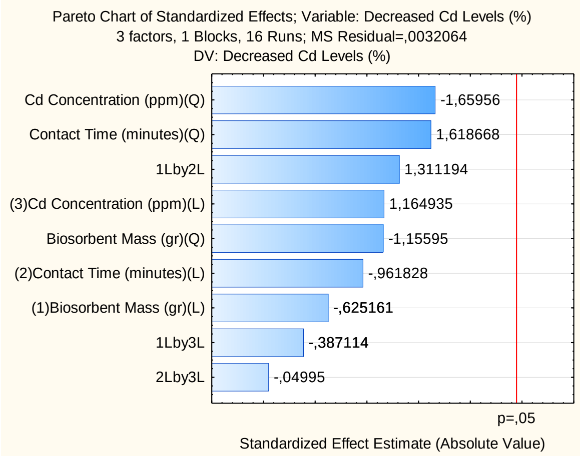

Figure 1. Pareto Chart Standarized Effect

From the pareto chart in Figure 1 it can be seen that the concentration of Cd gave the most significant effect on the decrease in Cd levels produced with p value is 0.05. After doing regression analysis on response surface design, it is necessary to see the residual plot against the decrease in Cd levels. Residual is the difference between the dependent variable or Y and the predicted Y. Y prediction is the value of Y based on the results of the regression equation.

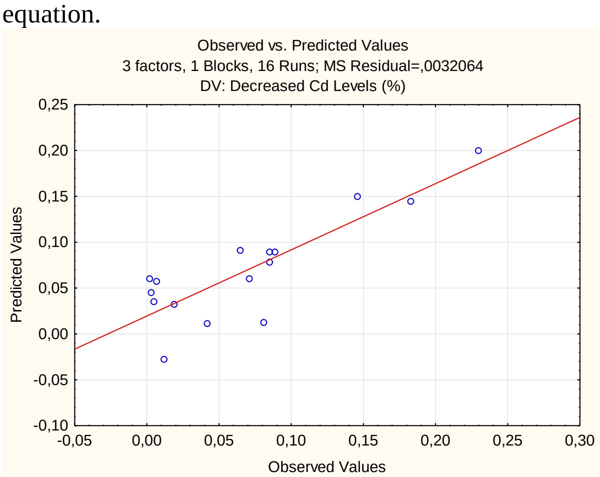

Figure 2. Observed Diagram vs Predicted Values

Figure 2 explains that the proximity of the estimated value to the model has been close to the value obtained from the results of the experiment. The value of the plot on the graph shows a good correlation between the values of the experiment and the estimate because the deviation between the values is close to the linear line. It can be concluded that the residual is normally distributed.

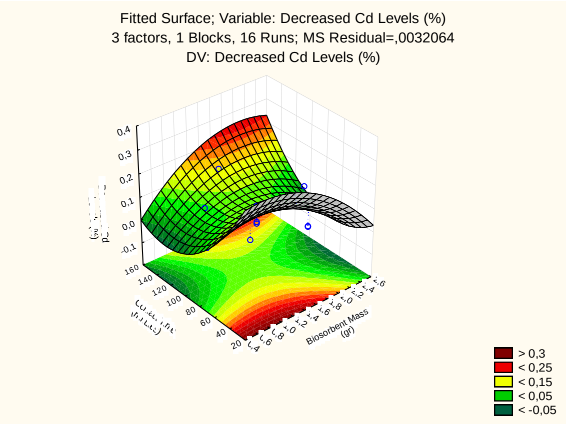

Figure 3. Surface Plot of Biosorbent Mass and Contact Time

Figure 3 explains the existence of a three-dimensional response surface on a dependent variable plotted with two independent variables with data processed using statistica software central composite design. Figure 3 ilustrates the surface plot of the variable biosorbent mass and contact time in the manufacture of biosorbent duck eggshell. To see the influence of other independent variables on dependent variables, we can use the statistica software

In the biosorbent mass vs contact time can be seen that the most optimum part is marked on the left end of the curve sheet, which is biosorbent mass 2.4-2.6 grams and contact time 100-160 minutes. The greater mass of biosorbent the Cd levels will be smaller. Variable contact time has an optimum value of around 100-160 minutes. Furthermore, analysis can be carried out using the ANOVA method. Analysis of Variance (ANOVA) is done to obtain a value that affects the significant percentage of CD levels decrease. In addition ANOVA performed for the adequacy of the model.

Fisher ratio variance or value F is a statistical measure calculation with several factors that describe the variation of some average data and the effect of the factor is estimated to be real. If the value of F is greater, it will show more similarity (Widhiarso, 2011).

Table 5. Analysis of Variance (ANOVA)

Factor	SS	df	MS	F	p
(1)Biosorbent Mass (gr)(L)	0,001253	1	0,001253	0,390826	0,554881
Biosorbent Mass (gr)(Q)	0,004284	1	0,004284	1,336215	0,291648
(2)Contact Time (minutes)(L)	0,002966	1	0,002966	0,925114	0,373279
Contact Time (minutes)(Q)	0,008401	1	0,008401	2,620086	0,156646
(3)Concentration Cd (ppm)(L)	0,004351	1	0,004351	1,357075	0,288261
Concentration Cd (ppm)(Q)	0,008831	1	0,008831	2,754134	0,148073
1L by 2L	0,005512	1	0,005512	1,719229	0,237734
1L by 3L	0,000480	1	0,000480	0,149858	0,712030
1L by 3L	0,000008	1	0,000008	0,002495	0,961783
Error	0,019238	6	0,003206		
Total SS	0,069238	15			

Based on the ANOVA table, the p-value for biosorbent mass, contact time and concentration of Cd solution is 0.554881, 0.383279 and 0.288261 can be interpreted that there is no variable close to the α value (0.05) however, the variable that is slightly close to the alpha value is the concentration of Cd variable. Besides that, this model shows a significant correlation on the F-value based on Fisher test (F table) biosorbent mass of 0.390826, contact time of 0.925114 and Cd solution concentration of 1.357075 while the value of F table is 1.258667 .If the F table is smaller than the F value, the interaction between variables can be ignored (Yirong & Vaurs, 2019).

To determine the optimization condition of the resulting Cd levels is determined with a critical value. Critical values can be seen in Figure 4.

Factor	Critical values; Variable: Decreased Cd Solution: saddlepoint Predicted value at solution: ,0902797 Observed Minimum	Critical Values	Observed Maximum
Biosorbent Mass (gr)	0,65910	1,45110	2,3409
Contact Time (minutes)	39,54622	98,76753	140,4538
Cd Concentration (ppm)	46,36410	85,93228	113,6359

Figure 4. Predicted Value

From figure 4, it can be concluded that the critical values for optimization conditions of Cd levels are achieved when the biosorbent mass is 1.45110 or 1.45 grams, the contact time is 98.76753 or 100 minutes and the Cd solution concentration is 85.93228 or 86 ppm.

CONCLUSION

The duck eggshell has the main component calcium carbonate by 94%, 4% organic matter and other minerals. Therefore, eggshell waste has the potential to be an efficient adsorbent. Physical activation is done by heating using a furnace that aims to enlarge the pore by breaking the chemical bond or oxidizing surface molecules so that changes in physical properties that the surface area increases and affects the adsorption power. With entrapment method by utilizing ca-alginate, biosorbent is expected to have advantages such as having mechanical strength, can form a strong aggregate, rigidity, size and porosity characteristics. Based on the results obtained, the percentage of optimum Cd levels reduction using duck egg shell was obtained with operating conditions of egg shell biosorbent mass of 1.5 grams, contact time of 90 minutes and solution concentration of 80 ppm with a percentage decrease in Cd levels of 89%.

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