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Optimization of Pb(II) Metal Adsorption on Pomelo Peel Biosorbent by Immobilization in Ca-Alginate

Zulfa Wulandari Rasyid[1*] and Vita Paramita[1]

[1]Department of Technology and Industry, Vocational School, Diponegoro University
Jl Prof Soedarto. SH, Tembalang, Semarang, 50275, Indonesia

*) Corresponding author: zulfawulandari16@gmail.com

Abstract *– Industrial wastewater is a source of water pollution that dominates today. Wastewater is known to cause damage to the environment, health and threatens the availability of clean water. Industrial wastewater is a problem because it contains a lot of dangerous heavy metals, one of which is Lead or Pb(II). Adsorption technology has become one of the most exciting technologies because of its good performance. Adsorption media currently popular for the study is adsorption using agricultural waste. One of the agricultural wastes that can be used as biosorbent is grapefruit peel (Citrus maxima). The functional groups in grapefruit peel are ether, pedophilic, carboxyl, carbonyl, and hydroxyl. These functional groups are essential in binding heavy metals from the aquatic environment. In this study, grapefruit peel was modified into a Ca-alginate immobilized biosorbent. The adsorption process was optimized using RSM then followed by an adsorption isotherm study to determine the absorption mechanism of the biosorbent.The analyzes carried out includes the include the characteristics of the biosorbent, namely the water content and ash content test, the FTIR test to determine the functional groups contained in the biosorbent, the SEM-EDX test to assess the appearance of the biosorbent, as well as analysis of the initial and final levels of Pb(II). Based on the results obtained, the best percentage decrease in Pb(II) levels was obtained with operating conditions of pH 4.7, contact time of 90 minutes, and Pb(II) concentration of 100 mg/L with a percentage decrease in Pb(II) levels of 89%. Through RSM, it can be seen that the most influential variable is the pH of the solution used, then the value of* $R^2 = 0.9954$ *on the adsorption isotherm is obtained.*

Keywords: *Immobilization, Biosorbent, Pomelo Peel, Pb(II)*

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INTRODUCTION

Industrial wastewater is a source of water pollution that dominates today. Wastewater is known to cause damage to the environment, health and threatens the availability of clean water. Regulation of the Minister of the Environment of the Republic of Indonesia No. 5 of 2014 has regulated wastewater quality standards, especially for industrial wastewater. Industrial wastewater is a problem because it contains a lot of harmful heavy metals. Heavy metals that are often found in wastewater that pollute the environment are mercury (Hg), lead (Pb), copper (Cu), cadmium (Cd), arsenic (Ar), chromium (Cr), nickel (Ni), and iron (Fe) (Sekarwati et al., 2015). Lead is considered a severe heavy metal because of its high toxicity, carcinogenicity, and bioaccumulation and will be very detrimental to the human body and ecosystem (Huang et al., 2021).

Adsorption technology has become one of the most attractive technologies due to its excellent performance, low power consumption, and easy operation (Huang et al., 2021). One of the adsorption media currently popular for the study is adsorption using agricultural waste. One of the agricultural wastes that can be used as biosorbent is grapefruit peel (*Citrus maxima*). The pomelo production in Indonesia is spread over several areas, with yields reaching 511 kg/ton per year. From these results, the number of grapefruit peels gets 208 kg/ton (Rafsanjani & Putri, 2015). More grapefruit peel waste is produced than other citrus fruits because grapefruit has a higher number of skin and membrane fragments. As a result, grapefruit peel accounts for more than 50% of the total weight, has a bitter taste, is considered inedible, and is not utilized further (Yu & He, 2018). Pomelo peel consists mainly of hemicellulose, cellulose, and lignin. The functional groups in pomelo cultivars are ether, phenophilic, carboxyl, carbonyl, and hydroxyl. These functional groups are essential in binding heavy metals from the aquatic environment (Kumar et al., 2021).

Research on the use of grapefruit peel as a biosorbent has been carried out, one of which by Dinh et al. (2020) investigated the primary adsorption mechanism of lead (II) and cadmium (II) cations to grapefruit peel in solution. One of the researchers who used the Ca-alginate immobilization method was Aichour & Zaghouane-Boudiaf, (2020), where an adsorbent made from orange peel was created using the activation method of acetic acid immobilized in calcium alginate then biosorben is used to adsorption methylene blue and crystal violet.

The research that be carried out in this paper is a biosorbent from grapefruit peel with the activation method of ca-alginate immobilized acid for absorption of Lead (Pb).

METHODOLOGY

The main materials used in this study were grapefruit peel waste H_3PO_4, aquadest, sodium alginate, calcium chloride (CaCl2), $Pb(NO_3)_2$, HNO_3, and NaOH. The waste of grapefruit peel is obtained from peeled fruit in supermarkets. Other chemicals are received at the Indrasari chemical store, Semarang.

The equipment used in this study is: a measuring cup, watch glass, analytical balance, dropper, beaker glass, magnetic stirrer, funnel, spoon, thermometer, grinder, oven, sieve, desiccator, pH paper, Atomic Adsorption Spectrometer (AAS).), Fourier Transform Infra-Red (FTIR) and Structural Equation Model (SEM).

Biosorbent Preparation

The waste of pomelo peel is cleaned of impurities and then dried at 110°C for 24 hours used oven. After the pomelo peel is dried, it is grinded and sieved to obtain a size of 0.2 mm (Aichour et al., 2018).

Activation

Pomelo peel powder was activated using H_3PO_4 0.1 M in a ratio of 1: 10 (gr: mL). The mixture was stirred with a magnetic stirrer for 30 minutes, and the mixture was then centrifuged to separate the supernatant. After the mixture activated then dried at 50°C for 24 hours. Finally, the product was washed with distilled water to remove excess acid and put into a desiccator (Aichour et al., 2018).

Immobilization Biosorbent

Biosorbent was added to a 2% sodium alginate solution and stirred for 10 hours, then 4% calcium chloride was added to form beads; the beads were washed with distilled water, dried, and stored in a closed container (Aichour). et al., 2018).

Adsorption Process

Solutions containing Pb(II) with various concentrations are then mixed with grapefruit peel biosorbent which has been immobilized by Ca-alginate, then stirred using a magnetic stirrer (Aichour). et al., 2018).

Table 1 Experimental design using RSM

No	pH	Contact Time (Minutes)	Concentration of Pb(II) (mg/L) (L)
1	5	60	50
2	5	60	150
3	5	120	50
4	5	120	150
5	7	60	50
6	7	60	150
7	7	120	50
8	7	120	150
9	4.7	90	100
10	7.2	90	100
11	6	51	100
12	6	128	100
13	6	90	35
14	6	90	164
15	6	90	100
16	6	90	100

Adsorption process using an experimental design using Respond Surface Methodology (RSM) to determine the variables involved most influential which can be seen in Table 1. In this study, the variable pH of the solution, contact time, and concentration of Pb(II) solution were used.

RESULTS AND DISCUSSION

Biosorbent characterization

Biosorbent is characterized for its water content and ash content according to SNI 06-3730-1995.

Table 2 Results of Quality Analysis of Pomelo Peel Biosorbent Immobilized Ca-alginate

No	Parameter	Unit	SNI	Biosorbent Test Results
1.	Moisture Content	%	Max 4.4	21
2.	Ash Content	%	Max 2.5	9.74

Table 2 shows the water content in pomelo peels biosorbent at 21%. The water content value does not meet SNI 06-3730-1995, where the maximum number for the water content of the biosorbent is 4.4%. The water content still attached is due to the level of purity of the alginate used, where the higher the purity of the alginate, the more difficult it is for the water that has been adsorbed to come out of the matrix that has been formed (Sinurat and Marliani, 2017).

The results of the calculation of the ash content of the pomelo peel biosorbent can be seen in Table 1, where the levels reached 9.74%. This value does not meet SNI because it exceeds the maximum value of 2.5%. 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 could be due to the mineral content in the biosorbent at the activation time (Sa'diyah et al., 2020).

Characterization of Ca-alginate immobilized grapefruit peel biosorbent by FTIR

Biosorbent characterization analysis using FTIR was used to determine the main functional groups present on the biosorbent surface, where these functional groups were responsible for the binding of metal ions (Nurhidayah et al., 2020). The results of the FTIR test were analyzed by looking at the specific peaks seen at certain wavelengths; these characteristic peaks then indicated the type of functional group in the biosorbent compound.

Characterization of Ca-alginate immobilized grapefruit peel biosorbent can be seen in Figure 1, where the width of the absorption peak at 3272.91 cm^{-1} indicates the absorption of the hydroxyl functional group (OH), at 2928, 75 cm^{-1} shows the stretching of the alkane group (C=H), at 1597.73 cm^{-1} offers the absorption of the carbonyl group

Table 3 Regression Coefficient of Reduction in Pb(II)

Factor	Regression Coefficients	Standard Error	t(6)	P	-95% Cnf.Limt	+95% Cnf.Limt
Mean/interc	103.1436	30.78698	3.35024	0.015415	27.8106	178.4767
(1) pH (L)	-10.7755	9.26141	-1.16348	0.288806	-33.4374	11.8864
pH (Q)	0.9226	0.74775	1.23387	0.263387	-0.9070	2.7523
(2) Contact Time (Minutes) (L)	0.3343	0.19930	1.67751	0.144454	-0.1533	0.8220
Contact Time (Minutes) (Q)	-0.0009	-1.06174	0.329209	-0.00083	0.00083	0.0012
(3) Concentration of Pb(II) (mg/L) (L)	0.2210	0.10293	2.14709	0.075408	-0.0309	0.4728
Concentration of Pb(II) (mg/L) (Q)	-0.0011	0.00030	-3.59469	0.011439	-0.0018	-0.0003
1L by 2L	- 0.0354	0.02065	-1.71591	0.136997	-0.0860	0.0151
1L by 3L	-0.0068	0.01239	-0.54601	0.604754	-0.0371	0.0236
3L	0.0002	0.00041	0.60482	0.567452	-0.0008	0.0013

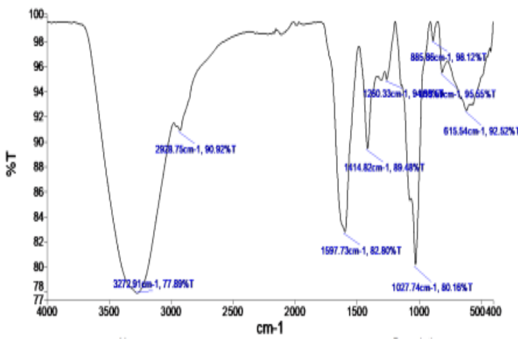

Figure 1. FTIR Spectrum of Ca-alginate Immobilized Pomelo Peel Biosorbent

(C=O) from aldehydes and ketones, 1414.82 cm^{-1} shows the absorption of the nitro group. The amide and alkyl carbonate peaks were at 1260.33 cm^{-1}, the rise at 1027.74 cm^{-1} was the absorption of (C-OH), and the increase at 615.54 cm^{-1} indicated the absorption (C-Cl) of the alkyl halide group (Aichour & Zaghouane-Boudiaf, 2020). The hydroxyl group (OH) has a negative charge and can bind to Pb(II), which has a positive group (Haqiqi, 2018).

Scanning Electron Microscopy (SEM) Characterization

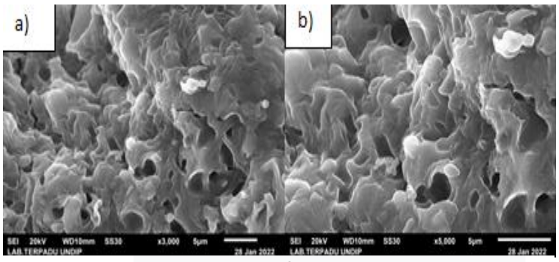

Figure 2. 3000X Magnification SEM Analysis Results (a) 5000X Magnification SEM Analysis Results (b)

With 3000x magnification (Fig. 2.a), there is an irregularly granular and porous structure. For more details, the porous surface of the grapefruit peel biosorbent is shown in Figure 2. b with a magnification of 5000x. With 3000x and 5000x magnification, it can be concluded that the pomelo peel biosorbent has a large porous surface.This porous surface is an important parameter of the biosorbent because the larger the pores of the biosorbent, the greater the absorption ability of contaminant compounds, which in the case of this study is Pb(II).

Pb(II) reduction analysis with RSM

Response Surface Methodology (RSM) is an analytical technique to develop and optimize the process where the response is influenced by several factors (independent variables). This study uses a central composite design (CCD). Based on the results obtained, the regression coefficient of the decrease in Pb(II) levels using RSM can be seen in table 3.

Based on the regression coefficient table, data interpretation should be made by looking at the numbers listed on the R-Square adjusted to determine the model's accuracy.

If more and more independent variables are used, a lot of "noise" will be formed in the model and cannot be explained by R-Square, so it becomes a weakness of R-Square itself. From the results shown by RSM, the R-Square adjust obtained 0.79723 or 79%, which means that 79% of the value of the dependent variable (decrease in Pb(II) levels) is influenced by the independent variables used in the study (pH, contact time, concentration). Initial Pb(II)).

For the remaining 21% influenced by other factors such as the quality of materials and quality of tools used. The regression equation can be written as:

$$y = 103.1436 + 0.9226x_1^2 - 10.7755x1 - 0.0009x_2^2 + 0.3343x_2 - 0.0011x_3^2 + 0.2210x_3 - 0.03541x_1x_2 - 0.0068\, x_1x_3 + 0.0001x_2x_3$$

In this equation, the value of x1 is the pH of the solution, x2 is the contact time, x3 is the initial concentration of Pb(II), and the importance of y is the percentage decrease in Pb(II) levels.

In identifying significant factors that affect the percentage decrease in Pb(II) levels resulting from the experiment, a Pareto diagram is used, which can be seen in Figure 3.

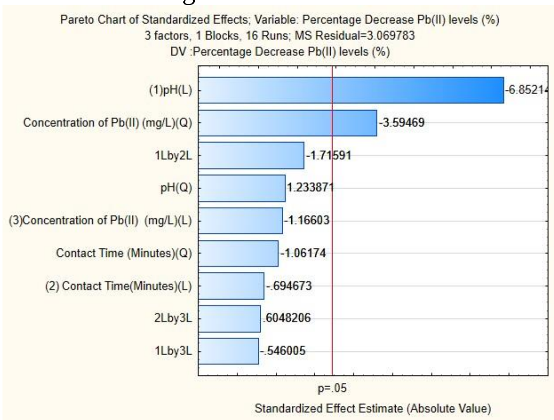

Figure 3. Pareto diagram of the effect of the independent variable on the percentage decrease in Pb(II) levels

Based on the resulting Pareto diagram, the pH factor of the solution used had the most significant effect on the percentage reduction in Pb(II) levels by Ca-alginate immobilized grapefruit peel biosorbent.

The variable that has an effect after pH is the initial concentration of Pb(II), and the variable with the most minor impact is the contact time variable.

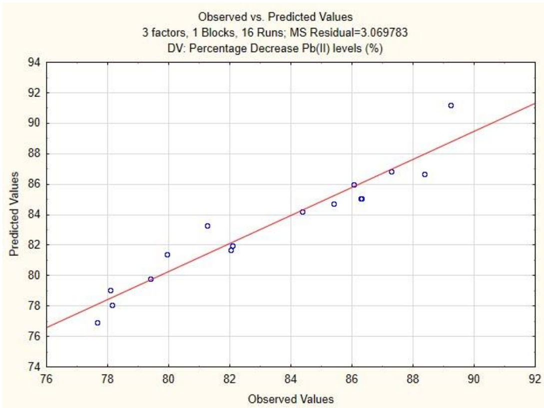

Figure 4. Comparison of Experimental Data with Estimated Percentage Decrease in Pb(II) Levels

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 residual plot can be seen in Figure 4.

It is known that the proximity of the estimated value to the model is close to the value obtained from the experimental results. Therefore, although the plotted value on the graph shows a pretty good correlation between the observed and estimated values, the deviations between these values are still close to a linear line and are not randomly distributed. Therefore, it can be concluded in this study that the residuals are normally distributed.

The ANOVA analysis obtained a value that significantly affects the study's results, in this case, the percentage decrease in Pb(II) levels.

Table 4 Values Predicted Percentage Decrease in Optimum Pb(II) Levels

Factors	Minimum	Critical Values	Observed Maximum
pH	4,71281	7,23926	7,2872
Contact Time (minutes)	51,38434	56,37091	128,6157
Pb(II) Concentration (mg/L)	35,64057	86,54621	164,3594

The critical value can be seen in table 4, where it can be concluded that the crucial matter in the optimization condition is the percentage reduction in Pb(II) levels achieved when pH is 7.23926, contact time is 56.37091, and Pb(II) concentration is 86.54621. Therefore, the predictive value obtained from ANOVA is 83%.

Adsorption Isotherm

Determination of adsorption isotherm aims to see the absorption mechanism of the adsorbent in the adsorption process (Sylvia et al., 2019). There are two models of adsorption isotherm: Langmuir adsorption isotherm and Freundlich adsorption isotherm. The selection of this isotherm model is based on research (Aichour & Zaghouane-Boudiaf, 2020) using the Langmuir model to show homogeneous adsorption and monolayers of methylene blue and crystal violet, which in the binary system shows that dye adsorption is affected by the simultaneous presence of dyes. In solution, it was found that the bio-adsorbent beads effectively removed the cationic dye's content and behaved as an excellent adsorbent in the binary system.

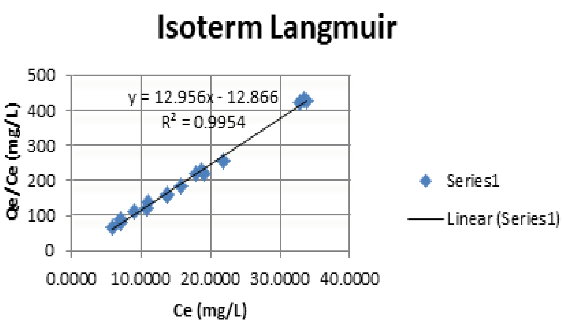

Figure 5 Graph of Langmuir Isotherm Pattern

Based on the graph shown in Figure 5, the resulting shape shows the trend of the Langmuir isotherm, so it can be stated that the results of the adsorption isotherm decreased Pb(II) levels using a Ca-alginate immobilized pomelo peel biosorbent following the Langmuir isotherm model. From the graph of the relationship between ce/Qe and Ce, an equation is obtained as a linear equation y = 12.956x - 12.866 with a value of R^2 = 0.9954. it can be concluded that the graph of the relationship between Ce/Qe and Ce is the Langmuir isotherm.

CONCLUSION

Biosorbent is a solid substance that can absorb (adsorption) from a fluid phase. This study focuses on the utilization of pomelo eel with the activation method of$_3PO_4$ ca-alginate immobilized

Based on the results obtained, the best percentage decrease in Pb(II) levels was obtained with operating conditions of pH 4.7, contact time of 90 minutes, and Pb(II) concentration of 100 mg/L with a percentage decrease in Pb(II) levels of 89%.

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