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# Synthesis of poly aluminium chloride (PAC) from aluminum cable waste through the polymerization process

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**ABSTRACT**

Cable waste is classified as inorganic waste that is difficult to decompose. Aluminum cable waste has good coagulant properties if it can be synthesized into Poly Aluminium Chloride (PAC) because the active aluminate groups can aggregate suspended materials in water into flocks during the coagulation-flocculation process in water purification. PAC is made by hydrolyzing aluminum samples with a 33% HCl solution. The sample is then left for one day to complete the hydrolysis process. After the formation of the $AlCl_3$ solution, polymerization is carried out by adding a $Na_2CO_3$ solution. In the research conducted, the best result was a turbidity reduction value of up to 2.96 NTU with the addition of 30 ml of $AlCl_3$ monomer and a $Na_2CO_3$ initiator with a concentration of 7N. After optimization using Response Surface Methodology (RSM) in the Design Expert 13 software, the most optimal result for the synthesized PAC was found to reduce wastewater turbidity to 2.609 NTU with variables of 25.992 ml of $AlCl_3$ monomer volume and 5.248N of $Na_2CO_3$ initiator concentration. Based on this research, the concentration of the initiator has a significant effect on the ability of the monomer to bind into a PAC polimer chain.

## 1. Introduction

As the industrial world develops, especially in the field of technology, the resulting electronic waste has become increasingly abundant. One type of waste is cable waste. Generally, copper cable waste is recycled into other electronic components. However, aluminum cable waste is rarely recycled because aluminum has lower conductivity than copper. Aluminum cable waste has good coagulant properties if it can be synthesized into Poly Aluminium Chloride (PAC), as the active aluminate groups can aggregate suspended materials in water into flocks during the coagulation-flocculation process in water purification [1,2].

PAC known as a group of aluminum chloride compounds, consists of complex organic chemicals with hydroxyl (OH) ions and aluminum ions. PAC has a polynuclear form, which differs from the standard chlorination form. PAC is a new type of coagulant resulting from research and development in water treatment technology. The general formula for PAC is $Al_m(OH)_n(Cl)_{3m-n}$. The basic element of PAC is aluminum, which associates with other elements to form repeating units in a long molecular chain [3].

The formation process of PAC involves hydrolysis and polymerization. The hydrolysis process includes the formation of the $AlCl_3$ monomer compound with the following reaction:

$$2Al_{(s)} + 6HCl_{(aq)} \rightarrow 2AlCl_{3(aq)} + 3H_{2(g)} \quad (1)$$

In aluminum-containing waste, metal cations derived from aluminum are extracted into hydrochloric acid, forming aluminum chloride salts, which are monomers that form PAC. This occurs because the acidic compound oxidizes aluminum metal into its ionic form, $Al^{3+}$ [4].

The formed $AlCl_3$ undergoes a polymerization process with the initiator $Na_2CO_3$, forming the PAC compound. In the production of PAC, the polymerization process that occurs is condensation polymerization. Condensation polymerization is based on the reaction between two or more molecules with different functional groups, resulting in a polymer containing new functional groups and producing by-products such as simple molecules like $H_2O$ and other by-products like NaCl and $H_2CO_3$.

The polymerization reaction of PAC is as follows:

$$4AlCl_{3(aq)} + 12H_2O_{(l)} + 5Na_2CO_{3(aq)} \rightarrow 2Al_2(OH)_5Cl_{(aq)} + 10NaCl_{(s)} + 5H_2CO_{3(aq)} + 2H_2O_{(l)} \quad (2)$$

The high degree of polymerization of PAC makes it an excellent coagulant for water with high alkalinity that requires rapid reaction times. The degree of polymerization is a comparison of the molecular weight of a polymer to its constituent monomers. It expresses the size of a polymer molecule based on the number of monomers composing it [5,6].

The coagulation effectiveness of PAC is influenced by the aluminum content in the material, while its application in water is influenced by pH. At pH 6.0-7.0, aluminum undergoes hydrolysis at high charge, making it highly efficient in coagulating suspended particles and dissolved organic particles in water. Thus, PAC exhibits superior coagulation performance compared to alum (aluminum sulfate) due to its higher pH

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range, lower sensitivity to water temperature, lower required dosage, and lower residual Al concentration [7].

The main topic of discussion in this article is the synthesis of PAC from aluminum cable waste using the polymerization process and the optimization of results using RSM (response surface method). The primary approach involves experimental optimization related to the utilization of aluminum cable waste as a raw material for PAC, including the quantity of monomers used in the polymerization process and the optimization methods employed.

## 2. Materials and Methods

### *2.1. Materials*

Aluminium cable waste have been sampled from Sambiroto Village (Gresik Regency, East Java Province, Indonesia), Hydrogen Chloride (33%), Sodium Carbonate, and Water.

### *2.2. Procedure for synthesizing PAC*

Aluminum cable waste undergoes a stripping process to remove its insulating rubber, followed by size reduction to facilitate dissolution. Once the sample size is appropriate, it undergoes the hydrolysis process. Five grams of the sample are weighed and placed into a 250 mL Erlenmeyer flask, then 250 ml of 33% HCl solution is added. The hydrolysis process takes place at room temperature. Successful hydrolysis occurs when the solution turns into a transparent yellow color, indicating the formation of $AlCl_3$ solution, and produces $H_2$ gas bubbles. The solution is then left to stand for 24 hours to complete the hydrolysis process.

After the 24-hour hydrolysis process, the sample solution undergoes the polymerization process. The sample solution is transferred to Erlenmeyer flasks with volumes of 10, 20, and 30 mL. Polymerization is carried out by gradually adding $Na_2CO_3$ solution with concentrations of 3, 5, and 7 N with a volume of 10 ml while stirring with a magnetic stirrer at a stirring speed of 30 rpm. The polymerization process is stopped when no more bubbles form upon adding the $Na_2CO_3$ initiator, and the formed PAC is a clear yellow solution that forms a precipitate.

### *2.3. Procedure for make synthetic wastewater*

The materials used to make synthetic wastewater include kaolin clay powder. 10 grams of kaolin powder is weighed and then dissolved in 1 liter of tap water. The synthetic wastewater is then stirred for approximately 1 hour [8].

### *2.4. Procedure for turbidity test*

The synthetic wastewater is measured at 500 ml into a beaker glass and then mixed with 1 mL of synthesized PAC. The mixture is then subjected to rapid stirring at 200 RPM for 1 minute, followed by slow stirring at 60 RPM for 15 minutes. The wastewater is then left to settle for approximately 1 hour. The clearest part of the wastewater is then tested for turbidity using a turbidimeter.

### *2.5. Optimization of turbidity response using RSM*

The results from experimental trials do not always meet expectations or are not optimal. Therefore, to find optimal conditions in experimental design, an optimization approach is often necessary. One optimization method that can be used is the RSM (Response Surface Method) (Sari, 2021). RSM functions to connect a response with several different variables that mutually influence each other through appropriate experimental design and analysis. RSM uses more than one polynomial regression equation to fit the functional relationship between factors and response values. Regression analysis serves to optimize process parameters and predict response values [9,10]. Response prediction in RSM will use the ANOVA (Analysis of Variance) method with a second-order polynomial equation approach expressed in the following equation:

$$y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_{11} {X_1}^2 + \beta_{22} {X_2}^2 + \beta_{12} X_1 X_2$$

Where :
y : predicted response (turbidity in this case)
$\beta_0$ : intercept coefficients
$\beta_1$ , $\beta_2$ : linear regression coefficients
$\beta_{11}$ , $\beta_{22}$ : quadratic regression coefficients
$\beta_{12}$ : interaction terms coefficients

## 3. Results and Discussion

### *3.1. Turbidity analysis*

The synthesized PAC will then be tested for its ability to clarify waste water using the turbidity analysis method with an initial turbidity level of 4400 NTU (Nephelometric Turbidity Units). The turbidity reduction values are presented in Table 1:

Table 1. Wastewater turbidity after the addition of PAC

| Concentration of $Na_2CO$ initiator (N) | Volume of $AlCl_3$ monomer (mL) | Turbidity (NTU) |
|---|---|---|
| 3 | 10 | 20.05 |
| | 20 | 9.45 |
| | 30 | 6.78 |
| 5 | 10 | 10.89 |
| | 20 | 4.68 |
| | 30 | 3.56 |
| 7 | 10 | 8.69 |
| | 20 | 3.74 |
| | 30 | 2.96 |

Table 1. shows the data on the reduction of wastewater turbidity after the addition of synthesized PAC. According to the table, the lowest final turbidity is 2.96 NTU, and the highest final turbidity is 20.05 NTU. Using this data, an optimization equation can be derived using Response Surface Methodology (RSM). This equation can then be used to create a graph depicting the relationship between the volume of $AlCl_3$ monomer and the concentration of $Na_2CO_3$ initiator in relation to the reduction of wastewater turbidity.

### *3.2. Analysis of the effect of monomer volume and initiator concentration on the reduction of wastewater turbidity*

Based on Figure 1, it can be observed that there is a turbidity reduction as the volume of $AlCl_3$ monomer and the concentration of $Na_2CO_3$ initiator increase. The optimal monomer volume that can significantly reduce wastewater turbidity is the addition of 30 mL of monomer and 7 N initiator concentration, resulting in a final turbidity of 2.96 NTU. The amount of monomer will cause the polymerization reaction rate to increase and more polymer to be produced. This allows for the formation of larger and more efficient flocs for removing water turbidity, which influences the effectiveness of coagulation. However, an excessive monomer volume will produce undesirable residues in the form of precipitates. These precipitates can be by-products or unpolymerized residual monomers during the reaction leading to overdosing and increasing turbidity levels [11,12].

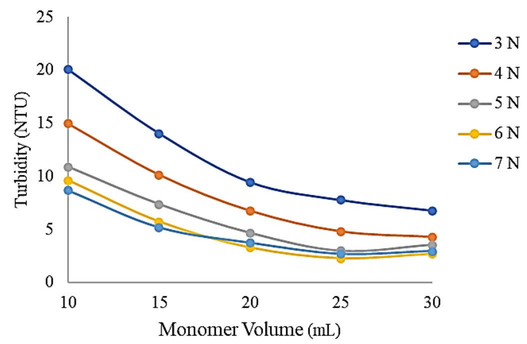


Fig. 1. Relationship between $AlCl_3$ monomer volume and $Na_2CO_3$ initiator concentration on turbidity

*3.3. Analysis model with ANOVA*

Based on Table 2, it is known that the F-value represents the distribution of independent variables, and the P-value represents the significance level, where the P-value is typically $\leq$ 0.05. The P-value indicates the significant influence of parameters on the addition of $AlCl_3$ monomer volume and $Na_2CO_3$ polymerization initiator concentration. A model with a P-value $\geq$ 0.1 indicates that the factor does not have a significant influence on the response. By looking at the table above, significant P-values are found for the AlCl3 monomer volume factor, which is < 0.0016 or < 0.16%, and the Na2CO3 polymerization initiator concentration, which is < 0.0031 or < 0.31%. The significance value of the model indicates how valid the equation model is. To obtain appropriate results, the $R^2$ value should be greater than 0.8 or 80% [13].

Table 2. Result of ANOVA analysis

| Source | Sum of Squares | df | Mean Square | f-value | p-valu |
|---|---|---|---|---|---|
| Model | 228.90 | 5 | 45.78 | 48.19 | 0.0046 |
| A-V.$AlCl_3$ | 115.54 | 1 | 115.54 | 121.62 | 0.0016 |
| B-C.$Na_2CO_3$ | 72.73 | 1 | 72.73 | 76.56 | 0.0031 |
| AB | 14.21 | 1 | 14.21 | 14.96 | 0.0306 |
| $A^2$ | 16.42 | 1 | 16.42 | 17.28 | 0.0253 |
| $B^2$ | 9.99 | 1 | 9.99 | 10.52 | 0.0477 |
| Residual | 2.85 | 3 | 0.9501 | | |
| Cor Total | 231.75 | 8 | | | |

*3.4. Analysis of the model equation adequacy*

Based on Table 3, a recommended model equation is obtained for determining the response based on the available two factors, namely the concentration of polymerization initiator ($Na_2CO_3$) and the volume of $AlCl_3$ monomer. The recommended model equation is a quadratic equation, where in this model equation, the values of Adjusted $R^2$ and Predicted $R^2$ do not have a significant difference, which is 0.115 (not more than 0.2). The tolerable $R^2$ value is between 0.8 to 1. The quadratic model equation is also chosen because it has sequential p-values below 0.05.

Table 3. Comparison of the recommended equation models by the software

| Source | Sequential p-value | Adjusted $R^2$ | Predicted $R^2$ | |
|---|---|---|---|---|
| Linear | 0.0066 | 0.7499 | 0.5124 | |
| 2FI | 0.1799 | 0.7980 | 0.2852 | |
| Quadratic | 0.0304 | 0.9672 | 0.8522 | Suggested |
| Cubic | 0.1895 | 0.9965 | 0.9195 | Aliased |

*3.5. Analysis of regression equation*

Optimization of Polymerization Process is conducted using RSM with the selection of the Central Composite Design (CCD) method. This is to obtain PAC with optimal coagulation ability to reduce the turbidity of synthetic wastewater. The equation obtained from the optimization results is a quadratic equation with an $R^2$ of 0.9672. The equation is as follows:

$$y = 56{,}90125 - 2{,}05608\, X_1 - 9{,}21333\, X_2 + 0{,}09425 X_1 X_2 + 0{,}02865\, X_1^2 + 0{,}55875\, X_2^2$$

Where :

y : Turbidity response (NTU)

$X_1$ : Volume of $AlCl_3$ monomer variable (ml).

$X_2$ : Concentration of $Na_2CO_3$ variable (N).

*3.6. Analysis of Contour Plot and Surface Plot*

A contour plot is a two-dimensional representation of the response presented using a predictive model for turbidity response values, whereas a 3D surface graph shows a three-dimensional depiction. Both the contour plot and the 3D surface graph illustrate how the combination of components affects the response yield values. The different colors on the contour plot indicate the optimized response turbidity.

Based on the Figures 2 & 3, the effect of the two factors in the PAC polymerization process is shown, allowing the optimal conditions for the PAC polymerization process to be determined. According to the two graphs, there are three colors indicating varying response results. The red color indicates a high turbidity level, caused by an incomplete polymerization process resulting in the insufficient ability of PAC to coagulate suspended substances in the wastewater. The green color indicates a medium turbidity level, and the blue color indicates a low turbidity level [14].

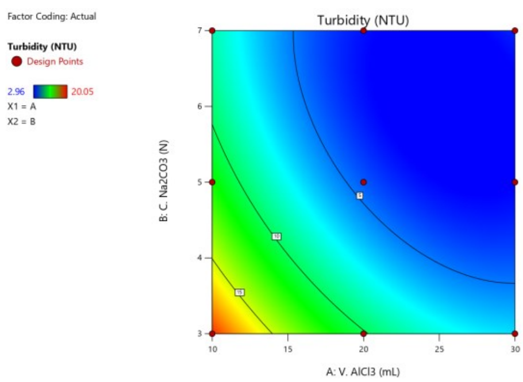


Fig. 2. Contour plot graph of $AlCl_3$ monomer volume versus $Na_2CO_3$ initiator concentration on turbidity

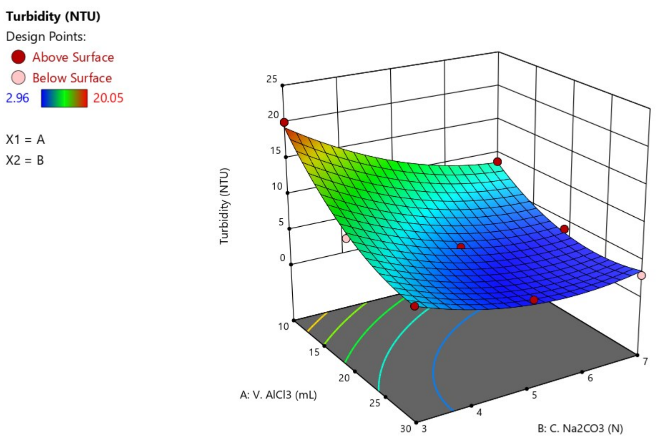


Fig. 3. 3D surface graph of $AlCl_3$ monomer volume versus $Na_2CO_3$ initiator concentration on turbidity

### *3.7. Optimizing results with RSM*

The most optimal response was obtained after meeting the specified constraints. For the $AlCl_3$ monomer volume factor of 10-30 mL and the $Na_2CO_3$ initiator concentration factor of 3-7 N, the most optimal point was achieved with a final turbidity of 2.6085 NTU. This optimal response value was obtained with an $AlCl_3$ monomer volume factor of 25.992 mL and an $Na_2CO_3$ initiator concentration factor of 5.248 N. This result yielded a desirability value of 1. The desirability value indicates how well the program meets the criteria set for the response. Desirability values range from 0 to 1, where a higher desirability value indicates that the optimization results are more accurate relative to the desired outcome [15].

Table 4. Optimalization result on turbidity response

| V.$AlCl_3$ | C.$Na_2CO_3$ | Turbidity | Desirability |
|---|---|---|---|
| 25.992 mL | 5.248 N | 2.6085 NTU | 1 |

### *3.8. Verification of optimal conditions results*

In the process of verifying optimization results, a comparison is made between the predicted values from the model and the actual values obtained from experiments. The validity of the model is evaluated through Confidence Interval (CI), Tolerance Interval (TI), and Prediction Interval (PI) analyses, which have lower and upper bounds at a confidence level of 95%. The verification results of the optimum conditions are presented in Tables 5. and 6.

Table 5. Verification results of confidence level and tolerance interval

| Analysis | Predicted Mean | Std Dev | SE Mean | 95% CI low | 95% CI high | 95% TI low | 95% TI high |
|---|---|---|---|---|---|---|---|
| Turbidity | 2.609 | 0.974 | 0.642 | 0.564 | 4.652 | -6.234 | 11.45 |

Based on Table 5, the optimization results obtained using the Response Surface Method (RSM) in Design Expert 13 software for the best turbidity response of 2.60852 NTU were achieved with an $AlCl_3$ monomer volume factor of 25.992 mL and an $Na_2CO_3$ initiator concentration factor of 5.248 N. For this response, a Tolerance Interval (TI) was obtained with a lower bound of -6.234 and an upper bound of 11.451. TI is an interval designed to encompass a certain proportion that covers 99% of the sample population. A 95% Confidence Interval (CI) for the lower interval is 0.5642 and for the upper interval is 4.6527. The CI value indicates 95% confidence that the calculated TI truly covers 99% of the population response. CI and TI are used as indicators of the standard mean error to help overcome random errors from data derived from a large number of observations. As the amount of data increases, random errors and the range of confidence intervals tend to decrease. In the case of sampling large quantities, the 95% CI produced will encompass the true mean value.

Table 6. Verification results of prediction interval

| Analysis | Predicted Mean | Std Dev | n | SE Pred | 95% PI low | 95% PI high |
|---|---|---|---|---|---|---|
| Turbidity | 2.609 | 0.974708 | 1 | 1.16733 | -1.106 | 6.3235 |

For this response, a 95% Prediction Interval (PI) was obtained with a lower bound of -1.1065 and an upper bound of 6.3235. In sampling large quantities, the 95% PI formed will encompass new observations. Therefore, comparing CI and PI is important to ensure that the verification results within the range indicate the level of accuracy of the response accordingly. Generally, the CI range is narrower than the PI range because PI measurements take into account diverse and unknown sample variations, providing an overview of future sample results with a certain level of confidence based on the observations that have been made.

## 4. Conclusion

The best reduction in synthetic wastewater turbidity from 4400 NTU to 2.96 NTU was achieved with volume of $AlCl_3$ monomer 30 mL and $Na_2CO_3$ initiator concentration of 7N. After optimization using the Response Surface Method (RSM), the predicted optimal turbidity response value was 2.609 NTU, with volume of $AlCl_3$ monomer 25.992 mL and $Na_2CO_3$ initiator concentration of 5.248 N. In the quadratic model equation resulting from the optimization, an $R^2$ value of 0.9672 was obtained, indicating that both variables have a significant influence on the turbidity response.

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