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Optimization of Geopolymer Compressive Strength Using Response Surface Methodology

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ABSTRACT

Geopolymers have issues related to cracking resistance and pore filling, decreasing their mechanical strength. However, the addition of nano silica and Cellulose Nanocrystals (CNCs) has been found to enhance their mechanical properties. This study focused on optimizing the utilization of nano silica and CNCs to enhance the compressive strength of geopolymers. This research employed Response Surface Methodology (RSM) with Central Composite Design (CCD). The concentrations of nano silica and CNCs used in the experiments ranged from 2% to 4% and 1% to 3%, respectively. The experimental results consist of 13 runs, including 5 center point runs. The model suggested concentrations of nano silica and CNCs of 3.98% and 1%, respectively, for an optimal compressive strength of 22.20 MPa. The proposed quadratic model exhibited high accuracy, as evidenced by an R^2 of 0.9865, Adj- R^2 of 0.9769, and predicted R^2 of 0.9168. The closeness of R^2 to 1 indicates a strong correlation between the actual and predicted values, thus highlighting the model's significant relevance. Ultimately, the model developed in this study holds the potential for predicting the compressive strength of geopolymers incorporating nano silica and CNCs.

I. Introduction

Geopolymer has become an alternative binder to the Ordinary Portland Cement (OPC). It has been widely applied as an advanced material in the construction sector. Currently, nanosilica composites have begun to be studied in geopolymer cement. Surface modification of nanosilica is proven to strengthen geopolymers and increase their mechanical strength. Natural fibers have also been used to prevent geopolymer cracking [1]. This condition shows that geopolymer is an alternative material to replace cement and is easily modified with other materials.

Using 5% nanosilica in cement paste increased its compressive strength by 35% compared to those without nanosilica [2]. Meanwhile, 2% nanosilica increased the control specimen's compressive strength from 53.2 MPa to 86.1 MPa at day 90. In comparison, adding 10% micro silica and 2% nanosilica increased the compressive strength to 92.1 MPa [3]. Researchers have also started focusing on cellulose as a geopolymer reinforcement material. Some researchers agree cellulose can prevent crack propagation in geopolymers [4][9]. Compositing nanosilica and Cellulose Nanocrystals (CNCs) requires suitable statistical methods to increase the mechanical strength of geopolymers. The Response Surface Methodology (RSM) is a statistical method many researchers recommend.

RSM is a collection of computational and scientific methods used to examine interactions between variables [10]. Central Composite Design (CCD) builds quadratic models from several variables in RSM. This statistical approach determines the relationship between the independent input variables, i.e., the percentage of nanosilica and CNCs, and the dependent output, i.e., compressive strength, through the RSM. The RSM method was selected due to its advantages,

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including fewer experiments, the model can be developed with many variables, and the optimization can be conducted in detail.

Zahid et al. used RSM to predict the mechanical strength of geopolymer composite by replacing it with OPC [11]. Ali et al. used the design and statistical modeling of concrete using Waste Foundry Sand as a sand substitute to evaluate its mechanical strength [12]. Al Salaheen et al. also used RSM to estimate and optimize the compressive strength of mortar by using heat-treated fly oil shale ash as an effective cementitious material [13]. Optimizing rice husk ash in geopolymer cement using RSM resulted in an optimal geopolymer composition of 11.67% RHA when cured for seven days at room temperature [14].

Nanosilica fills the pores in geopolymer, while CNCs function as reinforcement and prevent crack propagation. The composite of nanosilica and CNCs can mutually affect geopolymers; however, the literature shows that research on optimizing nanosilica and CNC addition to geopolymers has yet to be available. Therefore, this study aims to determine the percentage of nanosilica and CNCs in optimizing the compressive strength of geopolymer cement. RSM was employed as the method with CCD model using the Design Expert 11 software.

II. Method

A. Materials

The material was fly ash obtained from PLTU Nagan Raya, Aceh. White rice husk ash was processed in a ball mill for ten hours to prepare nanosilica based on the previous study [8]. CNC was made from the fibers of the typha plant by the acid hydrolysis method following previous studies [1][5]. Sodium hydroxide from Merck® and sodium silicate were used in the geopolymer mixture.

B. Procedures of Mixing and Testing

Two hundred and sixty grams of sodium hydroxide was mixed with 650 ml of water and added with 260 grams of sodium silicate to make an alkaline solution. The alkaline solution was added slowly to a 1000 g fly ash while stirring. The concentration ratio of fly ash and alkaline solution in the geopolymer cement paste was 74%: 26%. Next, nanosilica and CNCs were added following the experimental design recommended by RSM.

C. Formula Design

The design was prepared using the CCD method with Design Expert 11 software. Table 1 shows the variables. The nanosilica variables inputted into the RSM were 2% - 4%, while the percentage of CNCs was 1% - 3%. The optimized response variable was the geopolymer cement's compressive strength (Y1).

Table 1. Independent Variables and Treatment Symbols

Independent Variable	Notation	Range and level		
		-1	0	1
Nanosilica	NS	2	3	4
Cellulose nanocrystals	CNCs	1	2	3

III. Results and Discussion

A. Central Composite Design

The Design Expert software using the CCD method produced an experimental design with thirteen experimental runs and a center point of five runs. The next step was formulating or manufacturing the geopolymer cement mixture based on the obtained combination of treatments. Figure 1 shows the hardened geopolymer paste.

Fig. 1. The hardened geopolymer, a result of mixing according to the RSM method

Table 2 shows the compressive strength test result analyzed using RSM. The extraction variable was adjusted to the variable proposed by the RSM method, which was then tested for compressive strength. Table 2 shows the variations in nanosilica and CNC concentrations in which five replications were carried out for 3% nanosilica and 2% CNCs. Next, the compressive strength was analyzed using the mathematical model, and the model was validated.

Table 2. Experimental design and the result of compressive strength test using RSM

Run	Variable Code		Extraction Variable		Compressive strength respon (MPa)
	X_1	X_2	Nanosilica (%)	CNCs (%)	
1	0	-1.414	3	0.58	20.38
2	-1	1	2	3	18.16
3	-1	-1	2	1	18.1
4	1.414	0	4.414	2	21.2
5	-1.414	0	1.585	2	18.18
6	0	0	3	2	19.89
7	1	1	4	3	18.83
8	0	1.414	3	3.414	17.11
9	1	-1	4	1	22.19
10	0	0	3	2	20.12
11	0	0	3	2	20.19
12	0	0	3	2	20.11
13	0	0	3	2	20.00

B. The Statistical Model for the Effect of Nanosilica and Cellulose Nanocrystals on the Geopolymer Paste Compressive Strength

Tables 3 and 4 show the statistical summary model suggested by the Design Expert and the statistical data on the model selection. The model was selected based on the resulting R^2 values.

Table 3. Summary of statistical model for compressive strength

Source	Sequential p-value	Lack of Fit p-value	R-Square	Adjusted R^2	Predicted R^2	
Linear	0.0010	0.0005	0.7480	0.6976	0.4972	
2FI	0.0179	0.0013	0.8692	0.8256	0.7112	
Quadratic	**0.0004**	**0.0512**	**0.9865**	**0.9769**	**0.9168**	**Suggested**

Based on Table 3, the suggested model was a quadratic model, which shows an R^2 value close to 1 (R^2 = 0.9865) with Adj-R^2 = 0.9769 and a predicted R^2 of 0.9168. This model is accurate because R^2 is close to 1; therefore, the correlation value is very suitable and shows an almost similar value between the actual and predicted values, while the other models have a more significant deviation.

Table 4. Statistical data on the quadratic model selection

Source	Value
Std. Dev.	0.2157
Mean	19.57
C.V. %	1.10
R^2	0.9865
Adjusted R^2	0.9769
Predicted R^2	0.9168
Adeq Precision	33.0825

Table 4 shows that the difference between Adjusted R^2 and Predicted R^2 is less than 0.2. Adeq Precision measured the accuracy ratio of prediction results to noise, with the desired ratio greater than 4 [16]. The obtained ratio was 33.0825, indicating an adequate signal. This model could predict the compressive strength of nanosilica and CNC-based geopolymer pastes. The actual mathematical model for predicting the compressive strength of geopolymer paste added with nanosilica and CNCs is:

$$Y = 20.06 + 1.13\ X_1 - 0.991\ X_2 - 0.855\ X_1X_2 - 0.160\ X_1^2 - 0.633\ X_2^2 \quad (1)$$

With: Y as the compressive strength (MPa), X_1 as the nanosilica concentration (%), and X_2 as the CNC concentration (%).

The mathematical model above explains the effect of each variable, namely nanosilica and CNCs, linearly and quadraticly, as well as the interaction between the two variables. The predicted compressive strength appeared to be close to the experimental results, indicating that the model has a slight deviation and can be used. The normal distribution of the residuals plots was assessed with the help of a graphical method as the normal probability plots, shown in Figure 2.

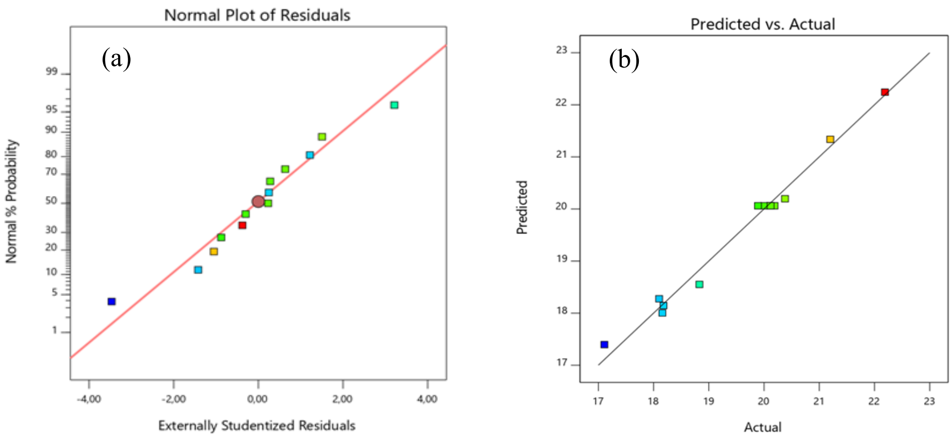

Fig. 2. (a) Normal plot from the residual and predicted values for compressive strength responses, (b) The predicted and actual values for compressive strength responses.

Figure 2(a) shows that the data points are close to a straight line; therefore, the residual data are normally distributed. Figure 2(b) shows the plot of the predicted data with actual data. The figure demonstrates that the data plot also shows a similar trend, i.e., almost forming a 45-degree straight line; thus, the predicted values are in accordance with the actual values.

The compressive strength test results are plotted in 3D, as shown in Figures 3(a) and 3(b). The graph shows that adding nanosilica and CNCs increases the compressive strength, but a decrease in compressive strength also occurs due to the composite of these two materials. The increase in compressive strength is due to increased reaction products from the geopolymer matrix [17][18]. Nanosilica can react and form C-S-H or C-A-S-H and N-A-S-H gels and lead to stronger geopolymer pastes [19][20]. Nanosilica also improved the pore-filling mechanism by filling voids and making geopolymers denser [21][22]. Meanwhile, the compressive strength decreased due to the agglomeration of CNCs in the geopolymer paste. CNCs could not disperse evenly in the geopolymer paste because many CNCs agglomerate. Some researchers suggest using mechanical energy or ultrasonication to break the CNC agglomeration and separate the CNC particles [23][25].

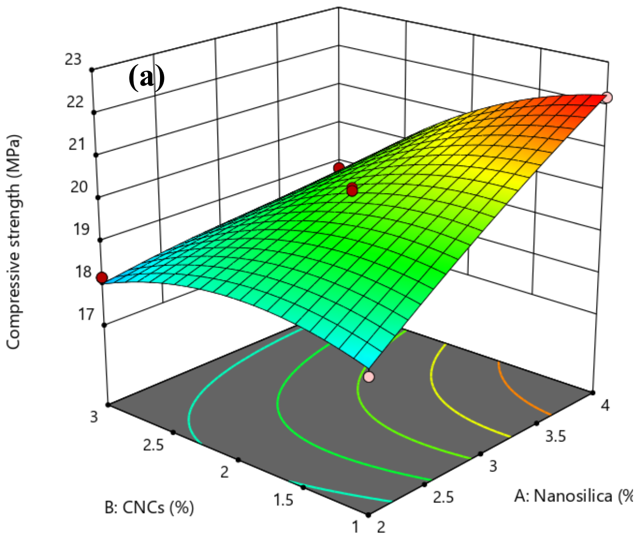

Fig. 3. The effect of nanosilica and CNC concentration on the compressive strength of geopolymer paste (a) 3D display of surface response (b) Display of contour diagram

Figures 4 and 5 show the desirability value, which indicates the achievement of the relationship between variables. The desirability value indicates the program's ability to fulfill the desire for the best achievement based on predetermined criteria. The desirability value was set at 0 to 1 [26]. It shows that the combination of the given treatments was appropriate and significant.

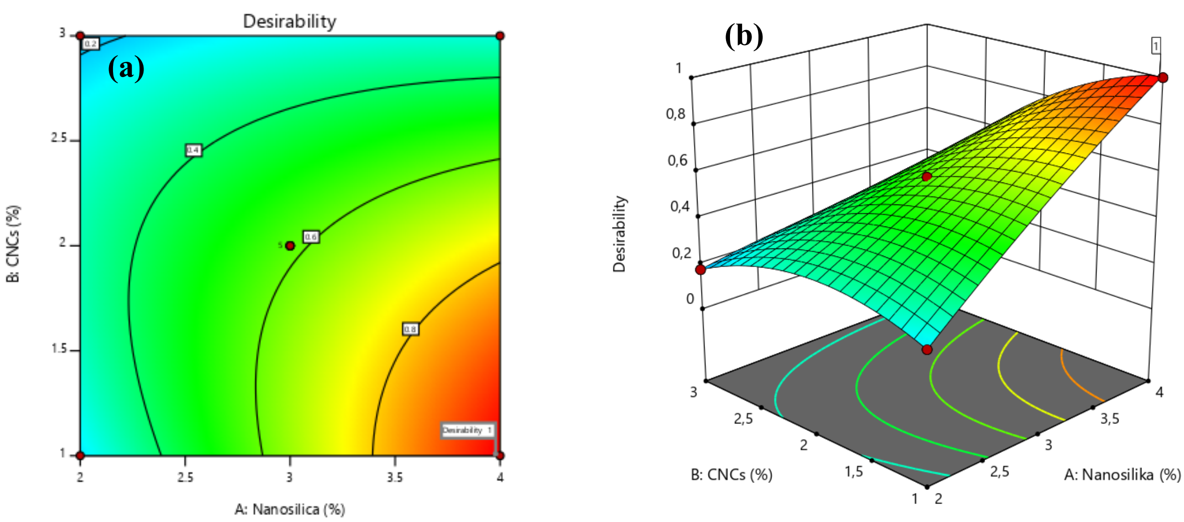

Fig. 4. The desirability of nanosilica and CNC-based geopolymer paste, (a) contour, (b) 3D display

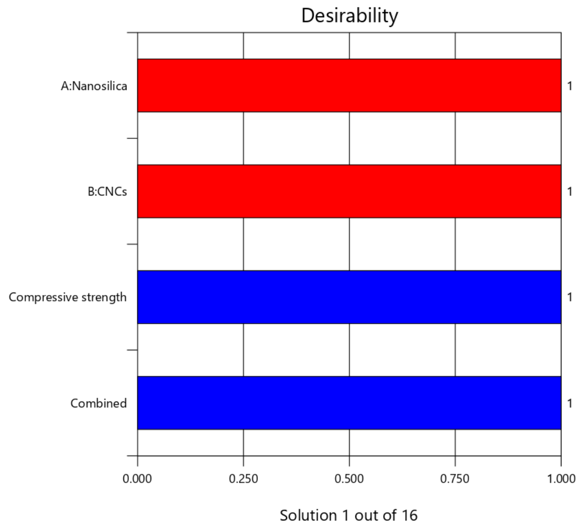

Fig. 5. Desirability diagram of nanosilica, CNCs, compression strength, and treatment combination.

Figure 5 shows that the program's ability to produce products according to wishes improves when the desirability value gets closer to 1. It shows that all variables have reached the best condition and can be applied to products. Another study also obtained a desirability value close to 1 [27]. Optimization aims not to obtain a desirability value of 1 but to achieve the best condition for all variables [28].

A numerical ramp was performed to assess the optimal compressive strength of nanosilica and CNC-based geopolymer pastes, as shown in Figure 6. The figure shows that nanosilica and CNCs influence the increase in compressive strength.

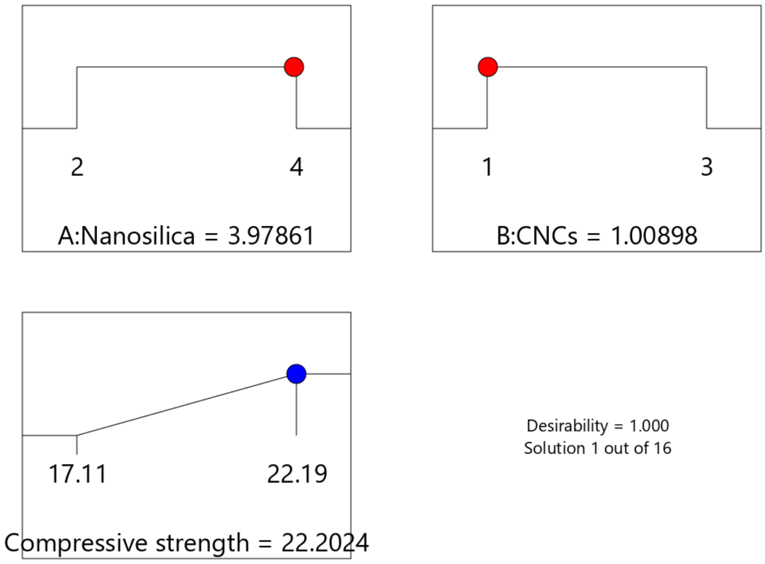

Fig. 6. Result of nanosilica and CNC-based geopolymer paste optimization based on the numerical ramp graph.

Figure 6 shows that the optimal compressive strength of 22.20 MPa was obtained by adding 3.98% of nanosilica and 1% of CNCs. The effect of nanosilica and CNCs on compressive strength can be observed from the perturbation curve plot in Figure 7.

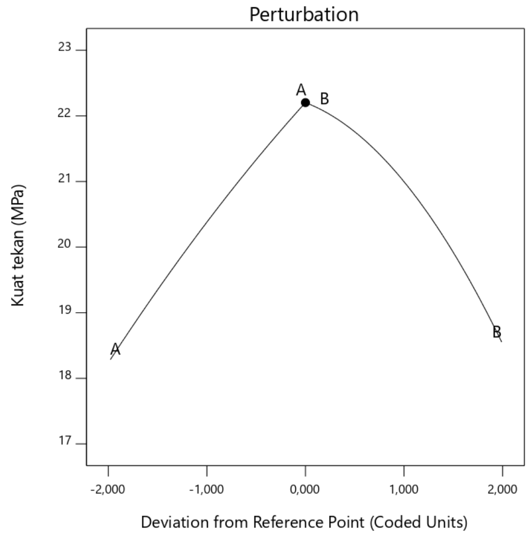

Fig. 7. The perturbation curve for compressive strength of nanosilica and CNC-based geopolymer paste

The steep slope is given by factors A (Nanosilica) and B (CNCs), which indicate the sensitivity of these two factors. The slope (gradient) on factor A (nanosilica) shows an increase, in contrast to factor B (CNCs), which shows the opposite. The graph shows that the addition of nanosilica continues to increase the compressive strength at a point, and if it is composited with CNCs, the optimal value will occur at a certain point. The optimal compressive strength for geopolymer paste occurs at a low CNC concentration.

C. Model Validation using ANOVA

Table 5 shows the analysis of variance for the effect of nanosilica (%) and CNCs (%) on the compressive strength of geopolymer paste. Based on the Central Composite Design, the ANOVA calculation shows linear and quadratic individual effects of nanosilica and CNC variables, as well as the interaction effect of each of these variables. The calculated F-Value was compared with the F Table value or p-value of the design expert itself for a 95% degree of confidence.

Table 5. ANOVA data for the effect of nanosilica and CNCs on the compressive strength of geopolymer paste

Source	Sum of squares	df	Mean square	F-value	p-value	Characteristics
Model	23.80	5	4.76	102.3	< 0.0001	significant
A-Nanosilica	10.19	1	10.19	219.12	< 0.0001	
B-CNCs	7.85	1	7.85	168.72	< 0.0001	
AB	2.92	1	2.92	62.85	< 0.0001	
A^2	0.1789	1	0.1789	3.85	0.0907	
B^2	2.79	1	2.79	59.89	0.0001	
Residual	0.3257	7	0.0465			
Lack of Fit	0.2702	3	0.0901	6.49	0.0512	not significant
Pure Error	0.0555	4	0.0139			
Cor Total	24.12	12				

Table 5 shows the validation result indicating that the compressive strength response model is appropriate and can be used. The high F value and the lower probability value (p), which is less than 0.005, confirm the significance of the model [10]. The model's lack of fit test result is not significant, meaning that the model is appropriate and can be used.

IV. Conclusion

An experimental design using the Central Composite Design (CCD) method with Design Expert 11 software on nanosilica and CNC-based geopolymer paste was conducted. The independent variables were 2% - 4% of nanosilica and 1% - 3% of CNCs, with compressive strength as the optimized response variable. The quadratic statistical model was selected with a normal distribution of residual plots, indicating that the predicted value is in accordance with the actual value. The mathematical model to predict the association between the percentage of nanosilica and CNCs with the compressive strength of geopolymer paste is $Y = 20.06 + 1.13 X_1 - 0.991 X_2 - 0.855 X_1X_2 - 0.160 X_1^2 - 0.633 X_2^2$ with X_1 as the percentage of nanosilica and X_2 as the percentage of CNCs. The optimal compressive strength of 22.20 MPa was obtained by adding 3.98% of nanosilica and 1% of CNCs. Model validation with ANOVA shows a p-value (p) of less than 0.005, indicating the significance of the model. There was an interaction between nanosilica, CNCs, and the compressive strength. Nanosilica appeared to work better on composites than CNCs. CNCs reacted less in geopolymers. Not all OH- bonds in CNCs bind to geopolymer. CNCs became non-reactive in the geopolymer composite due to agglomeration in the paste, while the fly ash could not bind to the alkaline solution properly, thus, disrupting the polymerization process.

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