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Operating Variables on Production of High Purity Bio-silica from Rice Hull Ash by Extraction Process

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Highlights:

- Indonesian rice hull biomass is abundantly available.
- Rice hull can serve as a good bio-silica source with low-cost raw material.
- This study investigated the effects of the operating variables of rice hull ash extraction.
- The bio-silica yield and purity were strongly affected by the acid concentration in the pretreatment.
- Variable screening can cut bio-silica production cost and time by half.

Abstract. The huge amount of rice hull biomass available in Indonesia can be utilized as raw material for bio-silica production. This study investigated the production of high-purity bio-silica from rice hull ash through an alkaline extraction process. A full factorial design (FFD) was used to screen for significant effects of the observed variables. Three operating variables – acid concentration, solvent to feed ratio ($R_{S/F}$), and extraction time – were investigated with the purpose of obtaining a high yield and high purity of bio-silica. Yield and purity above 96% were achieved by using pretreatment with 1 mol/L HCl. Employing an $R_{S/F}$ of 5 and a longer extraction time improved the bio-silica yield. The operating variable that enhanced the bio-silica yield and purity most was acid concentration. All variable interactions had an insignificant effect on purity, while two interacting variables had a significant effect on bio-silica yield. Based on the results of this study, rice crop residue can be optimally converted to a bio-silica product in terms of yield and purity by optimizing the most effective operating variables.

Keywords: *acid concentration; alkaline extraction; bio-silica; full factorial design; rice hull ash.*

1 Introduction

Developing countries in Southeast Asia have enormous rice crop (*Oryza sativa L.)* production [1-4], among them Indonesia. Rice processing often generates an abundant amount of rice hull, which is usually discharged to a landfill or open burned [5,6]. On the other hand, rice hull can serve as a bio-silica source as a low-

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cost raw material, which is frequently used in non-food industrial applications [7]. Even now, many silica-based products are used for pharmaceutical applications such as drug delivery systems, nanocomposite film for modified-release tablets, and microparticles for promising esophageal mucosal delivery systems [8,9]. Therefore, proper rice hull utilization is interesting due to its ability to replace fossil resources. It is economically attractive, has wide applications in terms of energy and chemicals, and has an environmentally friendly production process [10-13].

Rice hull utilization is usually executed through calcination followed by extraction with an alkaline solvent to produce water glass [14,15], also known as the sol-gel method [16-19]. Subsequently, the water glass is titrated with acid after which the obtained gel begins to precipitate. The precipitate is in a colloidal state, which is further aged and dried to obtain bio-silica [20]. The developed sol-gel method has been proven to be capable of synthesizing silica with altered properties such as nano-sized and doped nanocomposites for disinfectant purposes [17], UV-protective materials [18], and mesoporous thin film [21].

Due to the previously mentioned capabilities of the sol-gel method, this method was chosen in this study for the extraction of rice hull ash to produce bio-silica. Several variables affect the extraction process, such as acid washing time, acid concentration, solvent to feed ratio ($R_{S/F}$), solvent concentration, and extraction time and temperature [6,22-28]. However, not all of them have a significant effect. In addition, many studies only dealt with the development of rice hull extraction methods to obtain high-purity bio-silica [22,23,25,29,30] or to produce submicron bio-silica particles [31-34]. Rice hull utilization experiments with statistical analysis that have been done so far targeted bio-silica particle size distribution analysis [35], observation of the effect of bio-silica gel concentration on cement matrix compressive strength [16], phenolic compound production optimization [1], alkali pretreatment and enzymatic hydrolysis [3], β-blocker synthesis [7], lignin extraction [36], energy production [37], and de-lignification [38].

As mentioned above, the study on determining the significant operating variables in the rice hull ash extraction process to produce high-purity bio-silica through statistical analysis has not been done yet. Hence, this study intended to investigate the effects of three extraction operating variables – acid concentration, $R_{S/F}$, and extraction time – on bio-silica yield and purity. The significant main and interaction effects as well as the quantitative relationships between the operating variables were also studied.

2 Materials and Methods

2.1 Bio-silica Production Experiment

Rice hull was purchased from a rice milling industry in Bandung, West Java. Analytical-grade HCl and NaOH were procured from Merck. The rice hull was first calcined at 700 °C to form ash, which was then pretreated by an acid wash using HCl with concentrations varied at 0.1 and 1 mol/L. Subsequently, atmospheric chemical extraction of the treated rice hull ash was assisted with NaOH at 120 °C under $R_{S/F}$ of 5 and 6. The extraction time was varied at 1 h and 2 h. Afterward, the extract solution was filtered to obtain water glass and was slowly titrated with HCl at room temperature. The gel was aged, rinsed with distilled water, and finally dried. The experiment was carried out in triplicate. The desired responses were bio-silica yield and purity. The bio-silica yield (Y) is defined as the ratio of bio-silica obtained from the extraction to silica content in rice hull ash. The value is calculated with Eq. (1).

$$Y = \frac{m_p \times P_p}{m_a \times P_a} \times 100\% \tag{1}$$

where m_p is the mass of bio-silica, P_p is the bio-silica purity, m_a is the mass of rice hull ash, and P_a is the silica content in the rice hull ash.

2.2 Bio-silica Characterization

Silica content in rice hull ash (P_a) and bio-silica purity (P_P) were measured by a Rigaku ZSX Primus III+ X-ray fluorescent spectrometer equipped with a palladium X-ray generator and silicon detector. The sample should be pretreated by grinding and pelletizing, followed by drying. The external morphology of the obtained bio-silica was characterized by a Phenom proX desktop scanning electron microscope at 12.5 kV and a working distance of 9.6 mm.

2.3 Investigation Methods

A full factorial design (FFD) was employed to investigate, analyze, and screen for significant effects of the observed variables on rice hull ash extraction. The design had three observed factors (variables), here denoted as X_1, X_2, and X_3. Each factor was used at two levels; the values used for each level are tabulated in Table 1.

Table 1 Operating variables and level values used in the rice hull ash extraction experiment.

Factor	Variable Name [Units]	Low Level (-1)	High Level (+1)
X_1	Acid concentration [mol/L]	0.1	1
X_2	$R_{S/F}$ [-]	5	6
X_3	Extraction time [h]	1	2

The desired responses were analyzed separately and the outcomes of the FFD analysis involved the residual plot, the main plot, the interaction plot, and the response contour plot.

The statistical model development was generated using Eq. (2) for bio-silica yield and Eq. (3) for bio-silica purity. The significance of the main and interaction effects of the observed variables was evaluated under a P-value of < 5% to estimate the relative importance of the variables. Furthermore, insignificant variables were eliminated after the two-tailed T-test (Eq. (4)) and the simplified model was then assessed. Both simplified models were then validated with the experimental data.

$$Y = C_0 + \sum_{i=1}^{3} C_i X_i + \sum_{i=1}^{2} \sum_{j=2}^{3} C_{ij} X_i X_j + C_{123} X_1 X_2 X_3 \tag{2}$$

$$P_p = K_0 + \sum_{i=1}^{3} K_i X_i + \sum_{i=1}^{2} \sum_{j=2}^{3} K_{ij} X_i X_j + K_{123} X_1 X_2 X_3 \tag{3}$$

$$T_{value} = \frac{C}{SE_{,C}} = \frac{K}{SE_{,K}} \tag{4}$$

where Y and P_P are the responses for bio-silica yield and purity, C and K are the model coefficients, X_i are the main effects of the operating variables, $X_i X_j$ represent the interaction effects between the operating variables, and SE is the model coefficient standard error in the respective terms.

3 Results and Discussion

3.1 Effects of Extraction Operating Variables

Based on the XRF result, the rice hull ash had a purity of 87.69%. The average results, supplemented with standard deviation (ST. DEV), are outlined in Table 2. Pretreatment under 0.1 mol/L acid, extraction with $R_{S/F}$ 5-6, and extraction time 1-2 h yielded a purity in the range of 58-62%. On the other hand, rice hull ash pretreatment with 1 mol/L HCl prior to extraction increased the purity from 87.69% to approximately 96%. Thus, it can be said that only the acid concentration strongly affected the bio-silica purity, while $R_{S/F}$ and extraction time had a low impact. However, the bio-silica purity from this study was still slightly lower than the silica purity obtained from the research conducted by Maksum, *et al.* (2019), which was 99.93% [14]. They found that applying roasting-quenching before the acid wash contributed to significant removal of alkaline minerals, especially potassium.

Table 2 also reflects that bio-silica yield was in the range of 47-64% under an acid concentration of 0.1 mol/L and 72-97% under an acid concentration of 1 mol/L. For each acid concentration value and $R_{S/F}$ 5, a longer extraction time improved the bio-silica yield. The opposite behavior was found for $R_{S/F}$ 6, where the bio-silica yield was suppressed from 1-h to 2-h extraction. This phenomenon is in line with the simulation study by Ramli, *et al.* (2022) [19] as well as the study conducted by Steven, *et al.* (2021) [6], where the highest bio-silica yield was reached at $R_{S/F}$ 6 and 1-h extraction time.

Table 2 Average experiment results (± ST. DEV).

Coded X_1	Coded X_2	Coded X_3	Bio-silica Yield (%)	Bio-silica Purity (%)
-1	-1	-1	47 ± 2	58 ± 8
-1	-1	1	58 ± 2	62 ± 5
-1	1	-1	64 ± 2	62 ± 5
-1	1	1	56 ± 2	60 ± 8
1	-1	-1	72 ± 4	96 ± 1
1	-1	1	83 ± 3	96 ± 1
1	1	-1	97 ± 1	96 ± 0
1	1	1	84 ± 1	96 ± 0

FFD is an efficient experimental design for two or more variables that are varied together and usually used to explore the influence of main factors and their interactions [39,40]. FFD is also frequently used in industrial R&D due to its ability to screen the most significant variables, which further allows cost and time efficiency of industrial production [41,42]. Based on the FFD preliminary analysis, the extraction data were normally distributed (Figures 1(a)-(b)), whereas the residuals were randomly scattered, both for bio-silica yield and purity (Figures 1(c)-(d)).

The operating variables with a significant effect on the bio-silica yield were X_1 and X_2 (Figure 2(a)), whereas bio-silica purity was only influenced by X_1 (Figure 2(b)). A greater value of X_1 resulted in a higher yield and purity, whereas increasing X_2 only increased the yield. There was a bio-silica yield change along with a greater X_3, but the value was statistically insignificant for yield and purity. Hence, the acid concentration most strongly influenced the bio-silica yield and purity. If the effect of interacting operating variables is significant, the main effect cannot be interpreted without considering the effects of the interactions. A significant interaction between the variables is represented by non-parallel lines. The more non-parallel the lines are, the more notable the interaction effect's strength [43,44].

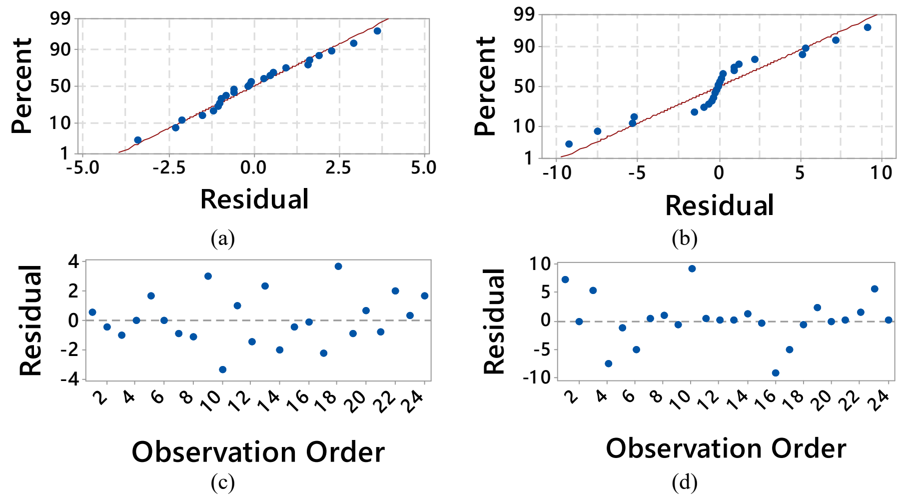


Figure 1 Normal probability plot for yield (a) and purity (b); residual plot for yield (c) and purity (d).

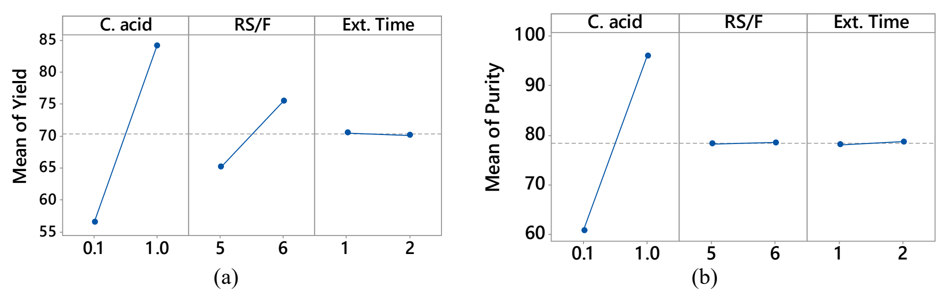


Figure 2 Plots of the effects of the operating variables on (a) yield and (b) purity.

In Figure 3(a), the X_1X_2 interaction lines are arguably close to parallel, while the lines in X_1X_3 are parallel and coincide. Thus, it can be said that X_1X_2 interaction had a slightly significant effect on the bio-silica yield and X_1X_3 interaction had no effect on it. The crossing lines of X_2X_3 indicate that the yield enhancement due to the interaction effect of X_2X_3 was weaker than the main effect of X_2. This tells us that interaction between $R_{S/F}$ and extraction time occurs and depends on the extraction time value [44]. There was a bio-silica yield decrease of about 8-10% under higher values of X_2 and X_3. Conversely, all interaction variables gave an insignificant change in purity, as can be seen in Figure 3(b), as all lines are parallel and coincide.

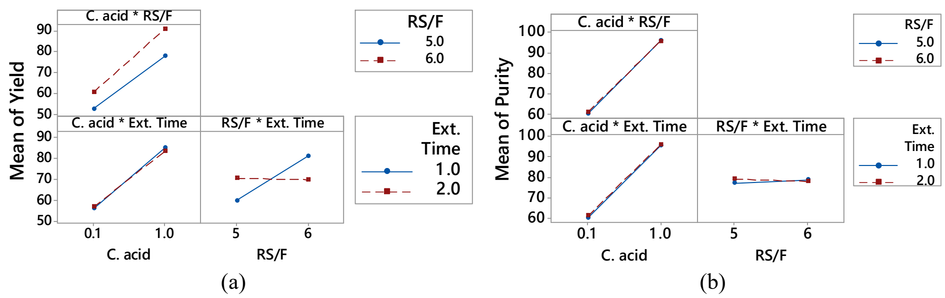


Figure 3 Plots for the effects of interacting operating variables on yield (a) and purity (b).

The response contour plots for bio-silica yield and purity are shown in Figures 4 and 5. Figure 4(a)-(b) imply that for each constant value of X_2 and X_3, increasing X_1 from 0.1 to 1 increased the bio-silica yield, exceeding 90%. For $X_3 = 1$ and at every value of X_1, a higher value of X_2 increased the bio-silica yield. The yield slightly changed and even decreased with higher X_2 when $X_3 = 2$, as can be seen in Figure 4(c)-(d). After that, as noticed in Figures 4(e)-(f), the bio-silica yield increased with a higher value of X_2 only for $X_3 = 1$ and seemed to have a small change for $X_3 = 2$. Figure 5(a)-(f) indicate that only X_1 influenced the bio-silica purity. Increasing X_1 from 0.1 to 1 increased the purity to about 96%. A higher value of X_2, X_3 as well as the interaction effects between the variables gave an insignificant change of purity.

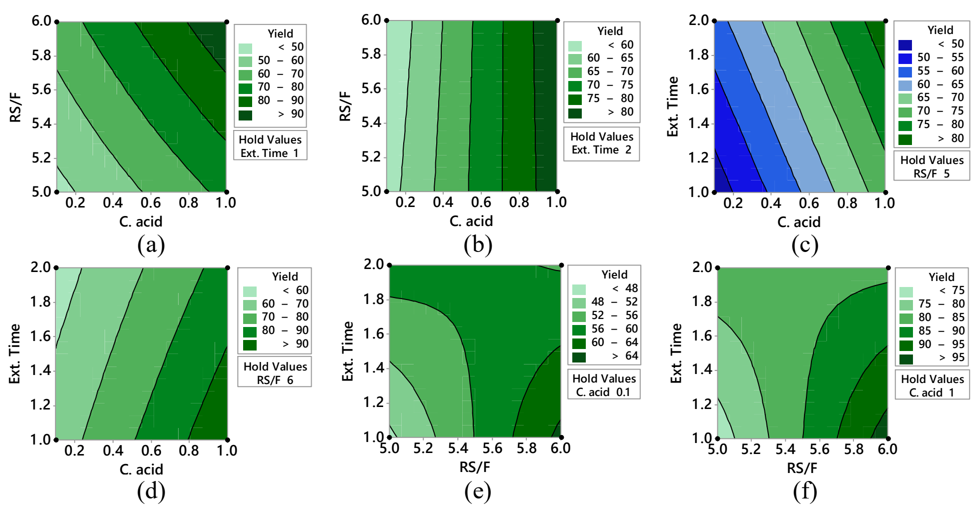


Figure 4 Response contour plot for bio-silica yield.

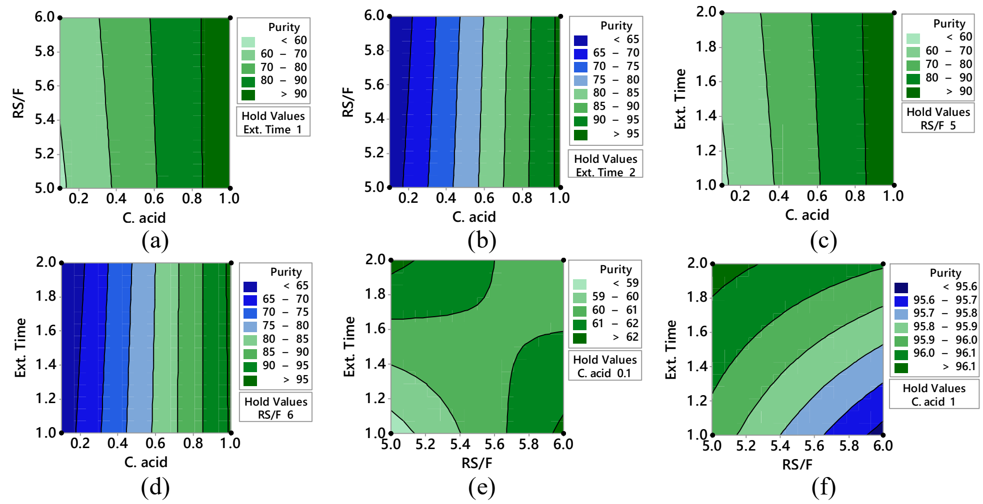


Figure 5 Response contour plot for bio-silica purity.

3.2 Quantitative Relation to the Extraction Operating Variables

The main and interaction plot of the operating variables above only indicates the magnitude of an effect without knowing the increasing or decreasing values. Statistical model development should still be performed to examine the magnitude and order of the effect. Apart from the effect, knowing the quantitative relationship between the response values and operating variables was also a goal of this study. This quantitative relationship is represented by the coefficients of each variable for both responses.

Figure 6 plots the T_{value} of all operating variables, which shows their significance order from the largest to the smallest. The red vertical dashed line at 2.07 is the T-critical regime as the criterion for null hypothesis rejection [44]. In this case, the statement for the null hypothesis is no difference in variance between one variable and another. The effect significance order was obtained as explained below.

When the bar length is below the T-critical regime (P-value > 5%), the null hypothesis fails to be rejected, which means there is no significant effect from the variables. Meanwhile, there is a significant effect on the variables when the bar crosses or exceeds the T-critical regime (P-value < 5%) so the null hypothesis is rejected [39,40,42,44]. Figure 6(a) shows that the bio-silica yield was influenced by X_1, X_2X_3, X_2, and X_1X_2 in order of decreasing significance. The other variables affected the bio-silica yield insignificantly, which confirms the results from Figures 2(a) and 3(a).

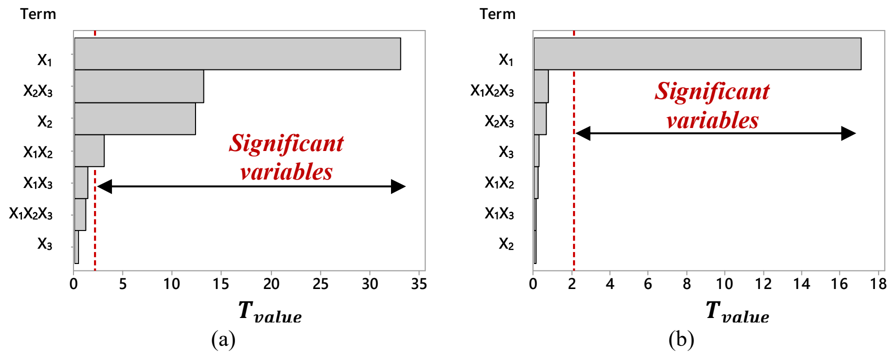


Figure 6 T_{value} of the operating variables for yield (a) and purity (b).

In Figure 6(b), X_1 is the only variable that strongly influenced the bio-silica purity, in line with the explanation in Figures 2(b) and 3(b). The poor bio-silica yield and purity under X_1 = 0.1 was provoked by the presence of significant impurities that existed in the product's pore structure. Increasing the acid concentration removes these impurities and leads to an improvement in bio-silica yield and purity [24,25,32,45-47].

The standard error for bio-silica yield ($SE_{,C}$) and purity ($SE_{,K}$) was 0.418 and 1.02, respectively. The T_{value} for each variable was then calculated with Eq. (4); the results are listed in Table 3. Then, the variables which had a T_{value} between -2.07 and 2.07 or P-value > 5% could be set aside because there was no statistically significant relationship between response and variable [48]. Moreover, the sum of squares of each eliminated variable was lower than the sum of squares of the residual, which confirms the elimination decision based on the T_{value} and/or P-value [41,48].

Table 3 Developed model parameters for bio-silica yield (Y) and purity (P_p).

Variable	C	K	T_{value}		P-value		Sum of Squares	
			Y	P_p	Y	P_p	Y	P_p
Constant	70.31	78.35	168.28	76.52	0.000	0.000	-	-
X_1	13.86	17.56	33.17	17.15	0.000	0.000	4610.94	7403.30
X_2	5.18	0.14	12.40	0.13	0.000	0.897	644.60	0.44
X_3	-0.19	0.29	-0.46	0.29	0.650	0.778	0.90	2.08
X_1X_2	1.30	-0.26	3.11	-0.26	0.007	0.800	40.51	1.67
X_1X_3	-0.57	-0.14	-1.36	-0.14	0.193	0.894	7.75	0.46
X_2X_3	-5.53	-0.71	-13.24	-0.69	0.000	0.501	733.94	11.93
$X_1X_2X_3$	-0.52	0.77	-1.24	0.75	0.233	0.462	6.45	14.32
Residual	-	-	-	-	-	-	67.03	25.16

The bio-silica yield was affected by X_1, X_2, X_1X_2, and X_2X_3, while only X_1 affected the bio-silica purity. A special case for the effect of X_1X_2 on the bio-silica yield was found. Even though the sum of squares was somewhat lower than the residual, the effect was still acceptable because the P-value was below 5%. Table 3 also shows that the coefficient of X_2X_3 had a minus sign, which implies that the yield increased due to the effect of X_2X_3 was weaker than the main effect of X_2. These explanations are all consistent with the aforementioned.

The simplified statistical model between the response and the operating variables has now been determined. The R^2 for both models was 0.9960 for the bio-silica yield and 0.9958 for the bio-silica purity, as shown in Figure 7. Both models were capable to predict the response, which is indicated by the R^2 value being close to 1 [7]. Then, both simplified models were validated. Figure 7 shows that the model's prediction appeared to be in good and reasonable agreement with the experimental data. From all the explanations above, it can be said that as much as 50% of the total experimental run could be eliminated in all experiments using pretreatment under 0.1 mol/L HCl.

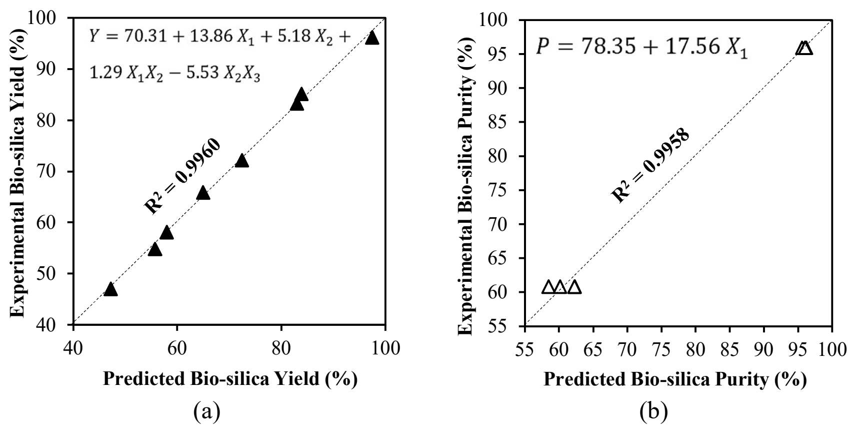
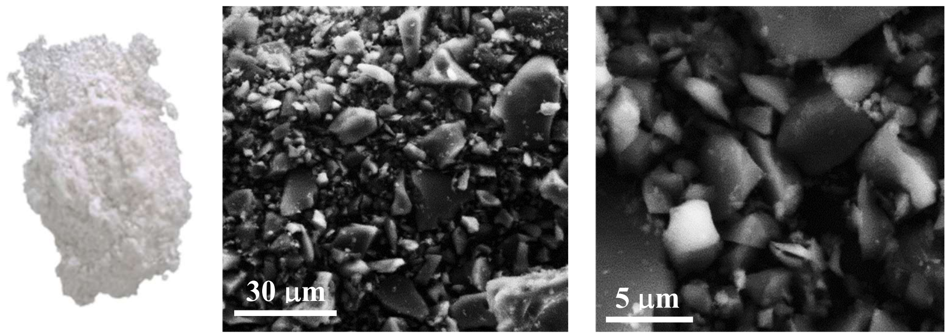


Figure 7 Simplified model validation check for bio-silica yield and purity.

3.3 Bio-silica SEM Result and Analysis

The bio-silica obtained from rice hull ash extraction is shown in Figure 8(a) and the external morphology is shown in Figure 8(b) for 1000X magnification and in Figure 8(c) for 5000X magnification. The bio-silica's external morphology mostly exhibits an irregular prism structure; only a few particles have a spherical shape and the particles are discernible in the absence of agglomeration or clustering [6,28,49]. Based on the 12.5 kV and a capturing distance of 9.6 mm, the average silica particle size was found to be in the range of 5-20 microns. A non-homogenous and non-uniform particle morphology is strongly caused by a brief hand-grinding process [32,49].



(a) (b) (c)

Figure 8 Bio-silica obtained from rice hull ash (a); external bio-silica morphology under 1000X magnification (b) and 5000X magnification (c).

4 Concluding Remarks

Rice hull ash extraction to produce high purity bio-silica accompanied by a full factorial design of the experiment was successfully investigated. The effects of three variables, i.e., acid concentration, $R_{S/F}$, and extraction time, on the bio-silica yield and purity were investigated. Pretreatment with 1 mol/L acid resulted in around 96% of bio-silica purity. Bio-silica yield reaching 97% was also majorly affected by acid concentration, while another main factor that also had a fairly significant effect was $R_{S/F}$. There was a decreased bio-silica yield of about 8-10% for extraction under $R_{S/F}$ 6 and 2-h extraction time, while simultaneously increasing the acid concentration and $R_{S/F}$ had a synergistic effect on the bio-silica yield. This study confirmed that high purity bio-silica with a particle size of 5-20 microns was successfully produced from rice hull ash. Moreover, variable screening was able to cut the industrial production cost and time by half.

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