Optimisation of bleaching time and $\text{H}_2\text{O}_2$ concentration of handmade paper from *Areca catechu* L. fibre

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**Abstract.** Areca nut (*Areca catechu* L.) is a type of palm used for commercial purposes because all parts of the plant have high economic value. Areca nut fibre contains 53.2% cellulose and therefore, it can potentially be used as raw material for pulp for paper craft. Bleaching is conducted in order to make colourful paper craft. Some factors to be taken into account while bleaching the paper craft are levels of chemicals used for bleaching and length of bleaching time. The purpose of this study was to determine $\text{H}_2\text{O}_2$ level and optimum bleaching time to create quality paper from areca fibres and cardboard paper. Quality of the paper was evaluated based on tensile strength, thickness, grammage and brightness. Response surface method (RSM) is implemented optimize the estimated response. The model used in RSM is CCD (Central Design Composite) with 2 factors, namely bleaching time and $\text{H}_2\text{O}_2$. The upper and lower limit for the first factor were 90 and 150 minutes consecutively. Those for the second factor were 5% and 15% respectively. The evaluate responses were tensile strength and brightness level. The findings showed that the most suitable combination was 150-minutes bleaching time and 15% $\text{H}_2\text{O}_2$. The combination resulted in 69.50% brightness and 14.71 kN/m$^2$ tensile strength. In addition, the paper grammage was 282 gr/cm$^2$, its thickness was 0.88 mm and the moisture content was 6.5.

1. **Introduction**

Areca nut (*Areca catechu* L.) is a type of palm that is used for commercial purposes due to its high economic value from all parts of the plant, such as leaf, stem, seed and fibre [1]. Areca nut is easily found in Southern and Southeast Asia particularly in Indonesia [2]. In 2014, Indonesia produced 42,201 tonnes of areca nut. Sumatra, the largest producer of areca nuts in Indonesia harvested 32,640 tonnes, while Nusa Tenggara produced 7,207 tons and East Java produced 203 tonnes of 872 ha area [3].

Areca nut’s seeds and leaves are commonly utilized, e.g. tanning [4], anti-oxidant [5], and medicine [6, 7]. However, other parts of the plant are remained unused and become waste or burned as a heat source [8]. Areca fibre contains cellulose (45.7%) and lignin (15.9%) [9]. Therefore, the cellulose can potentially be used as raw material for pulp and handmade paper.

Recent research shows that areca nut is used for cardboard production and has brownish colour with apparent fibre [10]. Therefore, bleaching is required to lighten-up the paper colour. The bleaching process aims to remove some lignin left on the pulp. The common chemical used in bleaching process is hydrogen peroxide ($\text{H}_2\text{O}_2$) [11, 12]. This chemical can brighten the paper colour and do not damage
the cellulose [11, 12]. The factors to take into account in bleaching process are the H$_2$O$_2$ concentration and the bleaching time [13].

In the present research, the optimum condition of chemical concentration and bleaching time was studied using Response Surface Method (RSM). The RSM is developed for determination of the optimum operating conditions [14]. RSM makes computational-based analysis easier, more practical, faster and more accurate. The method is suitable to analyse the optimum condition of bleaching time and hydrogen peroxide concentration to produce quality handmade paper.

2. Materials and Method

2.1. Materials

The raw materials used to make art paper were approximately a four-month old areca nut that has green fibres and was purchased from the sellers in Pasar Besar, a fresh market in Malang. Cardboard paper from a 200 mL UHT milk was also used. Other materials were 25% technical NaOH (w/v), purified water, and 35% technical H$_2$O$_2$ (v/v).

2.2. Process of handmade paper making

This paper making process was divided into 3 stages, namely the making of (1) areca nut fibre pulp, (2) pulp from the cardboard paper and (3) handmade paper. During the first stage, the areca nut shell was removed using a knife to obtain the fibre. The fibres were cut into a 3-4 cm long and 0.5 cm wide. The collected fibres were then air-dried in a baking sheet for 24 hours. A 10 g of the dried fibre were taken and cooked for delignification in 25% NaOH solution for 90 minutes at 100°C. Subsequently, the fibres were ground in a blender for 5 minutes. A filter cloth was used to sieve the pulp and rinse it with water to remove the remaining NaOH solution to get the areca nut fibre.

The second stage was the making of pulp from used cardboard box. The used cardboard boxes were cut into 1 cm$^2$ in size. A ten gram of the cut cardboard were blended for 2 minutes in addition of water to produce the cardboard pulp.

In the third stage, both the areca fibre and the cardboard pulp were mixed in blender for approximately 1 minute to evenly mixed. Water was added when necessary. For the delignification process, the mixed pulp was cooked in 5%, 10% and 15% H$_2$O$_2$ at 80°C for 90, 120 and 150 minutes. After the delignification process, the pulp went to a second homogenizing process until it is evenly mixed. The mixed pulp was then poured into a tub or bucket and moulded using a 120-mesh screen (20 x 15 cm) and manually pressed with a plywood. Finally, the pulp was sun-dried to produce the paper.

2.3. Experimental design

The present study used the RSM method with a Centralized Composite Design (CCD) with two factors, the bleaching time and the H$_2$O$_2$ concentration. The observed level and their range were as follows:

a. Bleaching time (A)
   - 90 minutes ($X_1 = -1$)
   - 120 minutes ($X_1 = 0$)
   - 150 minutes ($X_1 = +1$)

b. H$_2$O$_2$ concentration (B)
   - 5% H$_2$O$_2$ ($X_2 = -1$)
   - 10% H$_2$O$_2$ ($X_2 = 0$)
   - 15% H$_2$O$_2$ ($X_2 = +1$)

2.4. Analysis

The parameters used for optimization were tensile strength [15] and brightness level [16]. Thickness [17], grammage [18] and moisture content [19] were also measured for additional parameters. The analysis of tensile strength and thickness were conducted in Laboratory of Power and Machine,
Department of Agricultural Engineering, while the brightness level, grammage and moisture content were analysed in Laboratory of Agrochemical Technology, Department of Agro-industrial Technology, Faculty of Agricultural Technology, Universitas Brawijaya, Indonesia.

2.5. Data analysis
Data analysis was conducted using Design Expert version 7. The experimental data were analysed based on a 2-factor CCD [20]. The responses were tensile strength and brightness level. The data analysis using DE accommodated analysis of variance (ANOVA) and suggested the optimum condition of process. The optimum solution from the computation was then verified via laboratory experimentation.

3. Results and Discussion
3.1. Brightness and tensile strength
Based on Table 1, the highest brightness level was 69.22% which was obtained from the combination of 120 minutes bleaching time and 17.07% H₂O₂. Treatment with combination of 90 minutes bleaching time and 5% H₂O₂ resulted the lowest brightness level at value of 65.08% and the highest tensile strength (22.06 kN/m²). While the lowest tensile strength was 10.78 kN/m² obtained from the combination between 162.43 minutes bleaching time and 10% H₂O₂.

| H₂O₂ Concentrations (%) | Bleaching Time (minute) | Treatment ID | Brightness (%) | Tensile Strength (kN/m²) |
|-------------------------|------------------------|-------------|----------------|-------------------------|
| 5                       | 90                     | A₂B₂        | 65.08          | 22.06                   |
| 5                       | 150                    | A₂B₄        | 68.32          | 11.52                   |
| 15                      | 90                     | A₁B₂        | 65.44          | 20.07                   |
| 15                      | 150                    | A₁B₄        | 67.78          | 18.45                   |
| 2.93                    | 120                    | A₁B₃        | 63.57          | 14.46                   |
| 17.07                   | 120                    | A₃B₃        | 69.22          | 15.45                   |
| 10                      | 77.57                  | A₁B₁        | 65.93          | 12.26                   |
| 10                      | 162.43                 | A₁B₅        | 69.01          | 10.78                   |
| 10                      | 120                    | A₁B₃        | 66.33          | 17.45                   |
| 10                      | 120                    | A₁B₃        | 65.87          | 18.67                   |
| 10                      | 120                    | A₁B₃        | 66.81          | 16.67                   |
| 10                      | 120                    | A₁B₃        | 67.06          | 14.96                   |
| 10                      | 120                    | A₁B₃        | 66.64          | 13.56                   |

Figure 1 shows impacts of various treatment combination on brightness level, while Figure 2 shows the influence of various treatment combination on tensile strength. Figure 1 shows that bleaching time and H₂O₂ concentration influenced the brightness level. Increasing bleaching time followed by increasing H₂O₂ concentration resulted in an increase in brightness level of the handmade paper. This finding is in line with the report of Vaysi and Kord [11] who found that a longer bleaching time increases the H₂O₂ oxidation to remove molecular binding in lignin causing the brightness level to increase. Based on ANOVA analysis, P of the linear model was 0.0018 (P<0.05), indicating that the linear model can explain significant influence of both factors on brightness level of the art paper. P of the brightness Lack of Fit was 0.0652 (P>0.05), showing that the accuracy of the linear model was significant. The ANOVA analysis demonstrated that R² was 0.7182 representing 71.82% influence on brightness response of the handmade paper. The ANOVA analysis also resulted in actual variable, with the equation as follows:
Figure 1. The effect of the treatments on the brightness level based on H$_2$O$_2$ concentration (from the lowest to the highest)

$$Y = 59.13711 + 0.047399X_1 + 0.18035X_2$$ (1)

Where: $Y$ represents brightness, $X_1$ refers to bleaching time (minutes) and $X_2$ refers to H$_2$O$_2$ concentration (%).

Figure 2 shows that bleaching time and H$_2$O$_2$ concentration influenced tensile strength of the handmade paper. The longer bleaching time and the higher H$_2$O$_2$ concentration decreases the tensile strength of the art paper. This is in agreement with the literature that a decrease in tensile strength of fibre was because lignin that binds the fibre was dissolved [21]. As a result, microfibril bound in the fibre was declined. A reduction in the amount of lignin on the art paper could damage the surface of the fibre, it is therefore decreasing its tensile strength.

Figure 2. Influence of the treatments towards tensile strength based on bleaching time (from the lowest to the highest)
Based on the ANOVA analysis, P was 0.0297 (P<0.05), demonstrating that the model can explain the significant influence of bleaching time and H$_2$O$_2$ concentration on tensile strength of the handmade paper. The P lower than 0.05 means that the selected model can explain a significant influence of independent variable towards response [20]. P of tensile strength Lack of Fit was 0.2846 (P>0.05) and “not significant” which means that the model fits the experiment data well. The ANOVA table showed that R$^2$ was 0.61 which means that bleaching time and H$_2$O$_2$ concentration have 61.35% influence towards tensile strength of the handmade paper while the remaining 38.65% were not involved in the model. The ANOVA also resulted in actual variable, following the equation below:

$$Y = 54.61881 - 0.32330X_1 - 3.69100X_2 + 0.030233X_1X_2$$  \hspace{2cm} (2)

Where, Y is tensile strength (kN/m$^2$), $X_1$ represents bleaching time (minutes), $X_2$ refers to H$_2$O$_2$ concentration (%), and $X_1X_2$ represents interaction between bleaching time and H$_2$O$_2$ concentration.

### 3.2. Optimisation of tensile strength and brightness responses

Table 2 shows that the optimum bleaching time factor was in range between 90 and 150 minutes. H$_2$O$_2$ optimum concentration ranged between 5% to 15%. These combination resulted the tensile strength with the minimum value of 11.22 kN/m$^2$ and the maximum value of 17.1 kN/m$^2$ respectively [21]. The minimum brightness level was 64.02% and the maximum value was 74.61% [22]. Table 3 shows the optimum solution resulted from the Design Expert 7.1.5. The predicted optimum tensile strength was 18.78 kN/m$^2$ and the brightness was 68.95%. This is resulted from bleaching time of 150 minutes and H$_2$O$_2$ concentration of 15%.

### Table 2. Response optimization criteria

| Criteria          | Parameter                  | Objective | Minimum | Maximum |
|-------------------|----------------------------|-----------|---------|---------|
| Factor            | Bleaching time (minute)    | In range  | 90      | 150     |
| Factor            | H$_2$O$_2$ concentration (%)| In range  | 5       | 15      |
| Response          | Tensile strength (kN/m$^2$) | Maximize  | 11.22[21]| 17.1 [21]|
| Response          | Brightness (%)             | Maximize  | 64.02[22]| 74.61[22]| |

### Table 3. Optimum solution based on Design Expert 7.1.5

| Parameter                  | Predicted solution |
|---------------------------|--------------------|
| Bleaching time (minute)   | 150                |
| H$_2$O$_2$ concentration (%)| 15                |
| Tensile strength (kN/m$^2$) | 18.78             |
| Brightness (%)            | 68.95              |

### 3.3. Verification of the optimum condition from the predicted model

Verification was conducted to investigate whether the responses of the predicted optimum condition similar to that of the laboratory experimentation. When the responses differed from that of the suggested optimum condition, the responses were then compared to the lowest and highest prediction generated from the program. Table 4 shows the verification of the prediction and experimentation results.
Table 4. Predicted score and verification result

| Response                        | Verification Result | Deviation (%) | Match (%) |
|---------------------------------|---------------------|---------------|-----------|
|                                 | V1      | V2      | V1      | V2      | V1      | V2      |
| Tensile strength (kN/m²)        | 14.71   | 13.89   | 21.69   | 26.06   | 78.31   | 73.94   |
| Brightness level (%)            | 69.50   | 68.32   | 0.79    | 0.92    | 99.21   | 99.08   |

Notes: V1 First Verification, V2 Second Verification

Table 4 shows that the tensile strength in the first and second verification were 14.71 kN/m² and 13.89 kN/m², respectively. Compared to the predicted tensile strength, which was 18.78 kN/m², there were 21.69% and 26.06% deviations, resulting in only 78.31% and 73.94% of the model matched the experimentation result. The brightness level in the first and second verification was 69.50% and 68.32%, respectively. Compared to the predicted optimum brightness, which was 68.95%, there was less than 1% deviation, resulting in over 99% of the model matched the experimentation results.

3.4. Comparison of the physical properties of the optimum condition and the control

Based on the verification, the optimum condition was 150-minute bleaching time and 15% H₂O₂ concentration. This optimum condition was then tested for its physical properties and was compared to the control and commercial photo paper.

Table 5. Comparison of the physical properties of the handmade paper at the optimum condition, the paper without bleaching (control) and the photo frame paper (commercial paper)

| Physical properties | Handmade paper | Control | Commercial paper |
|---------------------|----------------|---------|-----------------|
| Brightness level (%)| 14.71          | 44.13   | 2.94            |
| Tensile strength (kN/m²) | 69.50          | 62.46   | 61.54           |
| Grammage (gr/cm²)   | 282            | 320     | 250             |
| Thickness (mm)      | 0.88           | 1.2     | 0.3             |
| Water content (%)   | 6.5            | 6.5     | 7               |

Table 5 showed that all physical properties of the handmade paper were better than that of the control. However, those properties remain behind compared to the commercial paper. These three types of paper had different tensile strength since the photo frame paper was made from cardboard paper or short fibre that has lower tensile strength. Both the handmade paper and the control had long fibre, producing a higher tensile strength. The control still has lignin in its fibre. Lignin binds and glues one fibre to another making tensile strength of this type of paper higher than the handmade paper.

4. Conclusions

The present paper investigated the optimum condition of the handmade paper using areca nut fibre. It can be concluded that the optimum condition for handmade paper production was using 15% of H₂O₂ concentration and 150 minutes of bleaching time. The combination resulted in handmade paper with the physical properties of tensile strength of 14.71 kN/m², brightness of 69.50%, weight of 282 gr/cm², thickness of 0.88 mm and water content of 6.5%.

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