Optimization of Reaction Conditions for Preparing Carboxymethyl Cellulose from Bamboo Scraps by Response Surface Methodology

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Abstract. Sodium carboxymethyl cellulose (CMC) is mainly prepared from cotton linter and wood pulp. The bamboo scraps is a kind of natural lignocellulosic material with rich cellulose content. In this paper, the manufacture process of CMC from pre-treated bamboo scraps was reported. Box-Behnken design and response surface methodology were implemented for optimizing the reaction conditions in the light of single factor experiments. The results proved that the optimal factors of carboxymethyl reaction were: pre-treated bamboo powder (contained 91.7% α-cellulose) was added into aqueous ethanol with sodium hydroxide solution, the alkalization kept at 33.6 °C for 120min; subsequently, etherifying agent chloroacetic acid was put into the system and etherification carried out at 54.6 °C for 138min. After this preparation process, the product’s viscosity of its 1% water solution was 233 mPa·s.

1. Introduction
Considered as one sort of crucial cellulose derivatives, sodium carboxymethylcellulose (CMC), due to its thickening, viscosity and some other properties, is widely applied in textiles, daily chemical industry, medicine, food, building materials and other fields[1, 2]. Currently, most of the raw materials for CMC preparation is cotton linter and wood pulp. The waste biomass, such as bamboo scraps (bamboo powder and shaving), bagasse and corn-cob, is a kind of natural lignocellulosic materials with rich cellulose content. The manufacture method of CMC made of varieties of cellulose sources could be detail explored. In recently years, it became an interesting topic and many achievements in related field were reported [3, 4, 5].
The aim of this research was to get optimal reaction factors of carboxymethylation for CMC manufacture from pretreated bamboo scraps, then obtain the increased viscosity value of CMC. During the research, response surface methodology (RSM), which known as a valid statistical method with more precise and economical than the other ways, was applied to optimize the synthesis process. RSM could survey assorted factors simultaneously and obtain data about the interaction between variates, so as to get rational optimal results [6, 7].

2. Materials and Methods

2.1. Reagents
All of the chemical reagents and enzyme applied in this study, including ethanol, sodium hydroxide, monochloro acetic acid, acetic acid, cellulose, were purchased by Zeheng Biotechnological Co. Ltd.. All of these reagents were applied without further purification.
2.2. Bamboo Scraps and Its Pretreatment Method

Bamboo scraps was gathered from a company of bamboo products manufacturing located in Anji, Zhejiang Province. Bamboo scraps should be baked at 70°C by a vacuum oven after washing, subsequently powdered and sieved by 0.5 mm mesh sieve. Afterwards, bamboo powder was soaked into 6.1% sodium hydroxide liquor with the ratio of 1:10, string, maintained 90min at 50°C, then disposed the sample with cellulase solution (200U/mL) for 30 min at 49.0°C. After these procedures, the α-cellulose content of pretreated bamboo powder enhanced from 45.2% to 91.7%.

2.3. CMC Preparation and Optimizing Study by RSM

CMC synthesis by refined bamboo powder (contained 91.7% α-cellulose) was implemented by alkalization and etherification in the system successively. Based on the single-factor test what was done before, we got the ranges of each factors. The powder was added into aqueous ethanol with sodium hydroxide solution to start the reaction. Then Plackett-Burman design (PBD) was employed to screen the remarkable effect factors. Table 1 demonstrated the design of steepest ascent path and corresponding conclusions. RSM was applied to optimise the most remarkable variable factors and analyze the relationship between the factors and the product’s viscosity value. Box-Behnken design (BBD) was employed for further studied on these independent factors, and table 2 showed the design and results. The model’s analysis was assessed by analysis of variance (ANOVA) with Design Expert version 7.0.0. The model’s quality was evaluated by the determination coefficient, R². The significance of the polynomial equation for the response variables was estimated by p value. In this experiment, the selected response value was CMC’s viscosity of its 1% aqueous solution.

3. Results and Discussion

Based on PBD experiment, it showed alkalization temperature (X₁), etherification temperature (X₂) and etherification time (X₃) were significant variables (p<0.05), accompanied with an extensive variation of viscosity. Therefore, X₁, X₂ and X₃ were chosen for further study to obtain the optimal response.

Table 1 showed the path of steepest ascent experiments and the consequences, it demonstrated Run 2 would be close to the scope of the maximum response, which could be selected for the next step optimal test.

Table 1. Steepest ascent design and the consequences

| Run | Alkalization temperature (°C) | Etherification temperature (°C) | Etherification time (min) | Viscosity (mPa·s) |
|-----|-------------------------------|---------------------------------|---------------------------|------------------|
| 1   | 37                            | 115                             | 60                        | 90.9             |
| 2   | 35.5                          | 120                             | 58                        | 107              |
| 3   | 34                            | 125                             | 56                        | 148              |
| 4   | 32.5                          | 130                             | 54                        | 186              |
| 5   | 31                            | 135                             | 52                        | 117              |

BBD for RSM was adopted to analyze the optimized values of the studied variables which influenced samples’ viscosity value remarkably. Table 2 illustrated the Box-Behnken design and the consequences. The latter was confirmed to a second-order polynomial equation:

\[ Y = +194.70 + 23.15 \times X_1 + 14.95 \times X_2 + 9.04 \times X_3 + 1.75 \times X_1 \times X_2 + 1.00 \times X_1 \times X_3 + 5.25 \times X_2 \times X_3 - 28.28 \times X_1^2 - 31.47 \times X_2^2 - 6.94 \times X_3^2 \]  (1)
Table 2. Box-Behnken design and consequences of CMC synthesis conditions

| Run | X₁ (alkalization temperature (°C)) | X₂ (Etherification temperature (°C)) | X₃ (Etherification time (min)) | Viscosity (mPa·s) |
|-----|------------------------------------|--------------------------------------|-------------------------------|------------------|
| 1   | 32.5                               | 54.0                                 | 120.0                         | 167              |
| 2   | 35.0                               | 52.0                                 | 140.0                         | 144              |
| 3   | 35.0                               | 52.0                                 | 140.0                         | 193              |
| 4   | 32.5                               | 54.0                                 | 130.0                         | 192              |
| 5   | 32.5                               | 54.0                                 | 130.0                         | 183              |
| 6   | 28.3                               | 54.0                                 | 130.0                         | 89.0             |
| 7   | 32.5                               | 54.0                                 | 130.0                         | 206              |
| 8   | 36.7                               | 54.0                                 | 130.0                         | 139              |
| 9   | 30.0                               | 52.0                                 | 140.0                         | 89.0             |
| 10  | 32.5                               | 54.0                                 | 130.0                         | 201              |
| 11  | 32.5                               | 54.0                                 | 130.0                         | 187              |
| 12  | 32.5                               | 50.6                                 | 130.0                         | 77.0             |
| 13  | 30.0                               | 56.0                                 | 120.0                         | 101              |
| 14  | 30.0                               | 56.0                                 | 140.0                         | 122              |
| 15  | 35.0                               | 56.0                                 | 140.0                         | 187              |
| 16  | 30.0                               | 52.0                                 | 120.0                         | 86.0             |
| 17  | 32.5                               | 54.0                                 | 130.0                         | 207              |
| 18  | 35.0                               | 52.0                                 | 120.0                         | 140              |
| 19  | 35.0                               | 56.0                                 | 120.0                         | 159              |
| 20  | 32.5                               | 57.4                                 | 130.0                         | 133              |

Table 3 showed the analysis of variance (ANOVA) for this model. R-Squared, the determination coefficient value was 0.9626. It meant 96.26% of the total variance could be illuminated according to this model. Generally, a regression model of R² exceeds 0.9 clarifying a high correction. The adjusted determination coefficient (Adj R²=0.9289) was high as well, it was enough to demonstrate the significance of the model. Simultaneously, in this model, p-value was less than 0.0001, showed the highly significant fitness. Additionally, the lack of fit score was only 0.2807, which meant non-significant, displayed it was suited to forecast the response and explicate the influence of variables on this response.

The adopted three-dimensional response surface diagrams (Figure 1, Figure 2 and Figure 3) confirmed the interaction among the variable factors. Every 3D diagram displayed associations between two experimental variables, while the other one was at the central level. An oval-shaped contour or saddle nature of the contour plots implied there was a statistically significant interaction between two variables. Based on the quadratic model, the maximum viscosity value was predicted as 234·4mPa·s, while the alkalinity temperature was 33.6 °C, and etherification temperature and etherification time were 54.6°C and 138min, respectively.
Table 3. The analysis of variance of quadratic model for CMC synthesis

| Source            | Sum of Squares | df | Mean Square | F Value | p-value | Prob > F |
|-------------------|----------------|----|-------------|---------|---------|----------|
| Model             | 35995.28       | 9  | 3999.48     | 28.60   | < 0.0001 significant |
| X₁                 | 7315.94        | 1  | 7315.94     | 52.31   | < 0.0001 |
| X₂                 | 3052.65        | 1  | 3052.65     | 21.83   | 0.0009  |
| X₃                 | 870.55         | 1  | 870.55      | 6.22    | 0.0317  |
| X₁ X₂              | 24.50          | 1  | 24.50       | 0.18    | 0.6844  |
| X₁ X₃              | 8.00           | 1  | 8.00        | 0.057   | 0.8158  |
| X₂ X₃              | 220.50         | 1  | 220.50      | 1.58    | 0.2378  |
| X₁²                | 11625.30       | 1  | 11625.30    | 83.13   | < 0.0001 |
| X₂²                | 14388.21       | 1  | 14388.21    | 102.88  | < 0.0001 |
| X₃²                | 436.51         | 1  | 436.51      | 3.12    | 0.1077  |
| Residual           | 1398.52        | 10 | 139.85      |         |         |
| Lack of Fit        | 886.52         | 5  | 177.30      | 1.73    | 0.2807  |
| Pure Error         | 512.00         | 5  | 102.40      |         |         |
| Cor Total          | 37393.80       | 19 |             |         |         |
| R-Squared          | 0.9626         |    |             |         |         |
| C.V. %             | 7.88           |    |             |         |         |
| Adj R²             | 0.9289         |    |             |         |         |

Figure 1. Three-dimensional response surface diagram: the interaction of alkalization temperature and etherification temperature
Figure 2. Three-dimensional response surface diagram: the interaction of alkalinity temperature and etherification time

Figure 3. Three-dimensional response surface diagram: the interaction of etherification temperature and etherification time

For purpose of verifying the model fitness for predicting the maximum response, a probative test was carried out for five times. With the predicted optimal conditions, the average experimental value was 233 mPa·s, which was conform to the model predicted. The viscosity of CMC was improved by 194% compared with that of original sample.

4. Conclusions
Importantly, our results provided evidence of synthesis conditions for CMC made from refined bamboo scraps. The effective mathematical model illuminated RSM could be applied to obtain the optimal factors about carboxymethyl reaction. The viscosity of CMC product increased significantly. This research could contribute to waste management and circular using of resource.

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