Optimization of Microwave-Hydrogen Peroxide Pretreatment of Cellulose

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A hydrogen peroxide (H_2O_2) solution was adapted for microwave pretreatment of microcrystalline cellulose, which can be further used for heavy metal adsorption. The H_2O_2 concentration, temperature, and retention time were the key factors affecting the microwave/hydrogen peroxide pretreatment process. A Box-Benhken design (BBD) with response surface methodology (RSM) was employed to design and optimize the microwave-hydrogen peroxide pretreatment process (H_2O_2 pretreatment) of cellulose. After the H_2O_2 pretreatment, the crystallinity of cellulose decreased by 20% and the degree of polymerization (DP) decreased by up to 30%. The optimal conditions obtained by BBD were a H_2O_2 concentration of 8.37%, a temperature of 90 °C, and a retention time 5.33 min. Under these conditions, a minimum DP of 91.74 was achieved. The results indicated that all three of the factors notably affected the reduction of cellulose polymerization degree and pronounced interactions existed among the response variables. The predictive model developed was able to optimize the pretreatment process for the reduction of cellulose polymerization degree, which could improve the cellulose modification reactivity.

Keywords: Hydrogen peroxide; Microwave; Response surface methodology (RSM); Cellulose pretreatment

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INTRODUCTION

Because of increasing concerns about energy consumption and environmental protection, cellulose is becoming a more commonly used renewable resource material. However, considerable hydrogen bonding in the intramolecular and intramolecular domains of the cellulose molecule and the complexity of the cellulose morphology and aggregate structures decrease its solubility with reagents; thus, cellulose exhibits low reactivity and poor uniformity during chemical reactions. A reduction in the crystallinity of cellulose must be achieved by various methods to improve the availability and accessibility of cellulose to reagents. There are several methods involving the physical and chemical pretreatment of cellulose (Zhao *et al*. 2006; Moharram and Mahmoud 2008; Peng *et al*. 2013). The most popular pretreatment incorporates physical and chemical methods, including microwave alkali treatment and ultrasonic alkali treatment (Khajavi *et al*. 2013; Peng *et al*. 2013; Ni *et al*. 2014, 2015). However, these pretreatment methods require large quantities of alkali and a long processing duration of 12 to 16 h (Gurgel *et al*. 2008a,b; Hokkanen *et al*. 2013).

Presently, research is focusing on the development of a pretreatment method that combines a reduction in crystallinity with an improvement in process efficiency and environmental protection.

Hydrogen peroxide (H_2O_2) is a type of chemical oxidant that is referred to as a green oxidant (Wang *et al.* 2009; Sheldon 2015). Some resistant materials can be oxidized using oxidation products containing only water and oxygen, which are compounds that result in minimal environmental damage (Menova and Cibulka 2012; Hartman *et al*. 2015). The standard oxidation reduction potential of H_2O_2 is 1.8 V, which increases to 2.8 V after treatment with additional reagents (potassium permanganate, hypochlorite, and chlorine dioxide), producing the hydroxyl radical, $\cdot OH$. The hydroxyl radical has a strong oxidizing potential. Microwave pretreatment offers an alternative method to traditional heat-treatment, with the advantages of heating rapidly and minimal energy losses (Li and Xu 2013; Tyagi and Lo 2013; Ni *et al*. 2014). Similarly, microwave irradiation (with H_2O_2) is characteristically well-distributed, efficient, and highly penetrable (Hou *et al*. 2008; Hashem *et al*. 2014). Accordingly, this method is recommended for improving sludge disintegration (Wang *et al*. 2009), the hydrolysis of cellulose (Ni *et al*. 2015), and the pretreatment of cotton fabrics (Hashem *et al*. 2014). However, microwave irradiation (with H_2O_2), as a pretreatment of cellulose to obtain a modified material, has yet to be fully investigated.

Response surface methodology (RSM) is a useful tool based on statistical analysis that can be used to construct models and evaluate their influence on multiple factors and their interactions (Ya-Wei *et al*. 2015). Therefore, RSM has been employed in many studies as a powerful tool to explore the interactions among multiple factors. Predictive models, which are the most representative, have been used to analyze and optimize the operation parameters in many fields, including chemical (Adalarasan *et al*. 2015), medical (Chojnicka-Paszun and de Jongh 2014), and energy (Antonopoulou *et al*. 2012; Chen *et al*. 2012). This process could result in the development of desirable responses and reduce the number of experiments required. In comparison with the central composite design, the Box-Behnken design requires relatively few experiments and offers higher efficiency. The Box-Behnken design requires not all influencing factors to be at a high level at the same time and ensures that all the experimental conditions are within a safe operating area (Ragonese *et al*. 2002; Kehoe and Stokes 2011).

The present study investigated a pretreatment of cellulose using H_2O_2 and microwave irradiation. Response surface methodology was employed to determine the effect of the H_2O_2 concentration, temperature, and retention time on cellulose and to estimate the interactions among these factors. The RSM model contained 17 response variables to construct the optimal pretreatment conditions.

EXPERIMENTAL

Materials

Microcrystalline cellulose (Aladdin Inc., Shanghai, China), hydrogen peroxide (Chengdu Kelon Chemical Reagent Factory, Chengdu, China), and copper ethylene diamine solution (Paper Research Institute of China) were obtained for use in the study. A microwave accelerated reaction system (MARS6) was obtained from CEM Corp., North Carolina, USA.

Methods

To explore the optimal value of the influencing factors, a single-factor experiment was employed to determine the initial scope (Table 1). The Box-Benhken design (BBD) method was used to explore the importance of temperature, H_2O_2 concentration, and retention time on the cellulose polymerization degree. In theory, the decreasing trend of DP and crystallinity corresponding to the change of the pretreatment condition was consistent, and the decreasing trend of DP was more obvious. Therefore, the DP was selected as the response value. In comparison with the central composite design method, the BBD method requires fewer experimental parameters, which results in increased efficiency (de Almeida Borges *et al*. 2013). The other important reason for choosing BBD was that BBD avoids "the corner points", meaning experiments were avoided for all factors at extreme low or high levels, which ensures the operation safety. A three-level, three-factorial Box-Benhken design (BBD) was programmed using Design-Expert 8.0.6 software (Statease Inc., Minneapolis, USA). The H_2O_2 concentration (X_1), temperature (X_2), and retention time (X_3) were adjusted over a range of 6% to 12%, 80 to 100 °C, and 0 to 10 min, respectively, with corresponding optimal values of 9% (X_1), 90 °C (X_2), and 5 min (X_3). The X_i represented the actual values of the three variables (X_1, X_2, and X_3), according to the experimental design (Table 2). The parameters were standardized according to Eq. 1 (Li and Xu 2013),

$$x_i = \frac{X_i - X_0}{\Delta X_i} \qquad i = 1, 2, 3 \qquad (1)$$

where X_i is the coded value of the independent variable, X_i is the actual value of the independent variable, X_0 is the actual value of the independent variable at the center point, and ΔX_i is the step change of X_i corresponding to a unit variation of the dimensionless value.

Table 1. Treatment Levels

Variables	Treatment Levels						
	1	2	3	4	5	6	7
H_2O_2 concentration (%)	0	3	6	9	12	15	18
Temperature (°C)	0	60	70	80	90	100	110
Treatment time (min)	0	2	5	8	10	15	20

Table 2. Matrix of the Experimental Design

Run	Coded values			Actual values		
	H_2O_2 (%)	Temperature (°C)	Time (min)	H_2O_2 (%)	Temperature (°C)	Time (min)
1	0	1	1	9	100	10
2	0	0	0	9	90	5
3	1	1	0	12	100	5
4	0	-1	-1	9	80	0
5	-1	0	-1	6	90	0
6	1	0	1	12	90	10
7	0	-1	1	9	80	10
8	0	0	0	9	90	5
9	1	-1	0	12	80	5
10	-1	1	0	6	100	5
11	0	0	0	9	90	5
12	0	0	0	9	90	5
13	-1	0	1	6	90	10
14	1	0	-1	12	90	0
15	-1	-1	0	6	80	5
16	0	1	-1	9	100	0
17	0	0	0	9	90	5

Each response variable Y was assessed as a function of three, first-order effects (X_1, X_2, and X_3), three interaction effects (X_1*X_2, X_1*X_3, and X_2*X_3), and three, second-order effects (X_1^2, X_2^2, and X_3^2), and can be described according to Eq. 2,

$$\mathrm{Y} = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_{11}X_1^2 + b_{22}X_2^2 + b_{33}X_3^2 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3 \quad (2)$$

where Y is the predicted response, b_0 is the intercept coefficient, b_i is the linear term, b_{ii} is the squared effects term, and b_{ij} is the interaction term.

Data obtained from BBD for the optimization of the pretreatment conditions were used to generate regression coefficients for the second-order multiple regression models. Analysis of variance (ANOVA) was performed using Design-Expert 8.0.6 software. The coefficient of variation and the statistical significance were used to assess the quality of the fit to the polynomial model equation. Regression coefficient significance was assessed using F- and *t*-test parameters. The optimum values of the selected variables were obtained by analyzing the contour plot of the response surface and then solving for the regression equation.

A microwave reactor from the microwave accelerated reaction system was used for the cellulose pretreatment process. At full power, the microwave reactor delivered approximately 1800 W of microwave energy at a frequency of 2450 MHz and was controlled by a microcomputer that monitored the operations. According to the experimental design, the pretreatment was performed in a digestion tank with H_2O_2 solution (solid-liquid ratio 1:20) and microcrystalline cellulose at 80 to 90 °C for 0 to 15 min. The microwave reactor was digitally programmed to control the experimental conditions, which included a detection system to measure real-time temperature and power. After the reaction was complete, the mixture was cooled, centrifuged, and dried to a constant weight in an oven. Lastly, the microcrystalline cellulose (MCC) was treated with alkali (Hokkanen *et al*. 2013).

The degree of polymerization (DP) of the cellulose was determined according to the GB/T1548 (1989) (Halidan Manat *et al*. 2006) testing standard. The specific method to dissolve the cellulose in copper (Cu) ethylene diamine solvent involved mixing fully to obtain a certain concentration solution (0.5 g/L). The viscosity was determined using a Nordic standard viscometer (Beijing, China), and then the DP was calculated by Eq. 3,

$$\mathrm{DP}^{0.905} = 0.75[\eta] \tag{3}$$

where $[\eta]$ is the intrinsic viscosity.

The crystallinity index (CrI) was determined by the diffracted intensity of Cu radiation (1.54 Å), using an X-ray diffractometer (X-ray double crystal powder diffractometer, Smart Lab, RIGAKU, Japan). The operating voltage and current were set at 40 kV and 30 mA, respectively. The diffracted intensity was measured at a scan rate of 8°/min for 2 h ranging from 10° to 50°, and the step size was 0.012°. Before the tests, the samples were dried to a constant weight at 50 °C. The *CrI* is an indicator of the amount of crystalline *versus* amorphous structures, calculated from the diffracted intensity data. This method assumes a two-phase structure (crystalline amorphous) and a line between the intensity minima to obtain an arbitrary background to the diffraction trace, thus separating an arbitrary crystalline phase from an arbitrary amorphous phase (Ju *et al*. 2015). The *CrI* was calculated using crystallinity analysis software MDI Jade 5(Materials Data Ltd, USA), according to Eq. 4 (Focher *et al*. 2001),

$$CrI(\%) = \frac{I_C}{I_{Total}} \times 100\% \tag{4}$$

$$I_{Total} = I_C + I_B$$

where I_c is the intensity of the diffraction from the crystalline region and I_B is the intensity of the diffraction of the amorphous area.

RESULTS AND DISCUSSION

Quadratic Models for All Response Variables

The model showed that the DP was a function of X_1, X_2, and X_3. The 17 variables were assessed using ANOVA second-order equations that incorporated the interactions between the three variables and the coefficients for each variable and fitted them to quadratic models. The ANOVA F-value described the significance of individual factors and their interactions, whereas the *P*-value illustrates the significance of the coefficient. The F-value of 1054 was large enough to signify that the model was significant. There was a 0.01% chance that the highly significant F-value could have occurred from noise. The original model from the Design-Expert 8 software, including the interaction terms, X_1*X_2, X_1*X_3, and X_2*X_3, indicated that the model terms were significant. In this case X_1, X_2, X_3, X_1*X_2, X_1*X_3, X_2*X_3, X_1^2, X_2^2, X_3^2 resulted in significance. Model parameters with a P-value less than 0.0500 indicate model terms are significant. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model. The ANOVA results are shown in Table 3.

A 'lack-of-fit F-value' of 0.67 signified that the model was not significant, which was related to the error rate. According to the model, there was a 61% chance that the F-value size occurred from noise.

The DP was predicted based on the results obtained from the simulation conducted and Eq. 2. The model in Table 3 was statistically significant. The sequence of influence of the three factors on the degree of polymerization was $X_1 > X_2 > X_3$. Figure 1 illustrates that the error between the actual value and predicted value was minimal, and the actual value and predicted value on both sides was evenly dispersed diagonally, suggesting that the equation well-described the model. In addition, the regression coefficient was high (R^2 = 0.99), indicating that the model successfully described the correlation relationship between the factors and the DP (Shukla *et al*. 2014). Therefore, a quadratic model was chosen in accordance with the experimental results.

Usually, if the coefficient of variation (CV) of a model is less than 10%, then the model has good repeatability. For the DP, the coefficient of variation was 0.41%, indicating that the model exhibited an excellent ability to predict the observed data. The adequate precision value (Table 3) was employed as a measure of the signal-to-noise ratio. The precision value compares a range of predicted values at the design points to the average prediction error. A precision value of 88.497 indicated that an adequate signal was produced (a ratio > 4 is considered desirable) (Ahmadi *et al*. 2005). Therefore, this model can be used to navigate the design space. The coefficients of the quadratic model were calculated using least-squared means, multiple linear regression analysis, and the model's goodness-of-fit, and were evaluated according to the R^2 coefficient. The value of square of the correlation coefficient (R^2) was 0.99, shows that the quadratic model described the experimental result well. Because of the high R^2 coefficient, the resulting quadratic model can be considered suitable for describing the relationship among H_2O_2 concentration (X_1), temperature (X_2), and retention time (X_3). The validity of BBD was checked by predicted values versus actual values and Normal Plot of Residuals (Fig. 1)

According to Eq. 2 and Table 3, Eq. 5 and Eq. 6 were produced. Eq. 5 was the final equation in terms of Coded Factors. Eq. 6 was the final equation in terms of actual factors.

$$\mathrm{DP} = 92.13 + 3.49X_1 - 1.22X_2 - 1.40X_3 - 2.67X_1X_2 + 3.90X_1X_3 + 1.49X_2X_3 + 8.83X_1^2 + 13.47X_2^2 + 9.14X_3^2 \tag{5}$$

$$\mathrm{DP} = 1225.80 - 9.79H_2O_2 - 23.72T - 8.75t - 0.09H_2O_2T + 0.26H_2O_2t + 0.03Tt + 0.98H_2O_2^2 + 0.13T^2 + 0.37t^2 \tag{6}$$

Equation 6 represents the actual factors in their original units. According to Eq. 3, the highest coefficient value resulted from the relationship between H_2O_2

concentration and DP, indicating that DP was dependent upon the H_2O_2 concentration. Moreover, the values of b_1 were positive, suggesting that the value of DP increased with increasing H_2O_2 concentration, while the opposite was true for X_2 and X_3. The value of b_{13} was greater than $b_{12,23}$, indicating that the effects of the interaction between X_1 and X_3 was more pronounced. This was supported by the F-values obtained when the interaction between the variables was considered (Table 3).

Table 3. ANOVA of the Surface Quadratic Model of the Degree of Polymerization

Source	Sum of squares	df	Mean square	F-value	*P*-value
Model	1813.05	9	201.45	1054.32	<0.0001
X_1	97.23	1	97.23	508.88	<0.0001
X_2	11.88	1	11.88	62.19	<0.0001
X_3	1.26	1	1.26	6.62	0.0369
X_1*X_2	28.46	1	28.46	148.96	<0.0001
X_1*X_3	61.00	1	61.00	319.23	<0.0001
X_2*X_3	8.82	1	8.82	46.17	0.0003
X_{12}	327.97	1	327.97	1716.51	<0.0001
X_{22}	764.05	1	764.05	3998.76	<0.0001
X_{32}	352.00	1	352.00	1842.23	<0.0001
Residual	1.34	7	0.19		
Lack-of-Fit	0.45	3	0.15	0.67	0.6130
Pure error	0.89	4	0.22		
Corrected total	1814.39	16			
Standard deviation	0.44			R^2	0.99
Mean	106.92			Coefficient of variation (%)	0.41
Adequate precision	88.497			PRESS	8.55

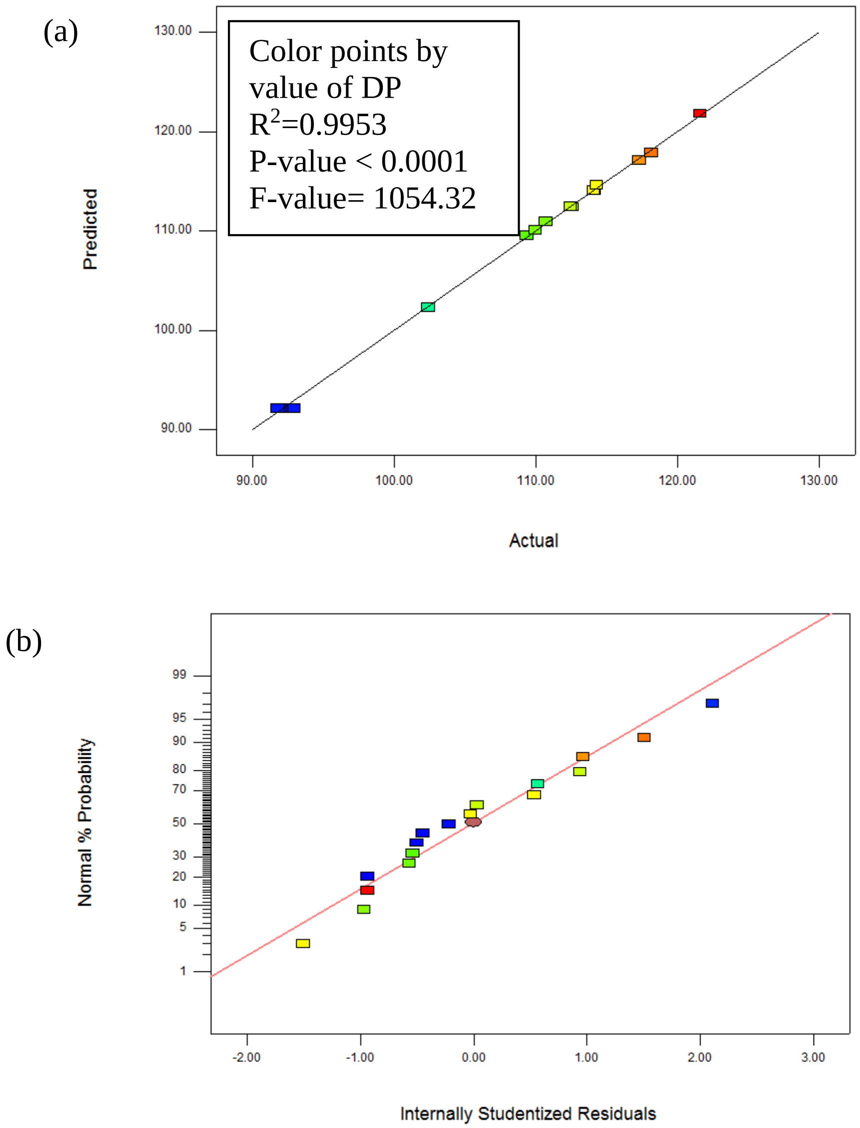

Fig. 1. Predicted values *versus* actual values for the polymerization degree (DP) (a); Normal Plot of Residuals for the polymerization degree (DP) (b).

Pretreatment Condition Optimization

The response surface plot and the contour map of DP are shown in Fig. 2. The DP of cellulose was dependent on X_1, X_2, and X_3. In comparison to the density of the contour plot in Fig. 2, the H_2O_2 concentration and microwave processing temperature exhibited the greatest influence on the degree of polymerization. This result was in agreement with the ANOVA results and the regression equation: the F-value of X_1*X_3 was greater than X_2*X_3. According to Eq. 5, the linear programming function was used to obtain the best pretreatment conditions, which included an H_2O_2 concentration of 8.37%, a temperature of 90 °C, and a retention time of 5.32 min. The minimum value of DP, obtained from these experimental conditions, was 91.74.

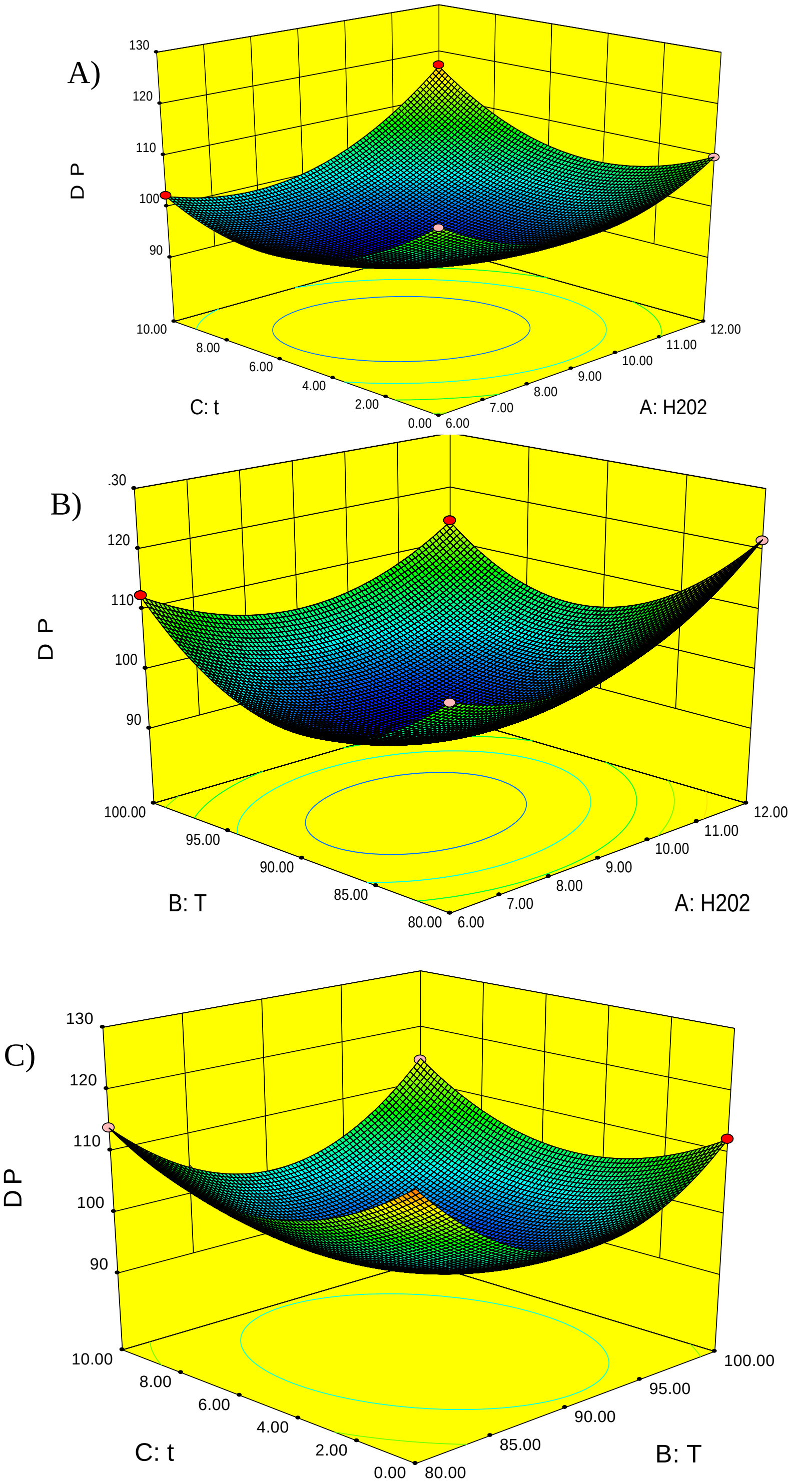

Fig. 2. Three-dimensional response surface plots for the degree of polymerization: A) H_2O_2 concentration and temperature; B) H_2O_2 concentration and retention time; and C) temperature and retention time

Cellulose Crystallinity

Crystallinity values pre- and post-treatment are listed in Fig. 3 and Table 4. Cellulose peaks, including cellulose I and cellulose II, appeared at different peak positions. The peaks of cellulose I were located at approximately 22.6°, 16.2°, and 22.6°. The peak at 16.2° was very close to the peak at 14.8°, forming a relatively wide diffraction peak. Meanwhile, the peaks of cellulose II were located at approximately 12°, 19.9°, and 21.7° (Nam *et al*. 2016).

Table 4. Crystallinity (*CrI*) of Untreated and Microwave-Hydrogen Peroxide-Pretreated Cellulose

Sample	*CrI* (%)	Peak (°)
Untreated	70.31	16.2, 14.8, 19.8, 22.8
Microwave-H_2O_2	56.07	15.9, 14.0, 22.8

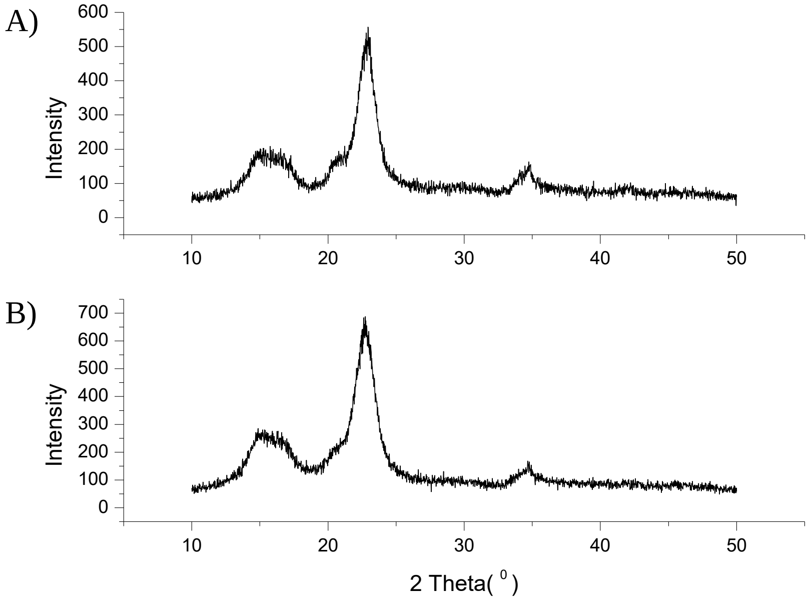

Fig. 3. X-ray diffraction patterns of A) untreated and B) microwave-hydrogen peroxide-pretreated cellulose

The characteristic peaks of the untreated microcrystalline cellulose were located at 2θ = 14.7°, 16.8°, 22.8°, and 34.7°. The diffractogram revealed a relatively ordered structure, with a narrow peak at 22.8° and a diffuse peak between 14.8° and 16.2°. The sharper diffraction peak at 22.8° indicates a region of higher crystallinity. Linear cellulose molecules are linked laterally by hydrogen bonds to form linear bundles, giving rise to a crystalline structure. Individual fibrillary units consist of long periods of ordered crystalline regions interrupted by disordered amorphous regions. The pretreatment of cellulose causes a rearrangement of the crystal packing of chains from native cellulose I (chains aligned in parallel) to cellulose II (anti-parallel arrangement). This change is irreversible and is normally accompanied by a decrease in crystallinity. The microwave-hydrogen peroxide pretreatment loosened the hydrogen bonding within the fiber bundles, causing the microfibers to move apart. After the pretreatment process, the crystallinity of cellulose decreased 20%, resulting from the activation of cellulose and the increase in accessibility of the fiber.

Degree of Polymerization of Cellulose

The results obtained in this study are listed in Table 5. The degree of polymerization for cellulose was determined by the Cu ethylene diamine solution viscosity method after the pretreatment process of cellulose. After processing, the degree of polymerization for cellulose declined, especially for the optimal value group (Runs 2, 8, 11, 12, and 17), by up to 30% (degree of polymerization for untreated microcrystalline cellulose was 132.6), which was similar to the effect of alkali pretreatment (NaOH 20 wt. %) with ultrasound for 12 to 16 h. The decrease of cellulose DP was mainly due to the oxidation of hydroxyl free radical. Hydroxyl free radical produced by the decomposition of hydrogen peroxide could cut off the long chain of cellulose and then reduce the DP. Low concentration (H_2O_2) and temperature were of no advantage to the reaction. High concentration would produce excess H_2O_2, and high temperature can achieve the response quickly though not completely. In a microwave frequency alternating electromagnetic field, the chance of cellulose hydrogen bond fracture was increased with the increasing of collision frequency between the molecules. However, with the extension of reaction time, a lot of heat would be generated within the molecules as a result of microwave heating. Then the hydrogen bonds which have been broken could form again, and thus the results backfire. Therefore, identifying the tendency of the decrease of DP and optimizing of experimental conditions were necessary.

Table 5. Degree of Polymerization (DP) of Pretreated Cellulose

Run	DP	Removal rate (%)
1	114.28	13.8
2	92.95	29.9
3	114.14	13.9
4	118.17	10.9
5	110.7	16.5
6	117.3	11.5
7	114.07	13.9
8	91.76	30.8
9	121.59	8.3
10	112.59	15.1
11	91.93	30.7
12	91.95	30.7
13	102.43	22.8
14	109.95	17.1
15	109.37	16.8
16	112.44	15.2
17	92.04	30.6

CONCLUSIONS

1. A quadratic model was established, according to RSM, based on the best fit to the experimental data. The model yielded a high coefficient of determination, indicating that the model was capable of predicting an optimized treatment process.
2. The effects of the three factors on the degree of polymerization for microwave-hydrogen peroxide pretreated cellulose were $X_1 > X_2 > X_3$, and the optimal conditions obtained by BBD were an H_2O_2 concentration of 8.37%, a temperature of 90 °C, and a retention time of 5.33 min. The crystallinity and DP values decreased by 20% and up to 30%, respectively.
3. In comparison with the alkali pretreatment, the microwave-hydrogen peroxide pretreatment obtained a similar effect. The optimal conditions required a shorter treatment time (5 min) and a lower reagent dosage (8.37%).

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