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Response surface method to optimize the preparation of carboxymethyl cellulose from corn peel agricultural waste

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ABSTRACT: Cellulose fibres were isolated from corn peel agricultural waste using NaOH extraction and converted to carboxymethyl cellulose (CMC) by carboxymethylation using monochloroacetic acid (MCA) in alkaline conditions. A Box-Behnken statistical design was used to evaluate the parameters (soaking time with NaOH solution, soaking time with MCA solution, and reaction time with MCA) affecting the degree of substitution (DS) of CMC. Optimization was carried out by using the response surface method. The optimized conditions for CMC production with a maximal DS of 0.90 were soaking with NaOH for 118 min, followed by soaking with MCA for 6.5 h, and reaction with MCA at 60 °C for 84 min. FTIR and XRD confirmed the successful carboxymethylation. This work demonstrates the feasibility of using corn peel agricultural waste as an alternative raw material for the production of CMC with high DS.

KEYWORDS: Box-Behnken statistical design, degree of substitution, carboxymethylation

INTRODUCTION

Cellulose is an abundant biological material that is extracted commercially from lignocellulosic materials in trees and other plants[1]. World production of cellulose is 10 000–100 000 million tons per year and the product is mainly used in the textile, paper, and material industries[2]. To increase the versatility of cellulose for wider applications, its properties need to be improved, especially water solubility.

Carboxymethyl cellulose (CMC) is an important derivative of cellulose. CMC is soluble in water and is used in applications such as tissue engineering[3], drug delivery systems[4,5], and adsorption of heavy metals[6] and dyes[7]. CMC is commonly synthesized by carboxymethylation of cellulose with monochloroacetic acid (MCA) in alkaline conditions[8,9], with the reaction starting from the conversion of cellulose to alkaline cellulose in the presence of NaOH and then reaction with MCA to form CMC as the sodium salt[10].

The typical raw materials for CMC production are cellulosic materials such as flax short fibres[11], sugar beet[12], wood, and cotton[13]. In recent years, with the goal of waste utilization, agricultural wastes have also been used as raw materials for CMC production. These wastes include rice straw[8], papaya peel[14], orange peel[15], sago waste[16], sugarcane bagasse[17], corn husk[9,18], banana stem[19], and vine stem[20]. However, only a few studies have examined CMC production using corn peel as a raw material and optimization of the conditions for CMC production from corn peel using statistical design has not been reported.

The response surface method (RSM) is an effective tool for optimization, since it allows evaluation of several factors simultaneously and reduces the number of experiments required compared with the traditional step-by-step approach[21,22]. In the current study, Box-Behnken statistical design was used as a method of RSM that is more efficient than factorial and central composite designs[23]. Optimization of CMC production from corn peel was carried out using RSM, with evaluation of the effects of soaking time with NaOH, soaking time with MCA, and reaction time with MCA on the degree of substitution (DS) of CMC. The DS is defined as the average number of free hydroxyl groups in the glucose unit of cellulose that undergo carboxymethylation.

MATERIALS AND METHODS

Fresh corn peel was collected from a central canteen at Chulalongkorn University, cut into lengths of 5 cm, and dried by sunlight before use. MCA was purchased from Acros Organics (Geel, Belgium). NaOH, hydrogen peroxide, ethanol and acetic acid were purchased from Carlo Erba (Rodano, Italy). All chemicals were of analytical grade and were used as received.

Cellulose extraction from corn peel

The 5-cm dried corn peel pieces were treated with 3% (w/v) NaOH solution at a liquid/material ratio of 20:1 (v:w) at 90–100 °C for 2 h, as described by dos Santos et al[24] with some modifications. The cellulose slurry was then filtered and washed with distilled water several times before drying it in a hot air oven at 80 °C. The obtained cellulose fibres were bleached with 0.7% (w/v) hydrogen peroxide solution in a liquid/material ratio of 15:1 (v:w) under alkaline conditions at 80–90 °C for 90 min. After cooling, the bleached cellulose fibres were washed with distilled water until neutral pH and dried in an oven at 80 °C.

Preparation of CMC

Bleached cellulose fibres (5 g) were suspended in 100 ml of 95% (v/v) ethanol, followed by addition of 10 ml of 45% (w/v) NaOH solution under continuous stirring at 750 rpm at room temperature for 30, 60, or 120 min. MCA (5 g) was then added to the fibre slurry under continuous stirring for 3, 6, or 18 h at room temperature. The slurry was incubated in a water bath at 60 °C for 30, 60, or 120 min, and cooled before neutralization with glacial acetic acid. The obtained CMC slurry was filtered and purified by Soxhlet extraction with 500 ml of 80% (v/v) ethanol for 4 h. Finally, the CMC product was dried in a hot air oven at 80 °C and ground.

Experimental design

A polynomial model for optimization of CMC production was constructed using Box-Behnken statistical design. Data were analysed using DESIGN-EXPERT 7.1 (Stat-Ease Inc., USA). The independent variables (factors) of soaking time with NaOH (X_1), soaking time with MCA (X_2), and reaction time with MCA (X_3) were used at 3 levels (−1, 0, +1) (Table 1). The dependent variable (response) was the DS (Y). Each experiment was performed in triplicate.

Table 1 Factors at various levels with the maximized degree of substitution as response (Y).

Factors	Level		
	Low (−1)	Medium (0)	High (+1)
X_1 (min)	30	60	120
X_2 (h)	3	6	18
X_3 (min)	30	60	120

The mathematical relationship of the response (Y) and the factors (X_i) was modelled by a second-order polynomial function:

$$\begin{aligned} Y = b_0 &+ b_1X_1 + b_2X_2 + b_3X_3 \\ &+ b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3 \\ &+ b_{11}X_1^2 + b_{22}X_2^2 + b_{33}X_3^2, \end{aligned}$$

where Y is the measured response (DS); b_0 is the intercept; b_1 to b_{33} are regression coefficients computed from observed experimental values of Y; X_1, X_2, and X_3 are coded values of the factors, and X_iX_j and X_i^2 ($i, j = 1$, 2, and 3) are interaction and quadratic terms, respectively.

Data analysis using the regression model and plotting of response surface graphs was performed in DESIGN-EXPERT. ANOVA with an F-test was used to evaluate the effect of each factor on the response, with $p < 0.05$ considered significant. The qualitative fitness of the polynomial equation was evaluated using multiple correlation coefficients (R^2) and adjusted R^2. Then 3D surface plots were used to show the relationship and interaction between the factors and the response. Numerical experimental regions were used to find the optimal formulation using the constraint that DS should reach a maximal level. Finally, the optimized formulation was prepared and the experimental result was compared with the predicted value obtained from the equation to evaluate the precision of the model.

Characterization of cellulose fibres and CMC

Lignin content, cellulose content in various forms, and DS of CMC were analysed based on TAPPI T 222 om-22, TAPPI T 203 cm-99, and ASTM D 1439-03, respectively. Functional groups were identified using Fourier transform infrared spectrometry (FTIR, spectrum 400; PerkinElmer, SpectrumOne, USA) in transmittance mode at 4000–400 cm^{-1}, with a scan number of 16 times/sample and resolution of 4 cm^{-1}. Samples were also subjected to wide-angle X-ray diffraction (XRD, PW 3710; Philips, Netherlands), using a detector operating at a current of 30 mA and a voltage of 40 kV, with Cu K$_\alpha$ radiation (1.54 Å) and a scanning speed of 0.2° 2θ/step at room temperature.

RESULTS AND DISCUSSION

Preparation of cellulose from corn peel

Corn peel was used as raw material because of its high α-cellulose content of about 35% (Table 2). The quality of the cellulose fibres mainly depends

Table 2 Chemical compositions of corn peel and prepared cellulose fibres.

Composition	Corn peel	Cellulose fibres
Lignin (%)	5.8	no data
α-Cellulose (%)	34.7	70.6
β-Cellulose (%)	12.0	24.9
γ-Cellulose (%)	24.0	4.5
Others (%)	23.5	no data

on the NaOH concentration and reaction temperature[25]; hence corn peel was treated with 3% (w/v) NaOH at 90–100 °C for 2 h[24]. Water pollution during bleaching is also a concern; hence hydrogen peroxide was used instead of chlorine. After pulping, the α-cellulose content increased to 71%, whereas hemicelluloses (β- and γ-celluloses) decreased from 36% to 29% (Table 2).

Preparation of CMC

Preparation of CMC involved an initial stage in which cellulose fibres were treated with NaOH in the presence of ethanol, which functions as a swelling agent to enhance penetration of NaOH into the cellulose structure, followed by a second stage, in which the resulting alkaline cellulose was reacted with MCA to form CMC as a sodium salt[24]. Soaking time with NaOH, soaking time with MCA, and reaction time with MCA could affect the DS of CMC. This is an important characteristic of CMC that indicates the number of substituted MCAs per glucose unit. Hivechi et al[25]. showed that the solubility of CMC increases with an increase in DS. Hence we chose DS as the criterion for optimal CMC synthesis.

The results in Table 3 show that the DS was in the range of 0.51–0.82 and the main factor affecting DS was the reaction time with MCA. An increase in reaction time with MCA up to 120 min resulted in an increase in DS, regardless of the soaking times with NaOH and MCA. A similar observation was made for sago waste[26]. This result is probably due to the prolongation of carboxymethylation allowing more time for MCA to react with the cellulose fibres, with a higher resulting DS.

Fitting data to a model

To select the best model for fitting the data, an F-value from ANOVA was used. Singare et al[27] showed that factors with $p < 0.05$ (prob > F-value) have a significant effect on the response. R^2 represents the percentage of data that is closest to the best fit line, and thus an R^2 close to 1 indicates a model that fits the data well. The results showed that a full quadratic polynomial fitted the data and that the lack of fit F-value of 0.13 was not significant in this response ($p > 0.05$) (Table 4). Multiple regression analysis showed that all linear, squared and interaction coefficients of the factors, including soaking time with NaOH and reaction time with MCA, were significant ($p < 0.05$) when DS was used as a response. The derived equation that fitted the data was

Table 3 Variables and response in Box-Behnken design for CMC production.

Run no.	Independent variables			Response
	X_1 (min)	X_2 (h)	X_3 (min)	Y_1
1	30	3	60	0.79 ± 0.01
2	120	3	60	0.71 ± 0.01
3	30	18	60	0.79 ± 0.20
4	120	18	60	0.74 ± 0.12
5	30	6	30	0.58 ± 0.01
6	120	6	30	0.62 ± 0.03
7	30	6	120	0.77 ± 0.03
8	120	6	120	0.82 ± 0.08
9	60	3	30	0.51 ± 0.01
10	60	18	30	0.59 ± 0.04
11	60	3	120	0.80 ± 0.01
12	60	18	120	0.70 ± 0.02
13[a]	60	6	60	0.75 ± 0.03
14[a]	60	6	60	0.78 ± 0.03
15[a]	60	6	60	0.82 ± 0.02

[a] Indicates the centre point of the design.

$$\begin{aligned} Y = 0.78 + 0.045X_1 - 0.016X_2 + 0.11X_3 \\ + 0.088X_1X_2 - 0.022X_1X_3 - 0.04X_2X_3 \\ - 0.018X_1^2 - 0.064X_2^2 + 0.084X_3^2, \end{aligned} \quad (1)$$

where Y is the DS, X_1 is the soaking time with NaOH, X_2 is the soaking time with MCA, and X_3 is the reaction time with MCA.

In the polynomial (1), a positive sign indicates a synergistic effect and a negative sign indicates an antagonistic effect[26]. The model was significant ($F = 37.40$, $p < 0.0005$) (Table 4). The values of $R^2 = 0.99$, predicted $R^2 = 0.93$, and adjusted $R^2 = 0.96$ were in reasonable agreement. The signal-to-noise ratio was satisfactory since the precision ratio of 20.008 is above 4 (data not shown). Thus this model could be used to navigate the design space.

From the polynomial (1), it is clear that factor X_3, the reaction time with MCA, affected DS of the CMC positively. This means that DS increased as the reaction time with MCA increased. This is

Table 4 ANOVA for DS.

Source	Sum of squares	df	Mean square	F-value	p value (prob > F-value)
Model	0.20	9	0.022	37.40	0.0005
X_1	0.016	1	0.016	27.54	0.0033
X_2	0.002113	1	0.002113	3.59	0.1166
X_3	0.099	1	0.099	168.29	< 0.0001
X_1X_2	0.031	1	0.031	52.05	0.0008
X_1X_3	0.002025	1	0.002025	3.44	0.1227
X_2X_3	0.0064	1	0.0064	10.88	0.0215
X_1^2	0.001241	1	0.001241	2.11	0.2061
X_2^2	0.015	1	0.015	25.84	0.0038
X_3^2	0.026	1	0.026	44.46	0.0011
Residual	0.002942	5	0.000588		
Lack of fit	0.00475	3	0.000158	0.13	0.9351
Pure error	0.002467	2	0.001233		0.0005
Cor total	0.20	14	0.022	37.40	0.0033
R^2	0.9854				
Adjusted R^2	0.9590				
Predicted R^2	0.9346				

probably because MCA has more time to react with cellulose fibres, resulting in greater substitution of the hydroxyl group. Factor X_1, the soaking time with NaOH, also had a significant effect, with a slightly positive value. An increased soaking time with NaOH produces more swelling of cellulose fibres and causes more alkaline saturation, which allows MCA to react with the alkaline cellulose more easily. However, the soaking time with MCA (X_2) at room temperature did not have a significant effect ($p > 0.05$) on DS. This may be because the temperature was not high enough for the reaction, since dos Santos et al[24]. showed that the temperature for carboxymethylation did affect the DS of CMC.

The 3D response surface plots of the effects of factors on the response (Y) are illustrated in Fig. 1. In each plot, the interaction of two variables was investigated simultaneously while the third factor was kept constant. The response surface curve in Fig. 1a shows an increase in DS with an increase of soaking time with NaOH. That is, quadratic coefficients of soaking time with NaOH in the model were significant, whereas the soaking time with MCA did not have a significant effect on DS. However, the interaction effect of soaking time with NaOH and soaking time with MCA was significant ($p < 0.05$). In Fig. 1b, the minimal DS occurs at low soaking time with NaOH and low reaction time with MCA. Increasing the reaction time with MCA from 30–120 min led to an increase in DS from 0.58–0.77. Fig. 1c also shows that DS increased as a function of the reaction time with MCA, but did not depend on the soaking time with MCA.

Optimization and validation of the model

The optimal conditions for CMC production with maximal DS were analysed by DESIGN-EXPERT based on the desirability coefficient close to 1. The results indicated that a soaking time with NaOH of 118 min, a soaking time with MCA of 6.5 h, and a reaction time with MCA of 84 min were optimal. The predicted DS was about 0.90. Comparison of the experimental DS (0.93 ±0.03) with the predicted value indicated only a slight difference, with a prediction error of 3%. Hence the Box-Behnken statistical design and optimization method used in the study were suitable to prepare CMC with a maximal DS. In addition, the other characteristics of CMC produced from the optimal condition could reach the specification of CMC in the market (Table 5).

Table 5 Characteristics of CMC produced from the optimal condition and commercial CMC.

Characteristics	Optimal condition	Commercial CMC
Appearance: form	Powder	Powder
colour	White	White to light yellow
Yield (%)	81.9 ± 1.1	–
Moisture (%)	7.54 ± 0.07	$\leqslant 8\%$
DS	0.93 ± 0.03	0.6–1.45
Sodium (ICP)	11.3 ± 0.7	10.5–12.0
Molecular weight (Da)	5.25×10^5	$(3.0–10) \times 10^5$
Viscosity (cps)[†]	275 ± 36	25–850

[†] at 2% in water, 25 °C.

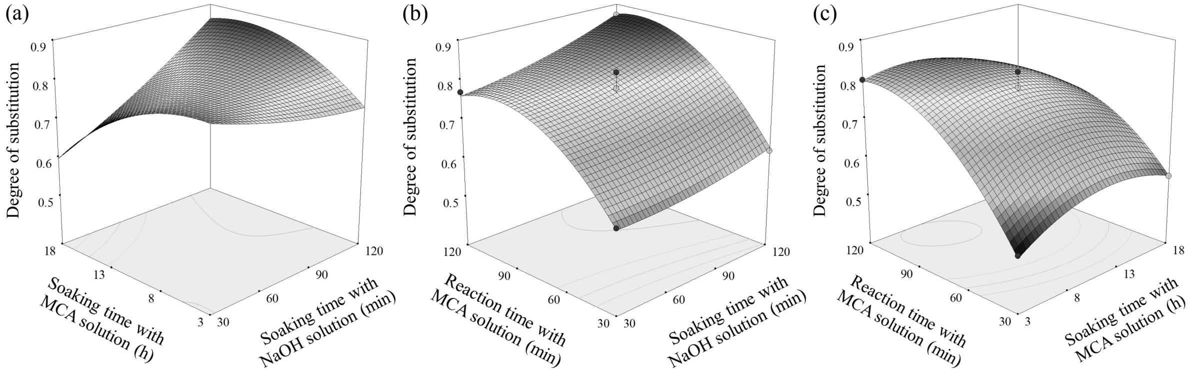

Fig. 1 3D response surface plots showing the effect of (a) soaking time with NaOH (X_1) and soaking time with MCA (X_2); (b) soaking time with NaOH (X_1) and reaction time with MCA (X_3); and (c) soaking time with MCA (X_2) and reaction time with MCA (X_3) on degree of substitution (Y).

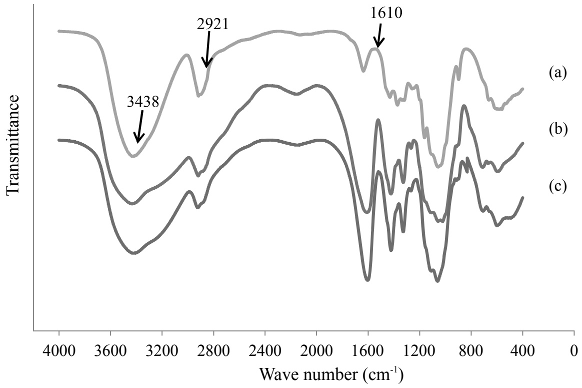

Fig. 2 FTIR spectra of (a) cellulose fibres extracted from corn peel, (b) standard CMC, and (c) CMC obtained under the optimized conditions.

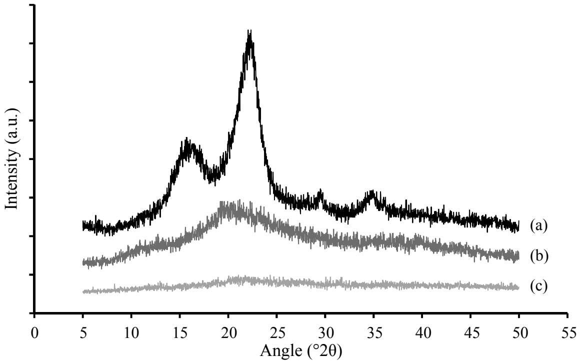

Fig. 3 X-ray diffractograms of (a) cellulose fibres extracted from corn peel, (b) standard CMC, and (c) CMC obtained under the optimized conditions.

Characterization of the optimized formulation

The IR spectrum of CMC produced using the optimized conditions (Fig. 2c) is similar to that of standard commercial CMC (Fig. 2b). However, some peaks of commercial CMC are broader compared to those in the spectrum of cellulose fibres extracted from corn peel (Fig. 2a). A broad peak in the region of 3000–3600 cm^{-1} represents the OH stretching with intra- and intermolecular hydrogen bonds, suggesting that the OH groups at C_2, C_3, and C_6 on the pyranose ring in CMC were substituted by CH_2COO^- [28,29]. In addition, the OH peak near 3500 cm^{-1} and CH peak at 2900 cm^{-1} decreased and the peak for —COO— at 1600 cm^{-1} was stronger in the spectrum of commercial CMC. The peaks at 1000–1460 cm^{-1} shows C—O and CH vibration bands of the pyranose ring, the skeletal structure of cellulose[29,30]. Except for additional peaks at 2880 and 2921 cm^{-1}, CH stretching bands were unchanged. This indicates that the CH groups of the pyranose ring did not react with MCA and that esterification mainly occurred at the OH at the C_6 position.

Fig. 3 shows the XRD pattern of CMC obtained under the optimized conditions, compared with those for standard CMC and cellulose fibres extracted from corn peel. The crystal structure of cellulose fibres extracted from corn peel decreased after carboxymethylation. Similar results were observed by de Santos et al[24], Chen et al[31], and Terinte et al[32]. The diffraction peak of cellulose fibres at 16° 2θ and 22° 2θ decreased and disappeared after the reaction with MCA and transformed into amorphous phase. This might be due to the substitution of OH groups in cellulose with CH_2COO^- groups.

CONCLUSIONS

Response surface method was successfully applied for optimization of preparation of CMC from corn peel. DS was affected by the reaction time with MCA and the soaking time with NaOH. The optimal conditions for preparation of CMC using RSM method were soaking with NaOH for 118 min, followed by soaking with MCA for 6.5 h, and reaction with MCA at 60 °C for 84 min, which produced a DS of 0.90.

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