Preparing a Novel Superabsorbent Based on Carboxymethyl Biocomposite: An Optimization Study via Response Surface Methodology

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A novel superabsorbent was prepared by utilizing carboxymethyl starch and carboxymethyl cellulose biocomposites as a grafting backbone. The scheme of the CMS-CMC double backbone structure was speculated. It was proposed that the superabsorbent possesses a three-dimensional network with an interpenetrating structure. The response surface methodology was used to optimize the parameters. Interactions among the most influential variables, *i.e.*, the dosage of CMC, the acrylic acid to acrylamide mass ratio, and the neutralization degree of acrylic acid were estimated. A mathematical model was developed, which fit the experimental results well for all of the response variables. The optimal conditions included 28.8 % of CMC dosage, a 1.6 mass ratio of acrylic acid to acrylamide, and 73.4 % of neutralization degree of acrylic acid to achieve 815.2 g/g of water absorbency.

INTRODUCTION

Superabsorbent hydrogels possess excellent properties, *i.e.*, water absorbency and retentivity, which is due to a lightly crosslinked network structure and a hydrophilic functional group (Ma *et al.* 2011). With valuable properties, superabsorbents have received significant attention, especially in the last 30 years, and potential has been shown for their application in many fields such as agriculture (Wu *et al.* 2008; Lokhande and Varadara 1992), personal care and hygienic products (Kosemund *et al.* 2009), drug-delivery (Sadeghi and Hosseinzadeh 2008; Pourjavadi and Barzegar 2009), waste-water treatment (Davies *et al.* 2004), and coal dewatering (Paiva *et al.* 2009). About 90% of all superabsorbent materials are used in disposable articles. Most of the superabsorbent materials are disposed of in landfills or by incineration, which may lead to increasing pollution concerns in the future (Kiatkamjornwong *et al.* 2002). Therefore, biopolymer materials derived from renewable agricultural resources have attracted great interest (Mohanty *et al.* 2002), and extensive attention has been directed toward superabsorbent polymers prepared through the graft copolymerization of vinyl monomers onto the chain of such natural polymers as starch and cellulose (Lanthong *et al.* 2006; Li *et al.* 2007; Feng *et al.* 2010; Prafulla *et al.* 2005).

Starch and cellulose are abundantly and cheaply available with the availability of high molecular grades and plurality of reactive hydroxyl groups (Godbole *et al.* 2003). However, the application of native starch is often limited by certain undesirable characteristics such as poor solubility, low mechanical properties, and instability at high temperatures, pH, and shear during processing (Wang *et al.* 2009). On the other hand, the

poor solubility of cellulose in water and most organic solvents, and the poor reactivity make it difficult to be directly modified to fabricate other useful materials (Wang and Wang 2010). Consequently, many treatments have been carried out in an attempt to modify the materials for the preparation of superabsorbents. These treatments include carboxymethylation and blending with other materials.

Carboxymethylation of the polysaccharides with an etherifying agent such as monochloroacetic acid in the presence of sodium hydroxide is the most popular method of conversion (Dutkiewicz 2002). Carboxymethyl polysaccharides are water soluble, biocompatible, and have various valuable features that can overcome the shortcomings of native polysaccharides. (Heinze *et al.* 2001). Moreover, the introduction of macro-molecular-branched chains affords various derivatives for enhanced applications, in particular, its potential for an application in a superabsorbent (Nagasawa *et al.* 2006; Ning and Sun 1993; Bao *et al.* 2011; Ibrahim *et al.* 2007).

Starch-based materials tend to form soft gelatinous masses when swollen with an aqueous solution. Blending natural polymers with clay to fabricate organic-inorganic superabsorbent composite is a convenient route to improve the properties of natural polymer-based hydrogels (Myung *et al..* 2008). Some articles related to the preparation of a starch/clay superabsorbent composite have been reported (Li *et al.* 2005, 2007; Beşün *et al.* 1997). Currently, although clay is low-priced and abundant, it is eventually non-renewable. Due to this, the comprehensive utilization of a renewable resource is essential. Some studies indicate that cellulose fibers blended with starch-based polymers for the formulation of biocomposites can provide a wide range of potential mechanical proper-ties, and the method has been widely used in starch-based film (Rosa *et al.* 2009; Kumar and Singh 2008), but only a few applications in superabsorbents. Carboxymethyl cellulose, with a similar structure to carboxymethyl starch, is another potential raw mater-ial for superabsorbent besides starch. With the excellent properties of the carboxy-methyl cellulose and the miscibility with the carboxymethyl starch, the processes could be feasible alternatives for the production of biodegradable superabsorbents from carboxy-methyl starch/cellulose biocomposites. Therefore, the synergistic effect of carboxymethyl starch/cellulose is expected to be observed in carboxymethyl biocomposite super-absorbents.

Response surface methodology (RSM) is a useful statistical technique that has been applied in research into complex variable processes. It can evaluate the interactions of the various parameters affecting the process. Therefore, it is becoming widely used for optimization studies. In the present study, a novel superabsorbent based on carboxymethyl biocomposites was prepared. The RSM approach was applied to study the combined effects of the main parameters to obtain maximum water absorbency. The morphology and structure of the superabsorbent were also investigated.

EXPERIMENTAL

Materials

Carboxymethyl starch, denoted as CMS, was prepared in the lab (degree of substitution 0.26; M_w 1.69×10^5). All of the other chemicals from the Tianjing Fuchen Chemical Reagent Factory, Tianjing, China, including carboxy-methyl cellulose (CMC, the degree of substitution 0.39; M_w 2.03×10^4), acrylic acid (AA), acrylamide (AM),

ammonium persulphate (APS), and N,N'-methylene-bisacrylamide, *etc*., were analytically pure. The water used was deionized water.

Preparation of Superabsorbent Biocomposites

A predetermined dosage of an NaOH solution (20 %, by wt) was added drop-wise to the stirred aqueous AA solution with an ice bath for partial neutralization. The other monomer, AM, was dissolved in the above AA solution. The monomer solution was then added drop-wise to the carboxymethyl biocomposites solution in a 250 mL four-necked flask equipped with mild agitation and nitrogen bubbling until a clear mixture was obtained. The reactor was placed in a water bath preset to 30 ^{o}C. The carboxymethyl biocomposites were prepared by the following procedure: CMS was dissolved in distillated water; in general the mass fraction of the CMS solute was 30%. Then, a predetermined weight quantity of CMC (mass fraction of carboxymethyl biocomposites, wt%) was added into the CMS solute directly with stirring. The carboxymethyl biocomposites to the monomer (AA and AM) mass ratio was 0.3 KPS (3.0% of monomers by wt), an initiator was added to the completely blended carboxymethyl biocomposites / monomers solution. After stirring for 10 min, MBA (0.08% of monomers by wt) was added to the reaction mixture. The mixture was continuously stirred for 20 min; simultaneously the water bath was heated to 75 ^{o}C and kept for 3 h. A nitrogen atmosphere was maintained throughout the reaction period. Then, the resulting product was washed several times with ethanol, immersed in ethanol for 4 h, and then dried at 60 ^{o}C to a constant weight. The dried product was milled and screened.

Water Absorbency Measurement

A superabsorbent composite (1.0 g) was immersed in distilled water at ambient temperature to reach a swelling equilibrium. The residual water was removed by filtration with a 100-mesh screen until no drops drained. The water absorbency (Q_{H2O}) of the superabsorbent composite was determined by weighing the weight of the swelled sample. The Q_{H2O} of the sample was calculated according to the following equation:

$$Q_{H_2O} = \frac{m_1 - m_0}{m_0}$$

(1)

where m_0 and m_1 are the weights of the dry sample and the swollen gel, respectively. Q_{H2O} was calculated as grams of water per gram of sample (g/g).

Design of the Experiments

The variables obtained in the preliminary experiments were screened using the Plackett–Burman design to identify those variables that most affected the water absorbency. Actual ranges and levels of the independent variables investigated in this study are shown in Table 1. The experiments were designed to find the interaction of three variables, *i.e*., the dosage of CMC (X1), the AA to AM mass ratio [m(AA):m(AM), X2], and the neutralization degree of AA (X3). The experiments were carried out in duplicate, and the results of the mean water absorbency were observed. The coded and non-coded values of the experimental variables are given in Table 2. The results of the mean observed and predicted responses are shown in Table 3. The relationship between the variables and the response was calculated by the second order polynomial equation,

$$Y = \beta_0 + \sum \beta_i \times X_i + \sum \beta_j \times X_i^2 + \sum \beta_{ij} \times X_{ij}$$

(2)

where Y is the predicted response, X_i is the independent variable, β_0 is the intercept term, β_i is the linear effect, β_j is the squared effect, and β_{ij} is the interaction effect.

The statistical software Minitab 16 was used for regression and graphical analyses of the data obtained.

Table 1. Preliminary Study of Preparation Conditions

Parameter (range)	Optimum
Mass ratio of biocomposites and monomers (0.1 to 0.5)	0.3
Mass ratio of CMC and biocomposites (0.1 to 0.5)	0.3
Mass ratio of AA and AM (1.0 to 3.0)	1.5
Neutralization degree of AA (50 to 90 %)	70
Mass ratio of Initiator and monomers (2.0 to 4.0 %)	3.0
Mass ratio of Initiator and crosslinker (0.04 to 0.12 %)	0.08
Reaction temperature (60-80 ^{o}C)	75
Reaction time (2.0 to 5.0 h)	3.0

Table 2. Coded and Uncoded Values of the Experimental Variables

Independent Variables	Coded Values		
	-1	0	1
The dosage of CMC (%)	20	30	40
m(AA):m(AM)	1	1.5	2
Neutralization degree of AA(%)	60	70	80

Table 3. Response Surface Central Composite Design and Experiments

Run	CMC Dosage (%)	m(AA):m(AM)	Neutralization degree of AA (%)	Water Absorbency (g/g) Observed	Water Absorbency (g/g) Predicted
1	-1	-1	-1	402.4	411.629
2	1	-1	-1	294.3	282.939
3	-1	1	-1	442.4	436.219
4	1	1	-1	240.8	249.429
5	-1	-1	1	470.3	456.649
6	1	-1	1	359.4	360.559
7	-1	1	1	530.9	537.239
8	1	1	1	397.3	383.049
9	-1	0	0	583.6	587.865
10	1	0	0	430.6	446.425
11	0	-1	0	724.5	739.125
12	0	1	0	757.2	762.665
13	0	0	-1	705.9	705.585
14	0	0	1	774.5	794.905
15	0	0	0	814.5	814.286
16	0	0	0	842.2	814.286
17	0	0	0	810.9	814.286
18	0	0	0	829.2	814.286
19	0	0	0	804.3	814.286
20	0	0	0	824.8	814.286

Characterization

An FT-IR spectrometer (Thermo Fisher Scientific Co.) was used for the FT-IR analysis, and the morphology of superabsorbent particles was observed on a XL30ESEM-TMP scanning electron microscope (SEM, Philips-FEI Co.) after gold coating.

RESULTS AND DISCUSSION

Regression Model Equation

The results obtained in the experiments are summarized in Table 3. The estimative response model equation of coded units can be stated as,

$$Y = 814.286 - 70.72X_1 + 11.77X_2 + 44.66X_3 - 297.14X_1^2 - 63.39X_2^2 - 64.04X_3^2$$
$$- 14.52X_1X_2 + 8.15X_1X_3 + 14.00X_2X_3$$

(3)

in which Y is the response value, water absorbency (g/g), X_1, X_2, and X_3 are the values of the independent factors, the dosages of CMC (%), m(AA):m(AM), and the neutralization degree of AA (%), respectively. The full regression models for water absorbency resulted in high R^2 values (0.9928), and the Adj R^2 was 0.9864, indicating an excellent fit of the data to the models. From the equation, water absorbency had linear and quadratic effects by the three process variables.

Statistical analysis based on the summary of the analysis of variance(ANOVA) for the response surface quadratic model is shown in Table 4.

Table 4. ANOVA for the Response Surface Quadratic Model Analysis of Variance Table

Source	Degree of freedom	F-value	Probe>F
Model	9	308.78	<0.0001
X_1	1	171.86	<0.0001
X_2	1	4.76	0.054
X_3	1	68.54	<0.0001
$X_1 X_2$	1	5.80	0.037
$X_1 X_3$	1	1.83	0.206
$X_2 X_3$	1	5.39	0.043
X_1^2	1	834.34	<0.0001
X_2^2	1	37.97	<0.0001
X_3^2	1	38.76	<0.0001
Residual	5		
Lack of fit	10	2.05	0.225
Pure error	5		

As can be seen from Table 4, the 'Probe>F' of the model was less than 0.05, indicating that it is a significant and desirable model. The value of P<0.0001 indicates that there was only a 0.01 % chance that a 'model F-value' this large could occur due to noise. In addition, the lack of fit 'Probe>F' was 0.225, which implied that a lack of fit was not significant in relation to pure error. From the ANOVA, it was also shown that 5 terms (X_1, X_3, X_1^2, X_2^2, X_3^2) related to linear and quadratic effects were significant, and X_1 was the most significant. Moreover, it is important to note that the interaction term of X_1X_2 and X_2X_3 were significant for the model.

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Parameter Effects for the Model

The regression model developed can be represented in response surfaces and contour plots to understand the interaction among the three variables, and to determine the optimum level of each variable for a maximum response.

Figure 1 represents the effects of different dosages of CMC and mass ratios of the monomers. It was observed that the dosage of CMC was a significant factor. At a constant monomer ratio, the water absorbency increased slowly within 28.8% of CMC, and then it dropped dramatically while the CMC was further increased. This finding may be explained by the fact that the network structure of the superabsorbent would be changed with the introduction of CMC. A lower CMC dosage was supposed to act as a lubricant (Mondragon *et al.* 2008), which results in a loose network and poor mechanical strength. An addition of CMC, in all of the concentrations, decreased the water solubility of the starch polymer; this effect was observed distinctly at the high levels of CMC (Ghanbarzadeh *et al.* 2010). On the other hand, CMC and CMS were blended to form double backbone biocomposites. Interpenetrating polymer networks might have formed due to the interaction among the groups of CMC and CMS. The incorporation of the appropriate dosage of a secondary biopolymer would improve the water absorbency by the formation of a superior network. The mass ratio of monomers was less influential, and the water absorbency varied within a small range at any designed mass ratio from 1 to 2. The interaction term of the dosage of CMC and the mass ratio of monomers was significant. The main reason was that the dosage of AA and the graft site in backbones were intrinsically linked. However, it was complicated; the interaction term was influenced by many aspects, which should be followed up on and studied. The appropriate maximal dosage was determined to be 28.8 % of the CMC dosage and a value of m(AA):m(AM) of 1.6.
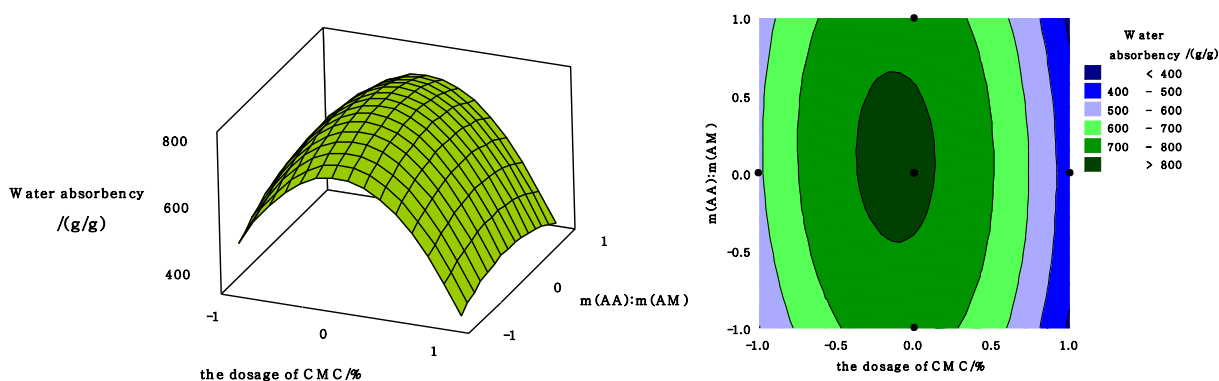

Fig. 1. Response surfaces and contour plots for water absorbency as a function of the dosage of CMC and the mass ratio of monomers. Other factors are constant at zero levels.

Figure 2 shows the response surfaces and contour plots for different dosages of CMC and the neutralization degree of AA. The figure also shows that the dosage of CMC was more influential. At low contents of introduced CMC, the water absorbency was slightly affected; whereas, at a high CMC content, the introduced CMC was extremely relevant to the reduction of the water absorbency. On the other hand, it was observed that increasing the neutralization degree of the AA did not have much of an effect on increasing the water absorbency. Although it was not readily apparent, at any dosage of CMC, the upper neutralization degree of AA possessed a superior contribution to the water absorbency to a lower degree. The proportion of ionized carboxymethyl groups

depended on the neutralization degree of the AA, which finally affected the water absorbency. The mechanism has been explained in a large amount of research (Chen *et al.* 2005; Ma *et al.* 2011).
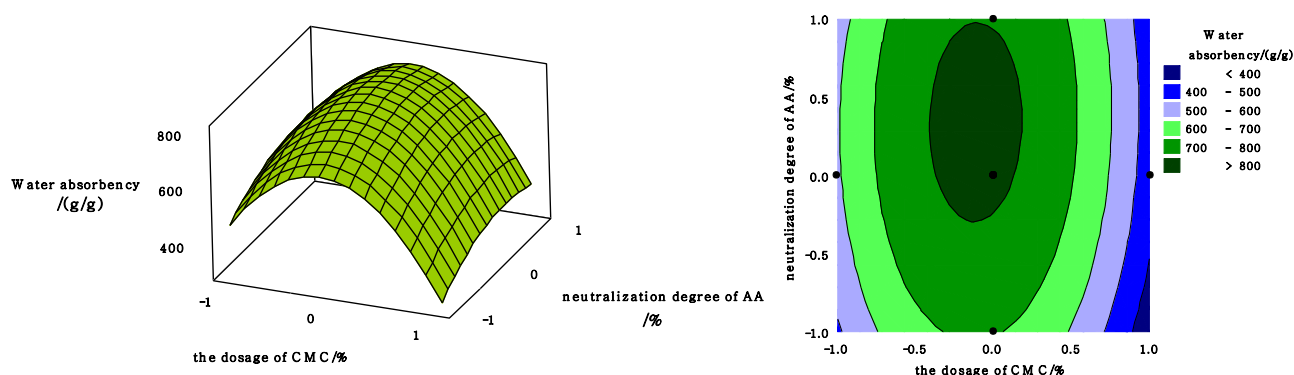

Fig. 2. Response surfaces and contour plots for water absorbency as a function of the dosage of CMC and the neutralization degree of AA. Other factors were constant at zero levels.

The effect of the AA-to-AM mass ratio and the neutralization degree of AA on the water absorbency and their reciprocal interactions are provided in Fig. 3. Compared with the dosage of CMC, the water absorbency was affected slightly by the AA-to-AM mass ratio and the neutralization degree of AA. At a low neutralization degree of AA, the water absorbency was still in the low-level. A high water absorbency was obtained with a higher mass ratio of AA to AM. The excellent water absorbency can be attributed to both the functional groups of ionic carboxylate (from neutralized AA) and the non-ionic carboxamide (from AM) (Mahdavinia *et al.* 2004). Some interactions between the neutralization degree of the AA and the AA-to-AM mass ratio could be deduced. The response surface suggests that there is a maximum water absorbency at approximately 1.6 of the AA-to-AM mass ratio, and 73.6 % of the neutralization degree of AA.
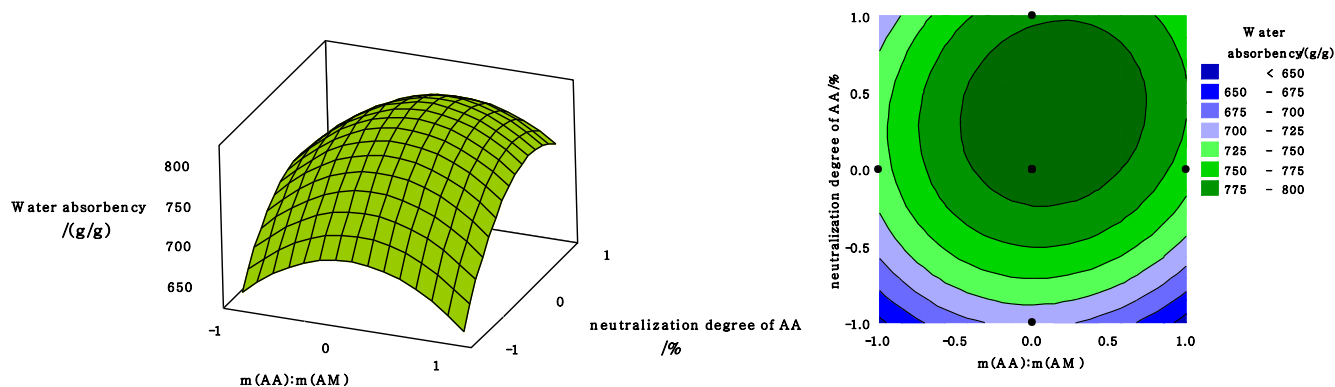

Fig. 3. Response surfaces and contour plots for water absorbency as a function of AA-to-AM mass ratio and t neutralization degree of AA. Other factors were constant at zero levels.

Process Optimization

As compared to the results shown in Figs. 1-3, the optimal condition for the maximal water absorbency was achieved with 26% to 32% of the CMC dosage, 1.5 to 1.6 of the AA-to-AM mass ratio, and 72% to 75% of the neutralization degree of AA. The optimal values of the selected variables were obtained by the Simulink Response

Optimization by Minitab 16 software. The optimal conditions were as follows: $X_1=28.8$ %, $X_2=1.6$, and $X_3=73.4$ %. The theoretical water absorbency predicted under the above conditions was $Y=827.6$ g/g. In order to verify the prediction of the model, the optimal reaction conditions were applied to three independent replicates for superabsorbent synthesis. The average water absorbency was 815.2 g/g. The experimental error was less than ±5 %, a figure well within the estimated value of the model equation. This demonstrated that response surface methodology with an appropriate experimental design can be effectively applied to the optimization of the process of factors in a chemical reaction. This study focused on the application of response surface methodology to further the optimization of the superabsorbent preparation conditions using double backbones (CMS and CMC) and double monomers (AA and AM). This may provide useful information regarding the development of a novel superabsorbent with economic and efficient characteristics.

Water Retention Behaviors

Water retention behaviors of the superabsorbent composite at room temperature are shown in Fig. 4. At room temperature (25 °C, relative humidity of 70 %), the water retention value of the superabsorbent composite was 87.6 wt% in 8 d, and it was 85.6 wt% in 16 d. Figure 5 shows that, at 60 °C, the water retention value of the superabsorbent composite was 64.3 wt% in 8 h, and it was 34.2 wt% in 16 h. This result showed that the water-holding effect of the superabsorbent composite was better at room temperature, and it was easy to dehydrate the material at high temperature.
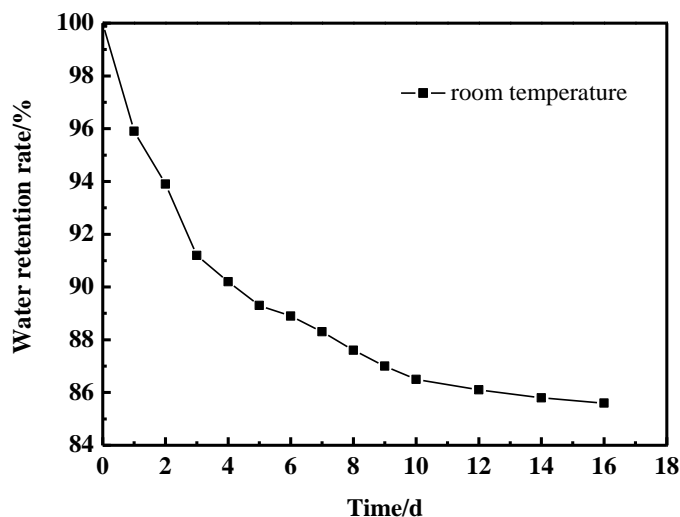

Fig. 4. The water retention rate of superabsorbent under natural conditions

Characterization

For the identification of the superabsorbent product, infrared spectroscopy was used. The IR spectra of the superabsorbent are shown in Fig. 6. The superabsorbent product comprised CMS and CMC backbones with side chains that carried sodium carboxylate and carboxamide functional groups. This is evident from peaks at 3576 cm^{-1} (N-H stretching), 1668 cm^{-1} (the extension vibration of C=O of amide I band), 1565 cm^{-1} (asymmetric stretching of COO$^-$), and 1403 cm^{-1} (symmetric stretching of COO$^-$). A

combination of absorption of the carboxylate and alcoholic O–H stretching bands appeared in the wide range of 3500 to 2550 cm^{-1}.
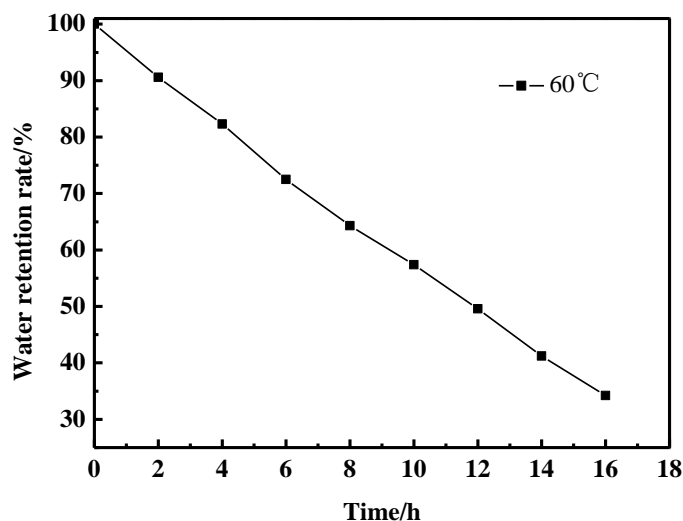

Fig. 5. The water retention rate of superabsorbent at 60 $^{\circ}$C

The surface appearance and structure of the superabsorbent were observed using SEM, and the results are shown in Fig. 7. Porous structure was observed, which structurally increased the surface area of the superabsorbent, and it is believed that these pores are the regions of water permeation. An interpenetrating network structure was formed after blending the backbones and grafting. According to the SEM, the CMC structure was distinct among the CMS; they were interpenetrating, which showed a double backbone structure.
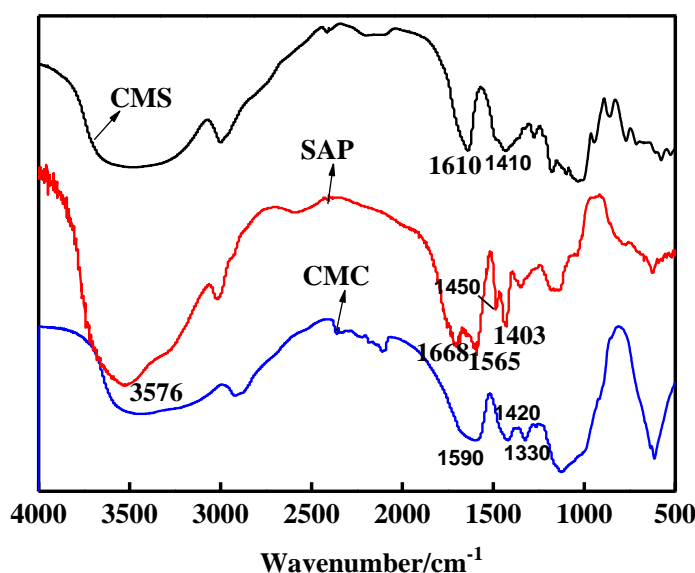

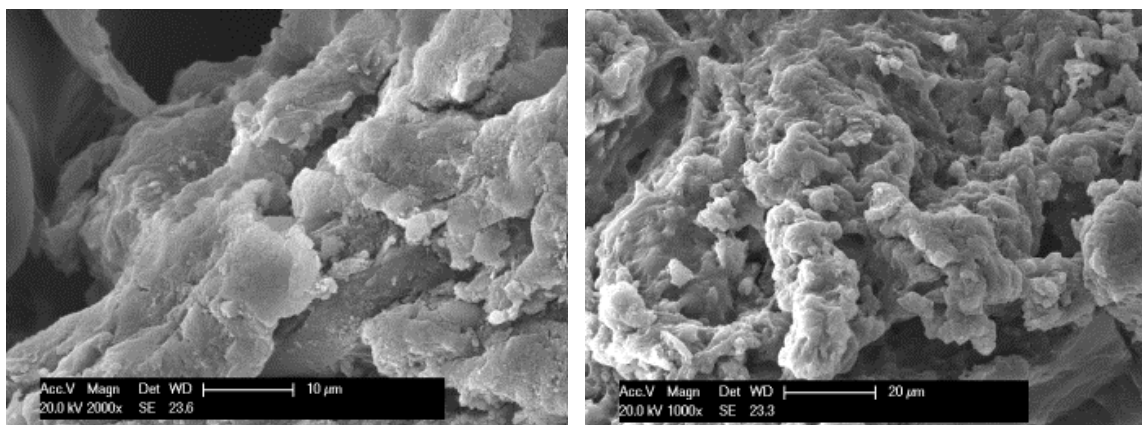**Fig. 6.** FTIR spectrum of CMC,CMS, and SAP

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Fig. 7. SEM of superabsorbent

CONCLUSIONS

1. A new approach was adopted in the utilization of double backbones (CMS and CMC biocomposites) for the preparation of a superabsorbent. The novel superabsorbent contains biodegradable starch and cellulose, which is quite economical and environment-friendly.

2. Optimal conditions were established using an RSM analysis. The dosage of CMC was found to be the most influential variable, and the interaction term of the dosage of CMC and the AA to AM mass ratio was significant.

3. In addition, the AA to AM mass ratio and the neutralization degree of AA also played roles in determining the maximal water absorbency. The values of three variables, the dosage of CMC (28.8%), the AA to AM mass ratio (1.6), and the neutralization degree of AA (73.4%), were found to be optimum for the preparation of a superabsorbent with the predicted 827.6 g/g of water absorbency. The average experimental water absorbency was 815.2 g/g, and the experimental error was less than ±5%. The mathematical model developed was validated and proven to be statistically adequate and accurate to predict the optimal water absorbency.

4. Moreover, the network with an interpenetrating network structure of CMS and CMC for poly-(AA-AM) was proposed.

ACKNOWLEDGMENTS

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