# Utilization of Xylan-rich Steam Explosion Liquid from Processing of Poplar for Hydrogel Synthesis

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A high-performance hydrogel was successfully fabricated using xylan-rich concentrated steam explosion liquid (CSEL). The method used was a freeradical graft copolymerization of acrylic acid (AA) and acrylamide (AM) onto a primarily xylan backbone in CSEL, with a redox system of ammonium persulfate/anhydrous sodium sulfite as the indicator and N,N'methylenebisacrylamide (MBA) as the cross-linker. The effects of independent parameters (the dosages of the indicator, AM, AA, and the cross-linker) on the swelling ratio of the as-prepared hydrogel were studied via an optimal design of the response surface methodology (RSM). Under the optimal conditions (80.9 mg of initiator, 349.6 mg of AM, 988.7 mg of AA, and 9.39 mg of cross-linker), the swelling ratio of the prepared hydrogel (Xyl-AM-co-AA) was 276.6 g/g, which was close to the predicted value (255.7 g). The swelling behaviors of Xyl-AM-co-AA at different temperatures and pH values were also analyzed. The results showed that the swelling ratios varied at different temperatures and pH values, implying their potential use as smart materials. Analysis by Fourier transform infrared spectroscopy and scanning electron microscopy confirmed the cross-linked and hygroscopic behavior of XyI-AM-co-AA.

Keywords: Hemicellulose; Steam explosion liquid; Hydrogels; Swelling ratio

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# INTRODUCTION

Hydrogels are polymers structured by hydrophilic networks formed by chemical or physical cross-linking. They swell in water or aqueous solutions without dissolving (Yang *et al.* 2011; Ahmed 2015). With many hydrophilic functional groups, such as hydroxyl, carboxylic acid, and amines, on the main chain of polymers, hydrogels can have excellent liquid adsorption ability (Wang *et al.* 2017; Liu *et al.* 2019). At the same time, the formation of cross-links between polymer chains often results in their insolubility (Ahmed 2015; Liu *et al.* 2019).

In recent years, the use of environmentally sensitive hydrogels as intelligent material has attracted considerable attention. Environmentally sensitive hydrogels are also called intelligent hydrogels (Yashin and Balazs 2006), and demonstrate response to environmental stimuli, such as temperature, pH, salt, and biomolecules (Peng *et al.* 2011; Dai *et al.* 2016). Their response behavior is mainly reflected in the changes in volume size and pore size of the hydrogel (Qiu and Park 2001). Of multiple environmentally sensitive hydrogels, temperature- and pH-sensitive hydrogels have attracted much attention by researchers in the biomedical field, especially in controlled drug delivery systems and immobilized enzyme systems (Qiu and Park 2001; Zhang *et al.* 2004; Kipcak *et al.* 2014). Risbud *et al.* (2000) synthesized a pH-sensitive hydrogel by cross-linking chitosan and

polyvinyl pyrrolidone with glutaraldehyde, and the result implied that the hydrogel could be a potential candidate for antibiotic delivery in an acidic environment.

Generally, hydrogels can be synthesized by various approaches, such as radicalinduced copolymerization, frontal copolymerization, graft copolymerization, crosslinking, and ionizing radiation from synthetic polymers or polysaccharides (Marandi *et al.* 2008). However, most of the synthetic polymers are petroleum-based, making the products unsustainable (Al-Rudainy *et al.* 2019). Therefore, many natural materials, such as biomass polysaccharides and inorganic clay minerals, have been developed as raw materials to realize low-cost, renewable, non-toxic, and biodegradable hydrogel production (Bao *et al.* 2011; Kabiri *et al.* 2011).

Hemicelluloses are the second most abundant polysaccharides in nature after cellulose, constituting over 20% of the cell walls in wood (Al-Rudainy *et al.* 2019). Considering the abundance of hydrophilic functional groups on hemicellulose backbones, hemicellulose could be a promising feedstock to produce hydrogels (Li and Pan 2010; Zhao *et al.* 2014). Recently, researchers have shown great interest in hemicellulose-based hydrogels, especially environment-sensitive hydrogels with light-responsive abilities. Peng *et al.* (2011) synthesized an intelligent hemicelluloses-graft-acrylic acid ionic hydrogel with N,N`-methylenebisacrylamide (MBA) as a cross-linker. Expansion of the network occurred at high pH, whereas shrinkage appeared at low pH, in salt solutions, and in organic solvents. Cao *et al.* (2014) prepared hemicellulose-based hydrogels by free radical copolymerization, which showed multiple response behaviors to pH, water/ethanol alternating solutions, and light.

However, in the cell walls of biomass, hemicellulose is closely linked with cellulose and lignin by intermolecular hydrogen bonds and covalent bonds, respectively, resulting in increasing the difficulty of hemicellulose separation, thus limiting the utilization of hemicellulose. Therefore, the efficient utilization of hemicellulose to extract hemicellulose by appropriate separation methods is highly important.

Steam explosion is a high-efficiency method used to separate hemicellulose (Ruiz *et al.* 2008). After steam explosion treatment, hemicellulose-based polysaccharides, mainly xylan-based polysaccharides (Xyl-P), are separated from biomass and dissolved in the steam explosion liquid. In this study, the concentrated steam explosion liquid (CSEL) of poplar was employed as the raw material to graft copolymerize with acrylic acid (AA) and acrylamide (AM) to prepare xylan-based hydrogels. By incorporating AA and AM into the network, hydrogels can have excellent water absorption ability. To explore the optimal preparation conditions of hydrogels, the response surface methodology (RSM) method was adopted. Then, the water swelling ratios of the prepared hydrogel in different pH and temperature were measured. The morphology and chemical properties were investigated by scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR).

#### EXPERIMENTAL

#### Materials

Poplar chips were provided by Sun Paper Co., Ltd. (Shandong, China), with an average size of  $30 \times 30 \times 5 \text{ mm}^3$ . Acrylic acid (99.5%), acrylamide (99.0%), and *N*,*N*<sup>-</sup> methylenebisacrylamide (98.0%) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). NaOH was supplied by Aladdin Reagent Co., Ltd. (Shanghai,

China), and ammonium persulfate (99.0%) and anhydrous sodium sulfite (98.0%) were purchased from Tianjin Damao Chemical Reagent Company (Tianjin, China). All the reagents were used without further purification.

#### Methods

#### Preparation of the steam explosion liquid

Steam explosion pretreatment was conducted in an explosion device comprised of a 5-L reaction chamber, a steam generator, and a sample collector. After 0.4 kg of poplar chips (dry base) were loaded into the reaction chamber, high-pressure steam was introduced to reach the temperature of 209 °C, during a processing time of 7 min. After steam-explosion pretreatment, the hemicellulose-rich liquid was separated from the solids. With a rotary evaporator, the CSEL was obtained. The components' contents of CSEL were also determined by high-performance liquid chromatography (HPLC) according to NREL protocol (Sluiter *et al.* 2006).

#### Preparation of hydrogels

A total of 5 mL of CSEL was added in a beaker as raw material. After simmering the  $N_2$  for 20 min to discharge oxygen, a certain amount of indicator (redox system of ammonium persulfate and anhydrous sodium sulfite) was dissolved in the CSEL, and the mixture was placed on a magnetic stirrer for magnetic stirring at 60 °C for 15 min to generate free radicals. Subsequently, AM and AA were added in succession at 60 °C and stirred for 15 min. Subsequently, a certain amount of MBA was added to the beaker as the cross-linker. Finally, the mixture was placed at 25 °C for 12 h to mold. After the reaction, the as-synthesized hydrogels were washed with 2 mol/L NaOH and distilled water.

#### Experimental design for preparing hydrogels

The experimental procedure for preparing hydrogels was designed with the RSM method. This method was adopted for optimizing the swelling ratio of hydrogels. In this study, the RSM method was used to evaluate the relationship among four experimental variables (dosages of initiator  $[X_1]$ , AA  $[X_2]$ , AM  $[X_3]$ , and MBA  $[X_4]$ ) and the swelling ratio of hydrogels, as well as to obtain the optimal hydrogel with the highest swelling ratio. A Box-Behnken design with four factors at three levels was considered. The range of these four independent variables (X<sub>1</sub>, X<sub>2</sub>, X<sub>3</sub>, and X<sub>4</sub>) and the center point values are presented in Table 1. The statistical software Design-Expert (Version 8.0.5; Stat-Ease Co., Ltd., Minneapolis, America) was used to analyze the regression analysis of the experimental data and the response surface plots. The mathematical model for the swelling ratio of hydrogel was fitted to the second-order polynomial model, as in Eq. 1,

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_4 X_4 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2 + \beta_{44} X_4^2 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{14} X_1 X_4 + \beta_{23} X_2 X_3 + \beta_{24} X_2 X_4 + \beta_{34} X_3 X_4$$
(1)

where *Y* is the swelling ratio of the hydrogel;  $X_1$ ,  $X_2$ ,  $X_3$ , and  $X_4$  are the independent variables;  $\beta_0$  is the regression coefficient;  $\beta_1$ ,  $\beta_2$ ,  $\beta_3$ , and  $\beta_4$  are the linear coefficients;  $\beta_{11}$ ,  $\beta_{22}$ ,  $\beta_{33}$ , and  $\beta_{44}$  are the quadratic coefficients;  $\beta_{12}$ ,  $\beta_{13}$ ,  $\beta_{14}$ ,  $\beta_{23}$ ,  $\beta_{24}$ , and  $\beta_{34}$  are the second-order interaction coefficients.

Independent Variables	Range and Le			
	Symbol	-1	0	1
Dosage of initiator (mg)	<i>X</i> <sub>1</sub>	50	70	90
Dosage of AA (mg)	X2	150	250	350
Dosage of AM (mg)	X3	500	750	1000
Dosage of MBA (mg)	X4	9	12.5	16

#### Table 1. Experimental Range and Levels for the Independent Variables

#### Characterization of the hydrogels

The surface morphology of freeze-dried hydrogels swelled at different swelling conditions were analyzed using a scanning electron microscope (JSM-6400; JEOL Co., Ltd., Tokyo, Japan). Prior to the observation, the hydrogel surfaces were coated with platinum (SB1361; Jieou Road Science and Trade Co., Ltd, Beijing, China) to render them electrically conducive. The FTIR spectra of the prepared hydrogel and dried CSEL were recorded on VERTEX 70 Fourier transform spectrometer (Bruker Optics, Karlsruhe, Germany) with a wavelength range of 4000 to 400 cm<sup>-1</sup>, using the KBr disk method with a mass ratio of sample to KBr 1:100.

#### Swelling degree of hydrogels

The gravimetric method was adopted to analyze the swelling ratio of the prepared hydrogels. The swelling ratios of the dehydrated hydrogel samples were measured at 25 °C. When the samples reached the equilibrium swelling state, the swollen hydrogels were removed from the water and immediately weighed after wiping off the excess water on their surfaces.

To explore the response behaviors of prepared hydrogels to pH and temperature, the dehydrated hydrogel samples were immersed in 40 mL of aqueous solutions with pH levels from 2 to 11 and immersed in distilled water at temperatures ranging from 5 °C to 45 °C, respectively. The swelling ratio (*SR*) and equilibrium swelling ratio ( $S_{eq}$ ) were calculated by Eqs. 2 and 3, respectively (Sun *et al.* 2013),

$$SR = (W_{\rm t} - W_{\rm o}) / W_{\rm o} \tag{2}$$

$$S_{\rm eq} = (W_{\rm t} - W_{\rm o}) / W_{\rm o} \tag{3}$$

where  $W_0$ ,  $W_t$ , and  $W_{eq}$  are the weights (g) of dried hydrogels, swollen hydrogels at the time t, and swollen hydrogels at equilibrium swelling state, respectively.

#### **RESULTS AND DISCUSSION**

#### **Component Analysis of CSEL**

Table 2 shows the components' contents of CSEL. As shown in Table 2, the main components of the steam expansion liquid were glucose-based polysaccharide (Glu-P), xylose-based polysaccharide (Xyl-P), arabinose-based polysaccharide (Arab-P), formic acid, and acetic acid. The Xyl-P content was the highest in steam expansion liquid, at 37.7 mg/mL.

Table 2. Component Concentrations of Concentrated Steam Explosion Liq	Juid
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Components	Glu-P	Xyl-P	Arab-P	Formic Acid	Acetic Acid
Concentration (mg/mL)	6.4	37.7	1.5	2.7	10.8

#### **RSM Study for Preparing Hydrogels**

Model analysis

A quadratic model was recommended to evaluate the responses as functions of independent variables and their interactions. According to Box-Behnken design, 29 groups of experiments were conducted to prepare hydrogels from CSEL; Table 3 shows the combinations of the preparation conditions. Based on the results, the following regression equation was obtained to describe the swelling ratio from the experimental responses,

 $Y = 205.36 - 16.56X_1 + 1.69X_2 + 8.34X_3 - 18.44X_4 + 18.75X_1X_2 + 27.17X_1X_3 + 5.60X_1X_4 - 0.48X_2X_3 - 16.90X_2X_4 - 26.27X_3X_4 - 20.74X_1^2 - 1.99X_2^2 - 9.81X_3^2 - 22.74X_4^2$ (3)

where Y is the swelling ratio of hydrogel; and  $X_1$ ,  $X_2$ ,  $X_3$ , and  $X_4$  are the independent variables of dosages of the initiator, AM, AA, or MBA, respectively.

 Table 3. Independent Variables of the Central Composite Design and the Results of Response Surface Analysis

 Duration V (ma)

Run	X <sub>1</sub> (mg)	X <sub>2</sub> (mg)	X₃ (mg)	X4 (mg)	Y (g/g)
1	50	250	500	12.5	205
2	50	250	750	16	156
3	70	350	1000	12.5	198
4	70	150	500	12.5	184
5	70	250	750	12.5	211
6	70	250	750	12.5	203
7	90	250	1000	12.5	196
8	90	250	500	12.5	124
9	70	150	750	9.0	172
10	50	250	750	9.0	190
11	50	350	750	12.5	185
12	70	250	1000	9.0	240
13	70	350	500	12.5	189
14	90	250	750	9.0	142
15	70	250	1000	16.0	137
16	70	250	500	16.0	166
17	70	350	750	9.0	216
18	90	150	750	12.5	150
19	70	250	750	12.5	203
20	70	150	1000	12.5	194
21	50	150	750	12.5	227
22	70	250	750	12.5	207
23	90	250	750	16.0	133
24	70	250	500	9.0	174
25	70	250	750	12.5	203
26	70	350	750	16.0	152
27	90	350	750	12.5	184
28	50	250	1000	12.5	168
29	70	150	750	16.0	176

The  $R^2$  value for this model was 0.9654 (Fig. 1). This result implied that 96.54% of the variability in the response could be explained by this model. A comparison between the predicted and observed swelling ratio was also conducted (Fig. 1). It showed that the observed swelling ratio was scattered relatively close to the straight line, thus demonstrating sufficient correlation between the experimental data and the theoretical values. Therefore, the quadratic model was used in this optimization study.

The variance (ANOVA) listed in Table 4 was used to check the F-value to assess the significance and adequacy of the models. As shown in Table 4, the F-value of the swelling ratio was 27.94. Generally, when the F value is greater than zero, it means that the obtained model is highly feasible, and a higher F value results in a more significant feasibility (Pourjavadi *et al.* 2004; Dil *et al.* 2016). The significance of each coefficient and the pattern of interactions between the factors were determined by the p-value (Prob > F). The p-value indicates the possibility of obtaining corresponding F-value due to error interference. As listed in Table 4, the p-value for the swelling ratio was < 0.0001, indicating that the model had statistical significance. The non-significant "lack-of-fit" was used to express the predictability of the model. In this experiment, the "lack-of-fit" value was 0.0600 > 0.05, which showed the low contribution compared with pure error (Asfaram *et al.* 2016). Moreover, the coefficient of variation (CV %) was 4.12%, less than 10%, further indicating that the fitting degree of the model was better. From the above, this model can be used for preliminary analysis and prediction in the preparation process of hydrogels.



Fig. 1. The actual coefficient of determination and the predicted coefficient of determination *versus* the observed swelling ratio

Sources of Variation	Sum of Squares	DF	Mean Square	F value	Prob > F	State
Model	22059.68	14	1575.69	27.94	< 0.0001	Significant
<i>X</i> <sub>1</sub>	3290.14	1	3290.14	58.35	< 0.0001	-
X2	34.34	1	34.34	0.61	0.4482	-
X3	835.00	1	835.00	14.81	0.0018	-
X4	4081.14	1	4081.14	72.37	< 0.0001	-
X <sub>1</sub> X <sub>2</sub>	1406.15	1	1406.15	24.94	0.0002	-
$X_1X_3$	2953.92	1	2953.92	52.38	< 0.0001	-
$X_1X_4$	125.44	1	125.44	2.22	0.1580	-
$X_2X_3$	0.90	1	0.90	0.026	0.9011	-
$X_2X_4$	1142.44	1	1142.44	20.26	0.0005	-
$X_3X_4$	2761.50	1	2761.50	48.97	< 0.0001	-
X1 <sup>2</sup>	2789.10	1	2789.10	49.47	< 0.0001	-
X <sub>2</sub> <sup>2</sup>	25.64	1	25.64	0.45	0.5111	-
X <sub>3</sub> <sup>2</sup>	624.66	1	624.66	11.08	0.0050	-
X4 <sup>2</sup>	3353.72	1	3353.72	59.47	< 0.0001	-
Residual	789.46	14	56.39	-	-	-
Lack of Fit	734.65	10	73.46	5.36	0.0600	Not significant
Pure Error	54.81	4	13.70	-	-	-
Total	22849.13	28	-	-	-	-

#### **Table 4.** Analysis of Variance (ANOVA) for Swelling Ratio

#### Effect of variables on the response

The 3D response surface plots are presented in Fig. 2, which depicts the effects of the dosages of the respective initiator, AM, AA, or MBA, on swelling ratio. As shown in Fig. 2a, the swelling ratio of hydrogel increased with increased initiator dosage, reached the maximum, and then decreased. The main reason for the final decrease may have been that less quantity of initiator led to less production of free radicals, thereby resulting in lower grafting rates of AA and AM. When the amount of initiator was too high, the excess initiator caused the free radical termination reaction. This reaction reduced the grafting rates of AA and AM and the swelling ratio of hydrogel.

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**Fig. 2.** Response surface graphs of the relationship between swelling ratio and variables: (a) the dosage of initiator and AM; (b) the dosage of initiator and AA; (c) the dosage of initiator and MBA; (d) the dosage of AM and AA; (e) the dosage of AM and MBA; and (f) the dosage of AA and MBA

According to Fig. 2, elevating the dosages of AM and AA increased the swelling ratio of hydrogels, but the degree of influence varied. The dosage of AA had a relatively large impact on the swelling ratio of hydrogels. This large influence mainly because, as the dosage of AA increased, more hydrophilic groups were introduced into the network structure of hydrogels and thus improved the hydrophilicity of the hydrogel (Zhang *et al.* 2015). Moreover, after washing with sodium hydroxide, —COOH in the structure of hydrogel was changed to COO<sup>-</sup>, which could generate higher electrostatic repulsion and expand its network to uptake more water (Du *et al.* 2016). However, the overdosed AA induced excessive cross-linking and resulted in decreased expansion ability and swelling ratio of the hydrogel (Zhang *et al.* 2015).

The dosage of the cross-linker (MBA) had great influence on the swelling ratio of the hydrogels. Increasing the dosage of MBA could increase the nodes of network and thus improve the swelling ratio of hydrogels. However, when the amount of the cross-linking agent was too high, the cross-linking degree was excessive, resulting in an extremely condensed network structure. When swelling, it was difficult for the pore size to expand, thus making the space for water molecules smaller and decreasing the swelling ratio (Mahdavinia *et al.* 2004; Pourjavadi *et al.* 2004).

Based on the results of the Box-Behnken model design, the predicted optimum swelling ratio was 255.7 g/g with the preparation conditions as follows: 80.9 mg of initiator, 349.6 mg of AM, 988.7 mg of AA, and 9.39 mg of MBA. To verify the predicted results, the hydrogel was prepared at the above preparation conditions, named Xyl-AM-co-AA, and the actual swelling rate was measured as 276.6 g/g. The experimental values for the welling ratios were close to the predicted values obtained from the fitted model.

# **FTIR Analysis**

The FTIR spectra of dried CSEL and the as-prepared Xyl-AM-co-AA are shown in Fig. 3. The peaks were assigned on the basis of previous literature (Sun *et al.* 2001; Wu *et al.* 2012; Zhang *et al.* 2015). In the spectrum of dried CSEL, the peak at 3413 cm<sup>-1</sup> was related to —OH in the structure of cellulose-based polysaccharide, hemicellulose-based polysaccharide, and lignin. The stretching vibration of 2931 cm<sup>-1</sup> belonged to C–H stretching vibration of methyl and methylene. The peaks at 1601, 1511, and 1422 cm<sup>-1</sup> were attributed to the stretching vibration of lignin's aromatic ring. The peaks at 1379 cm<sup>-1</sup> and 1260 cm<sup>-1</sup> corresponded to the C–H and C–O of the acetyl group, respectively, in the hemicellulose-based polysaccharide. A strong absorption peak emerged at 1051 cm<sup>-1</sup>, and was assigned to the asymmetric stretching vibration of the glycosidic bond C–O–C in the cellulose-based and hemicellulose-based polysaccharide.



Fig. 3. FTIR spectra of dried CSEL (a) and XyI-AM-co-AA (b)

Compared with CSEL, the spectrum of Xyl-AM-co-AA was markedly different. Given that AA and AM were added in the prepared process, new peaks emerged at 1665 cm<sup>-1</sup>, 1560 cm<sup>-1</sup>, 1450 cm<sup>-1</sup>, 1405 cm<sup>-1</sup>, and 1323 cm<sup>-1</sup>, which were the characteristic absorption peaks of the C=O bond of amide I band, the N–H bond of amide II band, the COO<sup>-</sup>, and the C–N bond of amide III band, respectively. From the analysis above, it was concluded that AA and AM were introduced into the structure of produced Xyl-AM-co-AA by graft copolymerization, induced by ammonium persulfate and anhydrous sodium sulfite as, respectively, the initiator and MBA as the cross-linker.

#### Morphology Analysis of Hydrogels

The SEM images of as-prepared Xyl-AM-co-AA are shown in Fig. 4, which illustrates that this hydrogel sample had good porous structure. Figures 4a, 4b, and 4c clearly show that the pore sizes of Xyl-AM-co-AA were different under swelling that occurred at 15 °C, 25 °C, and 35 °C. Because of the existence of -COOH, -OH, and -NH<sub>2</sub>, a good deal of H-bonds formed in the linking structures of Xyl-AM-co-AA. With an increase of swelling temperature, increasing number of these H-bonds would destroyed, followed by formations of hydrophilic residues which could link with H<sub>2</sub>O. Therefore, the pore sizes of hydrogels increased. Figures 4d, 4e, and 4f show the SEM images of Xyl-AM-co-AA swelling at pH levels of 2, 6, and 11, respectively. The pore size of Xyl-AMco-AA swelling, at pH of 2 (Fig. 4d), was lower than that of Xyl-AM-co-AA swelling at pH levels of 6 and 11 (Figs. 4e and 4f). This was probably because the pKa value of the carboxyl group was 4.6. When the pH value is less than 4.6, a majority of COO<sup>-</sup> is protonated into —COOH (Wu et al. 2012). After swelling in the solution with a pH of 2, there was a large amount of ---COOH in the structure of Xyl-AM-co-AA. Hence, a strong hydrogen bonding effect and shrinkage of the pore structure occurred in the hydrogel structure. At higher pH levels (pH > 4.6), the —COOH groups were ionized, and the electrostatic repulsion between COO<sup>-</sup> groups would lead to increased pore size (Yin et al. 2008).



**Fig. 4.** The SEM images of Xyl-AM-co-AA: (a) swelling at 15 °C; (b) swelling at 25 °C; (c) swelling at 35 °C; (d) swelling at pH = 2; (e) swelling at pH = 6; and (f) swelling at pH = 11

#### **Swelling Degree of Hydrogels**

The adsorption capability of Xyl-AM-co-AA was investigated in solutions with different pH levels ranging from 2 to 11, and in water at different temperatures between 5 and 35 °C, as shown in Fig. 5. Figure 5a shows that the swelling ratio of Xyl-AM-co-AA considerably increased when the pH increased from 2 to 4, and it slowly increased when the pH increased from 4 to 6. The swelling ratio decreased in the pH range of 9 to11. As the pH value increased from 2 to 11, more —COOH groups in Xyl-AM-co-AA were ionized into COO<sup>-</sup> groups. The electrostatic repulsion forces between COO<sup>-</sup> groups were strengthened, and the networks of Xyl-AM-co-AA were expanded with the greater increase

in pH, thus leading to the high swelling ratio (Cao *et al.* 2014). However, it was observed that in the solutions with pH levels of 9 and 11, the equilibrium swelling ratio decreased from 276.7 g/g (pH = 6) to 270.2 g/g and 247.9 g/g, respectively. This result was associated with the presence of a large number of metal ions in the alkaline solutions, resulting in electrostatic screening. In these cases, the electrostatic repulsion forces between COO<sup>-</sup> groups was weakened, which could reduce the network expansion capability of Xyl-AM-co-AA. As a result, the swelling ratio decreased (Lee and Wu 1996; Yin *et al.* 2008). Most notably, a low swelling ratio of 2.2 g/g emerged at a pH of 2. This ratio was closely related to the fact that, at highly acidic conditions (pH = 2), most of COO<sup>-</sup> was protonated into — COOH, which strengthened the H-bond effect and led to a shrinkage of the pore structure of this hydrogel. A low swelling ratio resulted.

From Fig. 5b, the swelling ratios of 197.3, 206.7, 276.6, and 282.1 g/g were obtained at the temperatures of 5, 15, 25, and 35 °C, respectively. This range illustrated that the swelling ratio of Xyl-AM-co-AA increased with the increasing temperatures. The swelling ratio at 35 °C was the highest (292.1 g/g). Because hydrophilic AM and AA were introduced into the hydrogels network, the contents of the hydrophilic groups in the hydrogel network increased, forming more H-bonds in the linking structure of hydrogel, and requiring more energy to break the H-bonds (Wang *et al.* 2013; Wang *et al.* 2019). It was possible that the increasing temperature broke an increasing number of H-bonds in the linking structure of hydrogel, and then hydrophilic residues produced a link with H<sub>2</sub>O, thus increasing the swelling ratio (Kipcak *et al.* 2014). Moreover, the rise in temperature could have resulted in thermal mobility of the polymer molecules inside the hydrogels, and then the swelling ratio increased (Rodriguez *et al.* 2006; Kipcak *et al.* 2014).



**Fig. 5.** The swelling ratios of Xyl-AM-co-AA in solutions with pH levels of 2, 4, 6, 9, and 11 (a), and in water at temperatures of 5, 15, 25, and 35 °C (b)

# CONCLUSIONS

1. To obtain hydrogels with high levels of swelling, RSM coupled with Box-Behnken design was used to optimize the swelling ratio of hydrogels. It was found that the predicted value (255.7 g/g) was close to the experimental value (276.6 g/g). Meanwhile, the optimum preparation conditions were obtained as follows: 80.9 mg of initiator, 349.6 mg of AM, 988.7 mg of AA, and 9.39 mg of MBA.

- 2. The electrostatic repulsion forces between COO<sup>-</sup> groups were an important factor in determining the swelling ratio and the pore size of the hydrogel. As the pH value changed, the degree of ionization of —COOH varied, further obtaining electrostatic repulsion with differing strengths, and thus resulting in different swelling ratios and pore sizes.
- 3. H-bonds played an important role in pore sizes. When temperature increased, an increasing number of H-bonds were broken. Thus, the swelling ratio of Xyl-AM-co-AA were also related to temperature.

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# ABBREVIATIONS

Full Name	Abbreviation
Concentrated Steam Explosion Liquid	CSEL
Acrylic Acid	AA
Acrylamide	AM
N,N'-methylenebisacrylamide	MBA
Response Surface Methodology	RSM
Xylan-based Polysaccharides	Xyl-P
National Renewable Energy Laboratory	NREL
Glucose-based Polysaccharide	Glu-P
Arabinose-based Polysaccharide	Arab-P

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