Preparation and Properties of Kraft Lignin-*N*-Isopropyl Acrylamide Hydrogel

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Kraft lignin was used to prepare kraft lignin-*N*-isopropyl acrylamide hydrogel (KNIAH). The results indicated that using a 1:2 mass ratio of KL-to-*N*-isopropyl acrylamide (NIPAM), 48 h reaction time, and 1.5 mL of crosslinking agent yielded KNIAH with the maximum swelling degree (209.3%). The crosslinking reaction was verified by C-N shifting at 1272 cm^{-1} and increased C=O bonding at 1720 cm^{-1}. KNIAH with a smooth and uniform surface was created. DSC demonstrated that free water combined with KNIAH at 200 °C, after which KNIAH began exothermic decomposition. TGA shows that KNIAH with good performance of heat resistance and degradation. Absorption was maximized at 20 °C; low temperature and neutral solution was conducive to water absorption. Decolorization increased with decreasing concentration and pH value.

Keywords: Gels; Grafting; Copolymers; Crosslinking

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INTRODUCTION

Lignin is the primary by-product from the preparation of pulp for papermaking, and it is found in the black liquor from the pulping process. It has excellent performance, high reactivity, good biocompatibility, and degrades easily to displace other phenolic compounds in formaldehyde-based adhesives (Gao *et al*. 2013). Kraft lignin extract from kraft straw black liquor collected using acid precipitation is typically negatively charged when in solution, and thus has the characteristics of an anionic surfactant (van Vlierberghe *et al*. 2011). Lignin is an attractive candidate in hydrogels because of its advantages due to their inherent properties such as biocompatibility, biodegradability, low toxicity, and eco-friendliness (Vijay *et al*. 2013, 2015). Feng *et al*. (2012) and El-Zawawy (2005) discovered that lignin introduced into resorcinol or polyvinyl alcohol creates a hydrogel, enhancing the hydrogel´s performance stability and biocompatibility compared with that without lignin. Kraft lignin can be made into a hydrogel in the form of an interpenetrating or semi-interpenetrating polymer network (IPN) to improve the hydrogel swelling degree and performance reliability (Li *et al*. 2010).

Hydrogels typically exhibit three-dimensional networks that affect absorption (Wang *et al*. 2010). *N*-isopropyl acrylamide (NIPAM) is widely utilized in studies as an environmentally-sensitive hydrogel because it is easily prepared and useful for such applications (Wang *et al*. 2005; Liu *et al*. 2013). Uraki *et al*. (2006) and Nishida *et al*. (2003) previously utilized NIPAM as a raw material to prepare hydrogels with good sensitivity to temperature. However, the swelling degrees of their hydrogels were low and they exhibited poor stability.

To improve the performance stability of hydrogels, the present work adopted NIPAM and KL as raw materials. Ammonium persulfate was used to initiate this double bond in the molecular structure of NIPAM grafted with the phenolic –OH group of lignin to prepare the copolymer (KNIAC) by graft copolymerization and to form a kraft lignin-*N*-isopropyl acrylamide hydrogel (KNIAH) after cross-linking using glutaraldehyde. FTIR, Kjeldahl, SEM, and DSC were used to characterize KNIAH, detect the environmental sensitive properties, and evaluate its capacity to adsorb methylene blue.

EXPERIMENTAL

Materials

The materials utilized in this work include kraft lignin (KL), a brown powdery substance with a distinct odiferous nature, a by-product of the papermaking industry, as well as various reagents including ammonium persulfate, sodium hydroxide, acetone, 50% glutaraldehyde, *N*-isopropyl acrylamide (NIPAM), and methylene blue. The instruments used in this work include an FT-IR-650 Fourier transform infrared spectrometer and a DF-4 tablet machine produced by Tianjin Port East Technology Development, Ltd., and by Share Ltd., China, respectively. A KDY-9810 Kjeldahl apparatus, produced by Beijing Think Better Electromechanical Technology Research Institute, China, was used. A TU-1901 double-beam UV spectrophotometer, produced by Beijing Purkinje General Instrument Co., Ltd., China, was also used.

Methods

Preparation of KNIAH

KL was dissolved in NaOH solution with pH at 10. Ammonium persulfate was added with NIPAM and the mixture was stirred for 2 h under the reaction temperature at 70 °C. The reaction solution was concentrated *via* acetone sedimentation and repeated extraction and vacuum-dried for 24 h at 40 °C to obtain the monomer (Zhang *et al*. 2009), KNIAC. The KNIAC was dissolved in distilled water at 1.0% mass concentration. 10 mL of the solution was removed from the container and a cross-linking agent, glutaraldehyde, was added at room temperature (25 °C) to form KNIAH (Singh *et al*. 2006).

Measurement of IR spectrum

The hydrogel was dried to constant weight and mixed with a sample of KBr at a 1:200 ratio. Next, it was tabletted by a DF-4 tablet machine and kraft lignin-*N*-isopropyl acrylamide hydrogel was tested with the FTIR-650 apparatus.

Determination of nitrogen content

The nitrogen content of the hydrogel was evaluated according to Chinese National Standard GB/T5009.5-2003 (2003). After being dried to constant weight, the hydrogel nitrogen content was determined using the KDY-9810 Kjeldahl apparatus.

Scanning electron microscopy (SEM) examination

The surface morphology of KNIAH was examined using a Quanta200 Electron Microscope after it was dried to constant weight. KNIAH was gold-coated prior to microscope observation.

Differential scanning calorimetry (DSC)

KNIAH was dried to constant weight and a DSC was performed using a NETZSCH DSC204 apparatus under a nitrogen atmosphere at a flow rate of 15 mL/min. The heating rate was 10 °C/min though the temperature ranges of 25 to 300 °C.

Thermogravimetric analysis (TGA)

The thermal properties of kraft lignin, KNIAC, and KNIAH were measured using thermogravimetric analysis (TGA). In preparation of samples for TGA, the hydrogels were ground to powder form. Decomposition profiles of TGA were recorded at a heating rate of 10.0 °C/min between room temperature and 600.0 °C in nitrogen.

Swelling capacity

The swelling ratios of KNIAH were measured according to the methods of Chang and Lin (2000): A dried piece of KNIAH was placed in water at room temperature for 24 h, the KNIAH swelled and reached equilibrium, the KNIAH was removed and surface water was removed with filter paper, and finally, the weight of the wet KNIAH was calculated using the following equation,

$$S = (W_s - W_d)/W_d \qquad (1)$$

where W_s is the wet KNIAH weight and W_d is dry KNIAH weight.

Adsorption properties on methylene blue

The adsorption properties of kraft lignin-*N*-isopropyl acrylamide hydrogel (KNIAH) on methylene blue were measured according to methods described by Uraki *et al*. (2006): KNIAH (0.1 g) was added to a concentrated methylene blue solution (0.02 L) and the pH was adjusted. The mixture was stirred for 2 h until adsorption equilibrium was achieved, at which point the supernatant was tested. The adsorption amount was calculated as follows,

$$Q = (c_0 - c_1) \times 0.02/\mathrm{m} \qquad (2)$$

where c_0 is the KNIAH concentration before adsorption, c_1 is the KNIAH concentration after adsorption, and *m* is the weight of KNIAH.

RESULTS AND DISCUSSION

The Main Functional Group Content of KL

According to the determinate method of the literature (Ren *et al*. 2008), the results are as follows: The experiment measured the acid-soluble kraft lignin content as 1.2% (mass percentage), the ash content as 14.27%, and the Klason lignin content as 64.55%. Table 1 presents the main functional group contents of KL.

Table 1. Characteristics of the KL Studied

	Total Acid	Carbonyl	Carboxyl Group	Phenolic Hydroxyl
Content (mass, %)	4.44	2.04	1.49	6.96

Preparation of KNIAH

In the presence of the ammonium persulfate initiator, the double bond in the molecule NIPAM initiates polymerization, and graft polymers are formed *via* H atom substitutions for hydroxyl groups on the lignin molecular chain and the more-reactive amino group (Feng *et al*. 2011). Glutaraldehyde is highly active, fast-responding, and has high binding capacity and product stability. As the cross-linking agent, glutaraldehyde can act as a bridge for cross-linked polymer materials, forming a polymer compound with a well-developed pore structure (Parajuli *et al*. 2005). The aldehyde can cross-link with the amino copolymer to generate N^+, preparing the KNIAH. The reaction mechanism describing the preparation of the hydrogel is presented in Fig. 1.

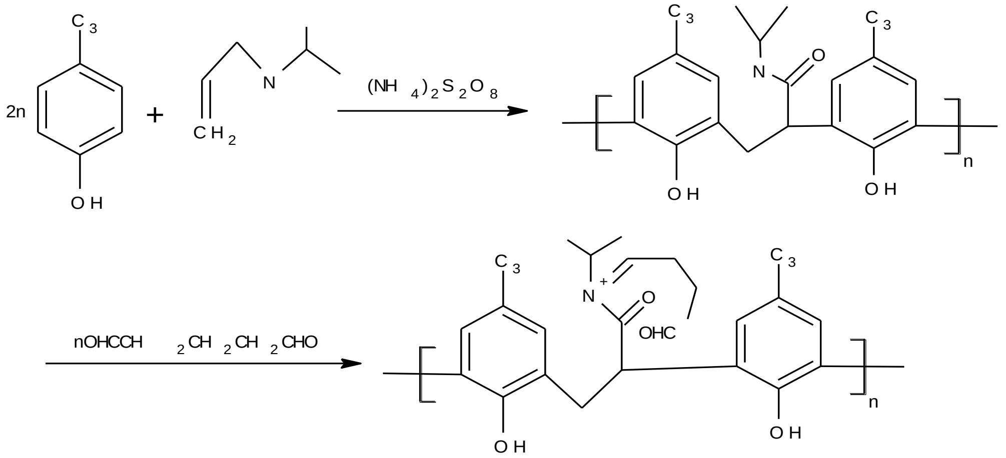

Fig. 1. The synthesis mechanism of KNIAH

Mass ratio of kraft lignin-to-N-isopropyl acrylamide

Figure 2 shows the effects of kraft lignin-to-*N*-isopropyl acrylamide mass ratio on the swelling degree of KNIAH prepared with 48 h reaction time, 1.5 mL of glutaraldehyde, at 25 °C. Under alkaline conditions, the ortho α-H groups of KL exhibit high reaction activity with the same NIPAM reaction mechanism. KL is a high-molecular weight polymeric material with high relative content and steric hindrance which did not facilitate the reaction.

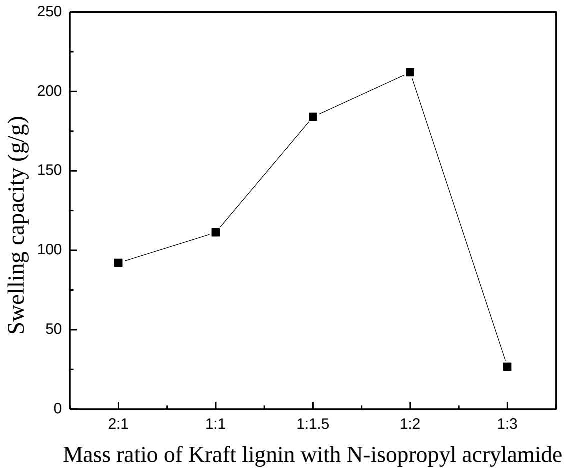

Fig. 2. Effect of Kraft lignin and N- isopropyl acrylamide mass ratio on swelling capacity of KNIAH

Increasing the NIPAM content can enhance the binding ability of the raw material, the graft point and grafting efficiency, and then increase the reaction volume and the swelling degree. When the NIPAM was too high, the graft point tended towards saturation and NIPAM homopolymerization occurred, surrounding the partial monomer. This in turn decreased the amount of hydrogels macromolecular chain that were produced under the action of the crosslinking agent, and the swelling degree sharply declined. The most effective mass ratio of kraft lignin and NIPAM was 1:2.

Reaction time

At a constant glutaraldehyde volume (1.5 mL), temperature (25 °C), and mass ratio of kraft lignin-to-N-isopropyl acrylamide (1:2), the swelling capacity as a function of cross-linking time is shown in Fig. 3. With the extension of reaction time, the swelling degree of the hydrogel rose slightly. The hydrogel has smaller steric hindrance in the preliminary stage and cannot form a half-interpenetrating network structure that is propitious to the crosslinking reaction. As the reaction continued, the molecular polymer participating in the reaction increased. A network structure was generated, increasing swelling degree. When the crosslinking time exceeded 48 h, steric hindrance became aggrandized, the cross-linking degree reached saturation, and water molecule penetration was abated. Further extending the cross-linking time had little effect on the KNIAH swelling degree. The cross-linking time of 48 h was selected to maximize production efficiency and minimize production costs.

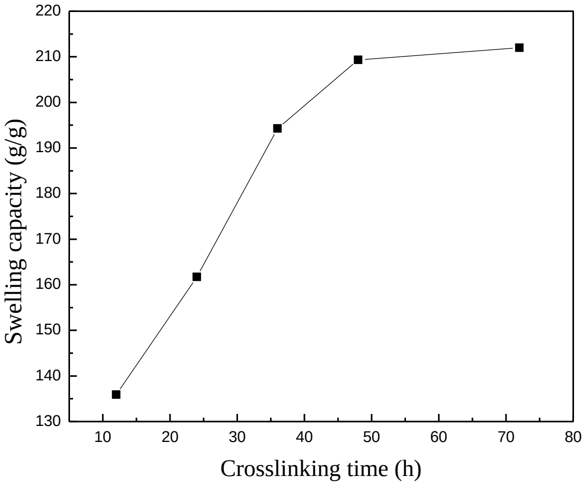

Fig. 3. Effect of reaction time on swelling capacity of KNIAH

Glutaraldehyde content

Under constant reaction time (48 h), temperature (25 °C), and kraft lignin-to-N-isopropyl acrylamide mass ratio (1:2), the swelling degree as a function of glutaraldehyde usage is shown in Fig. 4. Using glutaraldehyde to prepare the hydrogel destroyed intermolecular hydrogen bonding and the intermolecular copolymer, which normally combine to form the semi-interpenetrating amino copolymer. Thus, the hydrogel was prepared with semi-IPN. By decreasing the glutaraldehyde usage, KNIAH was created with low cross-linking degree but high steric hindrance, so forming a network structure was difficult and did not favor the reaction. By increasing the amount of glutaraldehyde, a network structure was formed and the molecular chain structure of hydrogel was destroyed, so the hydrogel's swelling degree increased. As cross-linking reached a maximum, the cross-link density grew and the molecular distance between network points was lower. As the network structure was filled, the swelling ratio decreased. The experimental results are consistent with those of Zhao *et al*. (2008).

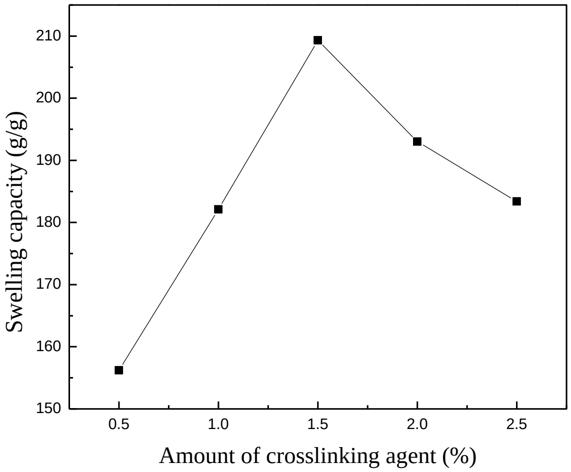

Fig. 4. Effect of glutaraldehyde content on swelling capacity of KNIAH

FT-IR Spectra

FTIR spectra for KNIAH are presented in Fig. 5. The peak at 1720 cm^{-1} is the C=O stretching absorption peak, the absorption peak of C-N stretching vibration is at 1272 cm^{-1}, and the C-N stretching vibration peak is at 1265 cm^{-1} (Chauhan *et al*. 2004). The unreacted NIPAM and KL were removed by repeated washing. The C-N stretching vibration absorption peak at 1265 cm^{-1} was observed, indicating that KL and NIPAM were well cross-linked. The C=O stretching absorption peaks at 1720 cm^{-1} increased in intensity significantly, as indicated by the reaction mechanism as C=O bonds were introduced. While the C-N stretching vibration absorption peak at 1272 cm^{-1} offset may be observed, copolymers were cross-linked with glutaraldehyde and KNIAH.

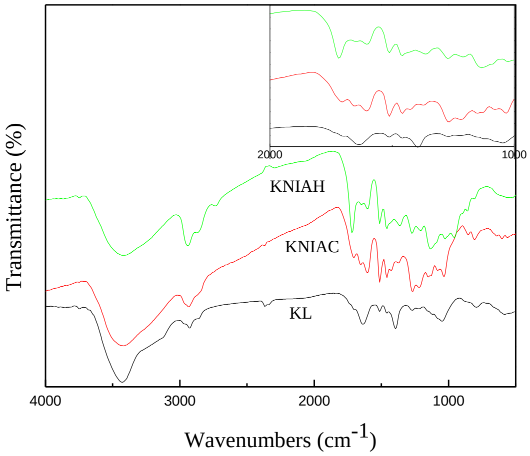

Fig. 5. FT-IR spectra of KNIAH

Nitrogen Content

Analysis with the Kjeldahl nitrogen instrument, *via* digestion-distillation-titration, measured the nitrogen content of KL as 0.85% and that of KNIAH as 4.06%, which is smaller deviations compared with theoretical prediction (4.26%). NIPAM not involved in the reaction was removed by washing.

SEM Analysis

SEM images of KNIAH are presented in Fig. 6. Based on a comparison of images (a) and (c), the KNIAC section had a more uniform pore structure and higher porosity, whereas the KNIAH section exhibited a relatively smooth and well-proportioned network structure with dense architecture and without any apparent microscopic phase separation. Images (b) and (d) reflected the surface morphology of the two substances. KNIAC had a non-continuous, closed-mesh structure and an uneven surface with significant concavity. The irregular pore structure of KNIAH provided channels for molecular flow and exhibited a smooth surface, reflecting the molecular glutaraldehyde hydrogel after absorbing water.

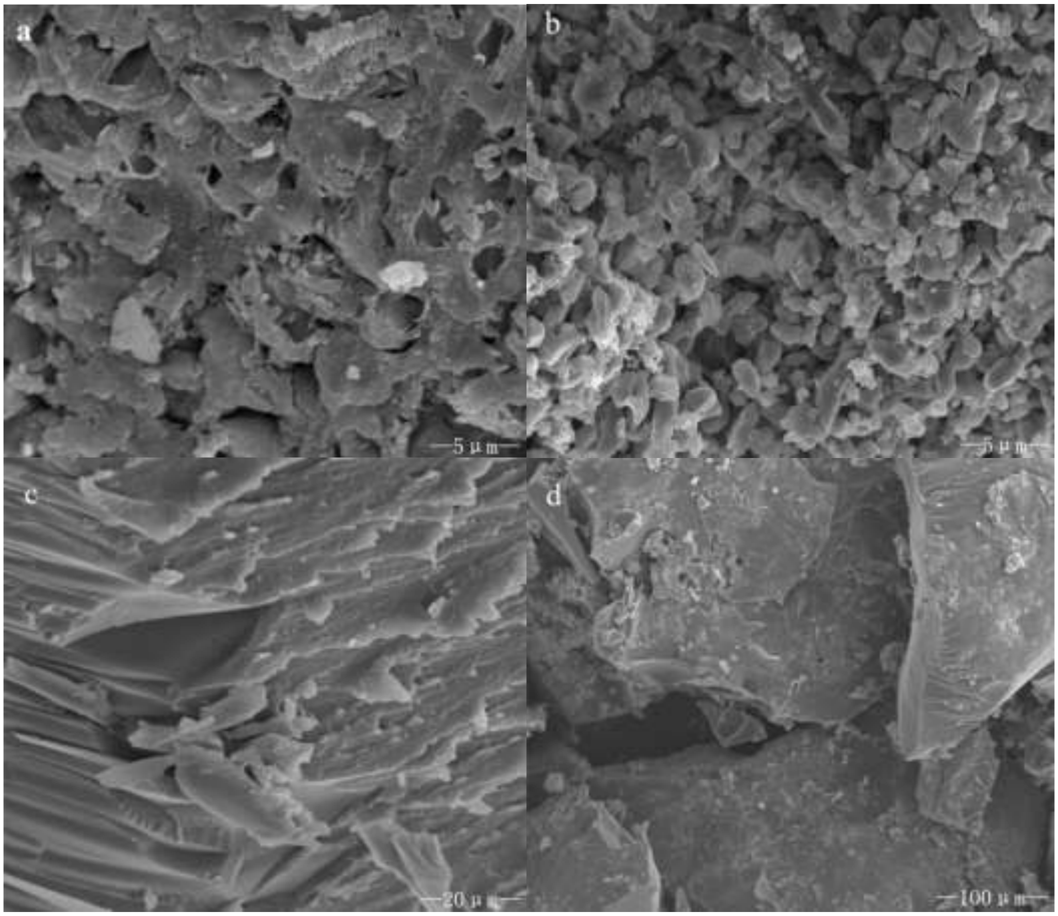

Fig. 6. SEM images of KNIAC and KNIAH under different magnification: (a) section of KNIAC; (b) surface of KNIAC; (c) section of KNIAH; and (d) surface of KNIAH

DSC Analysis

Figure 7 shows DSC curve of KNIAH. KNIAC and KNIAH both exhibited one endothermic peak and one exothermic peak. The endothermic peak of KNIAH grew larger due to the water in the intramolecular structure. Moisture evaporation absorbed heat within the temperature range of 50 to 100 °C, decreasing the exothermic peak at 180 °C. The temperature corresponding to the maximum rate was relatively low. The endothermic peak appeared in two sharp copolymer peaks, with three types of water existing in the copolymers: free water, intermediate water, and non-freezable water (Baba *et al*. 2004). The temperature of the endothermic phase transition was high because KNIAH retained existing free water and middle water, which contributed to its structural stability. As the phase transition occurred at 270 to 320 °C, heat release increased and molecular structure damage occurred. KNIAH stability was reduced by exothermic decomposition when the temperature exceeded 320 °C.

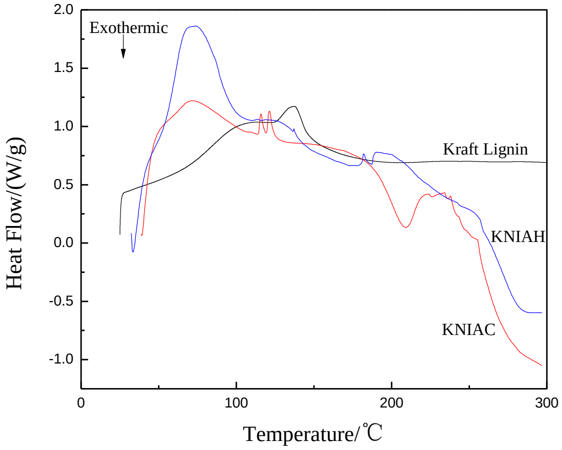

Fig. 7. DSC curves of KNIAC and KNIAH

TGA Analysis

The thermal degradation behavior of the hydrogels was studied in the range 25 to 600 °C under a nitrogen atmosphere. The thermogravimetry curves obtained with kraft lignin, KNIAC, and KNIAH are presented in Fig. 8. The first phase of the weight loss (25 to 150 °C) indicates evaporation of smaller molecules and shows that heat-resistant properties of KNIAH were improved.

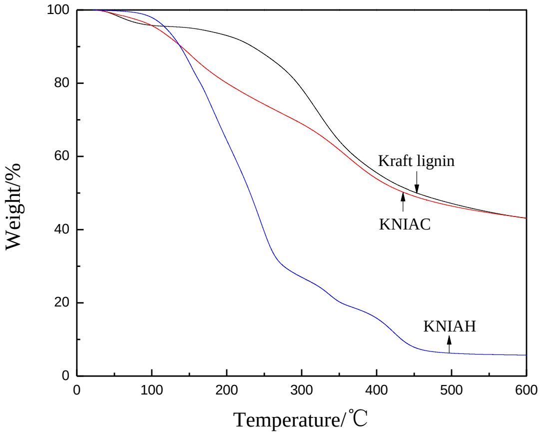

Fig. 8. TGA curves of KNIAC and KNIAH

For kraft lignin, the vast majority of the weight loss occurred at higher than 200 °C, with the maximum decomposition rate at 320 °C. For KNIAC, there are two decomposition phases, with maximum decomposition rate at 360 °C. The maximum decomposition rate of KNIAH occurred at 245 °C. The residual rate of KNIAH was much lower than that of kraft lignin and KNIAC, which indicates that the KNIAH with thermal degradation.

Response of Hydrogel to Environment

Hydroxyl radicals, as a hydrophilic functional group, generally have excellent water absorbing character. The O-H vibration peaks clearly indicated that KNIAH had excellent water adsorption performance (Cha *et al*. 2012). The response of hydrogels in water is demonstrated in Fig. 9. Figure 9A shows the effect of concentration on the adsorption capacity of KNIAH, while Fig. 9B shows the influence of pH. The temperature sensitivity was attributable to the branches of N-isopropyl molecules; repeated swelling and contracting did not occur as the temperature changed (Kim and Kadla 2010). At low temperatures, water activity was inhibited and swelling was poor. When swelling reached a maximum and temperature rose further, the sensitivity did not markedly change.

The hydrogel network shrinks in acidic solution, inhibiting water molecules from entering the gel and then reduces the swelling degree. By increasing the pH, ionic strength is increased, decreasing shrinkage of the hydrogel network structure and increasing the internal molecular osmotic pressure from the C＝O and N—H in the molecules. This creates a more conducive environment for water adsorption into the molecules. When the pH exceeded 7, ionic strength gradually decreased and the molecular osmotic pressure was reduced. Water absorption and swelling were highest at relatively neutral pH.

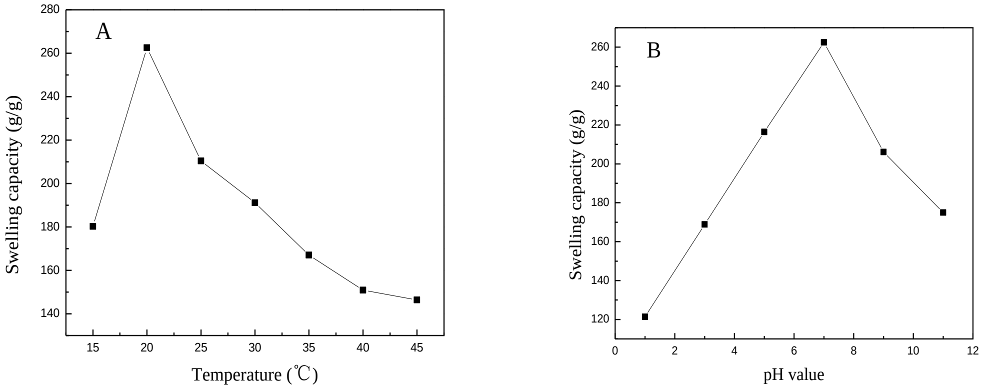

Fig. 9. Response of hydrogel to the environment: (A) effect of concentration; (B) effect of pH value

Adsorption Properties on Methylene Blue in Different Temperature and pH

KNIAH adsorption of methylene blue dye is demonstrated in Fig. 10. Figure 10A shows the effect of concentration on the adsorption capacity of KNIAH and Fig. 10B shows the influence of pH. From the IR spectra, it is known that KNIAH contains a large number of N atoms which hydrogen-bond and facilitate adsorption of the dye. Hydrogels can produce electrical attraction to the dye, further facilitating dye adsorption

(Vijayaraghavan *et al*. 2008; Liu *et al*. 2011). Hydrogels have a three-dimensional network structure which favors adsorbed molecules. When the dye concentration was low, the dye molecules made contact with the nitrogen atoms of the hydrogel, producing the hydrogen bond that triggers the adsorption effect. When the dye concentration increased, methylene blue molecules in the hydrogel adsorbed to nitrogen atoms in the molecules. Higher dye concentration allows for greater contact and higher adsorption capacity. When the dye concentration reached a certain value, adsorption onto the hydrogel reached saturation and the dyes were densely distributed. The intermolecular electrical attraction was reduced as absorption of external methylene blue with the gel molecular. The carboxyl groups in molecular hydrogel can electrostatically attract cationic methylene blue. When the pH was low, H^+ accumulated on adsorption sites with methylene blue and led to weak adsorption ability. The adsorption capacity decreased as the pH increased. The amount of H^+ adsorption increased the competition between the hydronium ion and the dye ionic species for the adsorption sites. When the pH was neutral, competition decreased and hydrogel ionization yielded negative charges. Hydrogel adsorption electrostatic interaction thus promoted methylene blue adsorption.

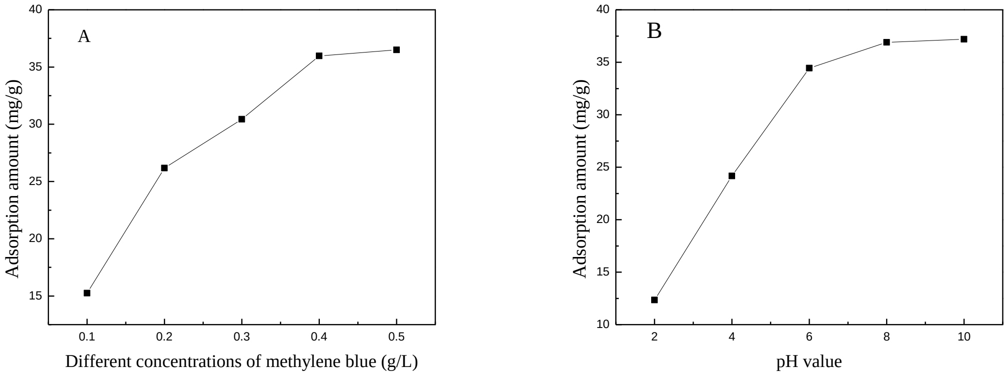

Fig. 10. KNIAH-methylene blue adsorption capacity: (A) effect of concentration; (B) effect of pH

CONCLUSIONS

1. The optimum kraft lignin-to-*N*-isopropyl acrylamide mass ratio, relative to the preparation of a high-swelling hydrogel, was 1:2. The cross-linking time was 48 h, and the usage of crosslinking agent was 1.5 mL. The maximum KNIAH swelling degree achieved 209.3%.
2. Occurrence of the graft reaction due to the C-N key and the cross-linked C-N bond shift increased, illustrating that KNIAH obtained through the cross-linking reaction.
3. The nitrogen content in the polymer was 4.06%, close to the theoretical value of 4.26%.
4. SEM revealed a crystalline KNIAH structure with a smooth, three-dimensional pore structure.
5. As shown by DSC, the hydrogel contained free water molecules, which exhibited an exothermic peak when the temperature exceeded 200 °C. TGA shows that KNIAH with good performance of heat resistance and degradation.

6. The performance of KNIAH was tested. Repeated swelling and contraction with temperature demonstrated no change. Water absorption was most efficiently at 20 °C, and elevated temperature hindered water absorption.
7. Neutral pH solutions were conducive to water absorption.
8. Methylene blue adsorption by KNIAH increased with methylene blue concentration and higher solution pH made the polymer more conducive to adsorption, until the pH became neutral and adsorption leveled off.

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REFERENCES CITED

Baba, T., Sakamoto, R., Shibukawa, M., and Oguma, K. (2004). "Solute retention and the states of water in polyethylene glycol and poly (vinyl alcohol) gels," *Journal of Chromatography A* 1040(1), 45-51. DOI: 10.1016/j.chroma.2004.03.065

Cha, R. T., He, Z. B., and Ni, Y. H. (2012). "Preparation and characterization of thermal/pH-sensitive hydrogel from carboxylated nanocrystalline cellulose," *Carbohydrate Polymers* 88(2), 713-718. DOI: 10.1016/j.carbpol.2012.01.026

Chang, K. L. B., and Lin, J. (2000). "Swelling behavior and the release of protein from chitosan pectin composite particles," *Carbohydrate Polymers* 43(2), 163-169. DOI: 10.1016/S0144-8617(00)00145-4

Chauhan, G. S., Lai, H., and Mahajan, S. (2004). "Synthesis, characterization, and swelling responses of poly(N-isopropyl acrylamide) and hydroxypropyl cellulose-based environmentally sensitive biphasic hydrogels," *Journal of Applied Polymer Science* 91(1), 479-488. DOI: 10.1002/app.13135

El-Zawawy, W. K. (2005). "Preparation of hydrogel from green polymer," *Polymers for Advanced Technology* 16(1), 48-54. DOI: 10.1002/pat.537

Feng, Q. H., Chen, F. G., and Zhou, X. S. (2011). "Preparation and characterization of a temperature-sensitive lignin-based hydrogel," *BioResources* 6(4), 4942-4952. DOI: 10.15376/biores.6.4.4942-4952

Feng, Q. H., Chen, F. G., and Zhou, X. S. (2012). "Preparation of thermo-sensitive hydrogels from acrylated lignin and N-isopropylacrylamide through photocrosslinking," *Journal of Biobased Materials and Bioenergy* 6(3), 336-342. DOI: 10.1166/jbmb.2012.1218

Gao, G. Z., Karaaslan, M. A., and Kadla, J. F. (2013). "Hydrogen-bonding based reversible polymer networks based on kraft lignin and poly(2-(dimethylamino)ethyl methacrylate) series polymers," *Macromolecular Materials and Engineering* 299(8), 990-1002. DOI: 10.1002/mame.201300364

GB/T5009.5-2003 (2003). "Determination of protein in foods," Chinese Standards Press, Beijing.

Kim, Y. S., and Kadla, J. F. (2010). "Preparation of a thermo responsive lignin-based biomaterial through atom transfer radical polymerization," *Biomacromolecules* 11(4), 981-988. DOI: 10.1021/bm901455p

Li, X. M., and Pan, X. J. (2010). "Hydrogels based on hemicellulose and lignin from lignocellulose biorefinery: A mini-review," *Journal of Biobased Materials and Bioenergy* 4(4), 289-297. DOI: 10.1166/jbmb.2010.1107

Liu, Y., Wang, W. B., Jin, Y. L., and Wang, A. Q. (2011). "Adsorption behavior of methylene blue from aqueous solution by the hydrogel composites based on attapulgite," *Separation Science and Technology* 46(5), 858-868. DOI: 10.1080/01496395.2010.528502

Liu, X. W., Zhu, S., Wu, S. R., Wang, P., and Han, G. Z. (2013). "Response behavior of ion-sensitive hydrogel based on crown ether," *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 417, 140-145. DOI: 10.1016/j.colsurfa.2012.09.044

Nishida, M., Uraki, Y., and Sano, Y. (2003). "Lignin gel with unique swelling property," *Bioresource Technology* 88(1), 81-83. DOI: 10.1016/S0960-8524(02)00264-X

Parajuli, D., Inoue, K., Ohto, K., Oshima, T., Murota, A., Funaoka, M., and Makino, K. (2005). "Adsorption of heavy metals on crosslinked lignocatechol: a modified lignin gel," *Reactive & Functional Polymers* 62(2),129-139. DOI: 10.1016/j.reactfunctpolym.2004.11.003

Ren, S. X., Jiang, G. Q., Qu, H. J., and Fang, G .Z. (2008). *Plant Fiber Chemistry Experiment Course*, Northeast Forestry University press.

Singh, D., Kuckling, D., Choudhary, V., Adler, H., and Koul, V. (2006). "Synthesis and characterization of poly(N-isopropylacrylamide) films by photopolymerization," *Polymers for Advanced Technologies* 17(3), 186-192. DOI: 10.1002/pat.713

Uraki, Y., Imura, T., Kishimoto, T., and Ubukata, M. (2006). "Body temperature-responsive gels derived from hydroxypropylcellulose bearing lignin II: Adsorption and release behavior," *Cellulose* 13(3), 225-234. DOI: 10.1007/s10570-005-9032-1

van Vlierberghe, S., Dubruel, P., and Schacht, E. (2011). "Biopolymer-based hydrogels as scaffolds for tissue engineering applications: A review," *Biomacromolecules* 12(5), 1387-1408. DOI: 10.1021/bm200083n

Vijayaraghavan, K., Mao, J., and Yun, Y. S. (2008). "Biosorption of methylene blue from aqueous solution using free and polysulfone-immobilized *Corynebacterium glutamicum*: Batch and column studies," *Bioresource Technology* 99(8), 2864-2871. DOI: 10.1016/j.biortech.2007.06.008

Vijay, K. T., Manju, K. T., and Raju, K. G. (2013). "Rapid synthesis of graft copolymers from natural cellulose fibers," *Carbohydrate Polymers* 98(1), 820-828. DOI: 10.1016/j.carbpol.2013.06.072.

Vijay, K. T., and Manju, K. T. (2015). "Recent advances in green hydrogels from lignin: A review," *International Journal of Biological Macromolecules* 72, 834-847. DOI: 10.1016/j.ijbiomac.2014.09.044.

Wang, Y. P., Yuan, K., and Pei, X. W. (2005). "Synthesis and swelling properties of poly (N-isopropyl acrylamide) nano-SiO_2 composite hydrogels," *Acta Polymerica Sinica* 4, 584-588.

Wang, J. Y., Xiao, F., Zhao, Y. P., Chen, L., Zhang, R., and Guo, G. (2010). "Cell proliferation and thermally induced cell detachment of galactosylated thermo-responsive hydrogels," *Carbohydrate Polymers* 82(3), 578-584. DOI: 10.1016/j.carbpol.2010.05.011

Zhang, H. F., Zhong, H., Zhang, L. L., Chen, S. B., Zhao, Y. J., and Zhu, Y. L. (2009).

"Synthesis and characterization of thermosensitive graft copolymer of N-isopropyl acrylamide with biodegradable carboxymethylchitosan," *Carbohydrate Polymers* 77(4), 785-790. DOI: 10.1016/j.carbpol.2009.02.026

Zhao, Z. X., Li, Z., Xia, Q., Bajalis, Q. B., and Xi, H. X. (2008). "Swelling/deswelling kinetics of PNIPAAm hydrogels synthesized by microwave irradiation," *Chemical Engineering Journal* 142(3), 263-270. DOI: 10.1016/j.cej.2007.12.009

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