

Microwave-assisted non-thermal hemp degumming

Lijun Qu^a, Shifeng Zhu, Mingwei Tian, Xiaoqing Guo, Guangting Han, Yan Zhang, Xiaoning Tang & Kaikai Sun

College of Textiles, Qingdao University, Shandong, China

Received 6 January 2014; revised received and accepted 1 July 2014

The microwave-assisted non-thermal degumming of hemp fibre has been studied and then compared with the water bath heating under different time and temperature conditions. The results show that the residual gum content of the lean hemp using microwave-assisted heating method is lower than that obtained using water bath heating. The residual gum content gap between the two degumming processes increases first and then decreases as the heating time and temperature are increased. This proves the existence of non-thermal effects in microwave heating process besides the thermal effects in water bath heating. In addition, the structures of the lean hemp fibres obtained from these two methods are also studied by scanning electron microscopy and fourier transform infrared spectroscopy.

Keywords: Hemp fibre, Microwave-assisted degumming, Residual gum content

Hemp fibre has been receiving a worldwide attention as a natural fibre because of its low cost and fast growing ability under various severe climate, soil quality and nutrients. Commonly, hemp bast consists of both cellulosic and noncellulosic substances, such as hemicelluloses, pectin, lignin and wax, and these noncellulosic substances might badly affect the spinning, weaving, dyeing and finishing processes of hemp fibres, yarns and fabrics. Therefore, extracting the high-quality hemp fibres from the bast is a crucial task for their applications in textile industry. Usually, hemp fibres are extracted from the bast via physical, bacterial, chemical and enzymatic methods. Specially, bacterial processing depends on the weather, water quality, and other factors and often results in inconsistent fibre quality¹. Enzymatic processing method was developed for flax in the 1980s, but found not a feasible method for processing hemp

fibres². Chemical processing is an effective and common method for removing noncellulosic substances, and considerable research has focused on this method to improve the quality of fibre³⁻⁵.

Recently, microwave-assisted extraction has been regarded as a novel extraction method for fibre degumming^{6,7}. As an alternative route of conventional heating technique, microwave irradiation has been proved as powerful techniques with more rapid, uniform and efficient of non-contact heating way. The microwave energy can easily penetrate into particle and all particles can be heated simultaneously, thus reducing the heat transfer problems⁸. The microwave heating of a dielectric material can convert electromagnetic energy into heat within the irradiated material which offers a number of advantages over conventional heating methods, such as non-contact heating, energy transfer instead of heat transfer, rapid and selective material heating, volumetric heating, quick start-up and stop, heating from the interior of the material body, higher level of safety and automation⁹. It has been widely used in the dyeing, finishing and curing processing of cellulose materials^{10,11}. To the best of our knowledge, seldom investigation has been reported on the effects of microwave irradiation on hemp degumming.

Keeping these in view, the present work was undertaken to compare microwave-assisted heating degumming with water bath heating degumming of hemp. Also, the effect of microwave-assisted hemp degumming on fibre quality was investigated.

Experimental

The hemp was obtained from Yunnan Province, China. The components of raw hemp used are grease wax 1.22%, water soluble matter 7.20%, pectin 5.99%, hemicellulose 17.27%, lignin 6.07% and cellulose 62.25%. The quantification of individual ingredients are carried out in our lab according to quantitative analysis of ramie chemical components. The step by step extraction details are given below:

- (i) The dried raw hemp (5g) was immersed in 150mL phenethyl alcohol and extraction was continued for 3h. The sample was then dried to constant weight. The grease wax was calculated using the following formula:

^aCorresponding author.

Present address: No.308, Ningxia Road, Qingdao City, Shandong Province, China.

E-mail: Lijunqu@126.com

$$W_1=(G_0-G_1)/G_0 \times 100 \quad \dots (1)$$

where W_1 is the grease wax content; G_0 , the weight of raw hemp; and G_1 , the weight of raw hemp after extraction. The results reported are the average of three measurements.

- (ii) After extracting the grease wax, the sample was immersed in 150mL distilled water and then boiled for 3 h. The water soluble matter (W_2) was calculated using the Eq. (1).
- (iii) Then the sample was put into 150mL ammonium oxalate solution (5g/L) and then extracted for 3 h. The pectin content (W_3) was obtained using Eq. (1).
- (iv) The sample was then immersed in 150mL sodium hydroxide solutions (20g/L) and then boiled for 3.5 h, the hemi-cellulose content (W_4) was obtained using Eq. (1).
- (v) The lignin content was calculated using the following method: one g raw hemp after extracting grease wax was put into stoppered conical flask, and 30mL 72% sulphuric acid was added slowly. After keeping the mix as such for 24 h at 8-15°C, the sample was moved to conical flask and then diluted to 300 mL with distilled water, then boiled for 1 h, filtered and scoured using glass filter until there was no sulphate ion. The glass filter was finally dried to constant weight. The lignin was calculated using the following formula:

$$W_5=(G''-G')/(G''-G^0) \times 100 \quad \dots (2)$$

where W_5 is the lignin content; G'' , the weight of lignin and filter glass; G' , the weight of filter glass and G^0 , the weight of raw hemp + stoppered conical flask, and G^0 , the weight of stoppered conical flask. The results reported are the average of three measurements. The weight (W_6) was calculated using the following relationship:

$$W_6=100-(W_1+W_2+W_3+W_4+W_5)$$

APEX microwave chemistry workstation was provided by Shanghai Yiyao Microwave Chemical Technology Co., Ltd., China. Digital constant temperature water bath was obtained from Shanghai Meixiang Instrument Co., Ltd. China. The longitudinal morphologies of the degummed fibres were observed with JSM-840 type scanning electron microscope (Hitachi, Ltd.). The structural properties of the resultant fibres were analyzed by a Fourier transform infrared (FTIR) spectrometer (NEXUS-670, Nicolet Company, USA).

The entire process of hemp degumming was as follows:

Hemp bast → acid pretreatment → washing → alkali-oxygen one bath degumming (water bath heating³ and microwave-assisted heating¹² separately) → washing → pickling → washing → hitting fibre → shaking loose → drying → lean hemp.

The parameters in each process step are explained below:

- Acid pretreatment— H_2SO_4 solution (1ml/L), temperature 50°C, liquor ratio 1:15, water bath heating for 60 min.
- Alkali-oxygen one bath degumming—NaOH solution (5g/L), $MgSO_4 \cdot 7H_2O$ solution (0.1 g/L), H_2O_2 solution (4g/L), ATMP (amino trimethylene phosphonic acid) and magnesium chloride ($MgCl_2$) as H_2O_2 stabilizer (1.2 g/L), liquor ratio 1:15.
- Microwave-assisted alkali-oxygen one bath degumming—NaOH solution (5g/L), $MgSO_4 \cdot 7H_2O$ solution (0.1g/L), H_2O_2 solution (4g/L), H_2O_2 stabilizer ($MgCl_2$) (1.2g/L), liquor ratio 1:15, microwave reactor (Apex, Shanghai EU Microwave Chemistry Technology, China) at 600W power. All the chemical reagents used were of analytical purity.

The existence of non-thermal effects in alkali-oxygen one bath degumming process was investigated with two parameters, namely heating time and temperature.

In Method I, two kinds of hemp fibres were extracted under water bath and microwave-assisted bath heating respectively. Their heating temperatures were set at 100°C, but the corresponding heating time was varied as 20, 40, 50, 60, 80, 100min. In Method II, their heating time was kept as 60min, but the heating temperature was varied as 40, 55, 70, 85 and 100°C.

Results and Discussion

Effect of Heating Time on Residual Gum Content

The effect of alkali-oxygen bath heating time on residual gum content is shown in Table 1. The results indicate that the residual gum tends to be lower with the increase in alkali-oxygen bath heating time. The longer the heating time, the more obvious is degumming effect. Compared to water bath heating, the residual gum content of microwave-assisted heating is distinctly lower.

It can be seen that the residual gum content of microwave-assisted heating is lower than that of water

bath heating under the same boundary conditions. This indicates that the non-thermal microwave-assisted heating process also affect the degumming. With the increase in heating time, the difference in residual gum content between the two heating methods increases first and then decreases. At the time of 20 min, the gap between the two heating methods is found very small, also the degumming effect is not found obvious. With the increases in heating time, the degumming effect of microwave-assisted heating becomes more obvious than that of water bath heating, this might be due to the fact that liquid penetration into hemp bast under microwave field is faster than in water bath heating. Hence, the physical activity and chemical reaction of alkali degumming are increased. At 60 min, the maximum discrepancy is achieved, indicating that there are strongest reaction between alkali degumming liquid and hemp bast. The difference decreases gradually with increasing time. At 100 min, the difference becomes relatively small because alkali degumming liquid in water penetrates into the fibre to reduce the difference in reaction rate between microwave-assisted heating and water bath heating. In conclusion, microwave-assisted heating degumming is found better than water bath heating under the same conditions.

Effect of Temperature on Residual Gum Content

The effect of heating temperature with alkali-oxygen processing on residual gum content is given in Table 1, showing the same tend as shown with the heating time.

Table 1—Residual gum content at different heating time and temperature

Parameters	Residual gum content, %	
	Water bath	Microwave
Heating time, min		
20	18.22	17.38
40	13.70	11.19
50	13.49	9.66
60	12.88	8.81
80	11.87	8.42
100	7.93	5.92
Temperature (°C)		
40	23.09	21.85
55	21.89	17.87
70	19.82	16.12
85	18.30	14.83
100	9.95	8.10

The residual gum content decreases with the increase in alkali-oxygen temperature. The higher the heating temperature, the more obvious is degumming effects. The residual gum content of microwave-assisted heating is relatively lower in comparison with water bath heating.

As observed, the residual gum content in two heating methods reduces with increasing heating temperature. Under the same conditions, the residual gum content of microwave-assisted heating is found comparative with water bath heating, which indicates the existence of non-thermal effects in microwave heating process. At 40°C, a very small discrepancy is found between two heating methods and degumming effect is not observed obvious, as the alkali liquid does not penetrate into hemp at low temperature to affect the residual gum content. When the temperature is increased from 40°C to 55°C, the alkali cooking liquid starts penetrating into the hemp fibre with driving force of microwave, then the reaction process strengthens and the residual gum content decreases. During 55-85°C, the residual gum content is decreased slowly, and the difference in residual gum content between two heating methods is found relatively large. Compared to water bath heating, microwave-assisted heating accelerates the diffusion of alkali cooking fluid into hemp fibres and promotes the reaction of hemp with alkali cooking liquid. The residual gum content decreases rapidly when the temperature changes from 85°C to 100°C. The residual gum content of microwave heating is found below water bath heating because microwave has changed the internal structure of hemp fibre, altered the path of reaction and speeded up the reaction process.

The degumming efficiency of microwave-assisted heating is found better than that of water bath heating, which attributes to the non-thermal effects besides thermal effects.

Longitudinal Morphologies on Hemp Fibre

To further validate the presence of non-thermal effects in the microwave-assisted heating, the longitudinal morphologies of hemp fibre has also been observed by scanning electron microscopy (Fig. 1).

As seen from Fig. 1(a), raw hemp bundles contain a large number of pectin before degumming. After degumming under the same conditions, the hemp fibre using microwave-assisted heating becomes

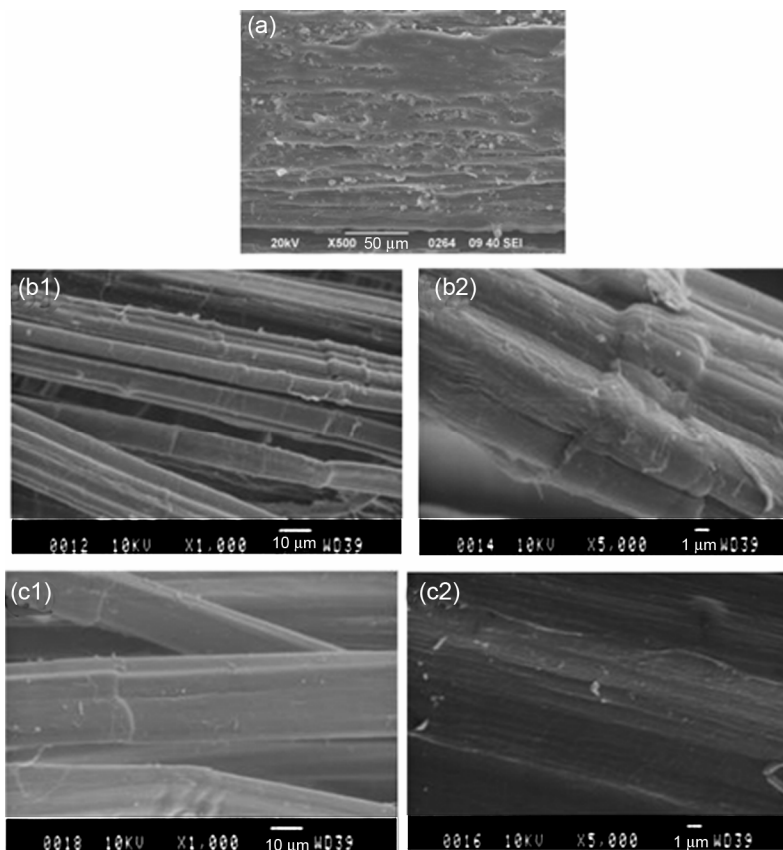


Fig. 1—The longitudinal morphologies of hemp fibre by SEM (a) raw hemp, (b1) lean hemp fibre after water bath heating ($\times 1000$), (b2) lean hemp fibre after water bath heating ($\times 5000$), (c1) lean hemp fibre after microwave heating ($\times 1000$), and (c2) lean hemp fiber after microwave heating ($\times 5000$)

smoother with clearer surface [Figs 1(c1)(c2)] in comparison to water bath heating [Figs 1(b1)(b2)]. It can be seen that there is still a small amount of pectin adhesion on the surface of degummed hemp fibre in case of water bath heating, while there is almost no pectin adhesive on the fibre surface and the surface texture is very clear in case of microwave-assisted degumming, showing that microwave heating is better than water bath heating. It shows indirectly that there is corresponding non-thermal effect to the same thermal effects during the heating.

FTIR Analysis

The FTIR spectra of the lean hemp fibre degummed for 60 min at 85°C using two heating methods are shown in Fig. 2.

It is observed that the characteristic peaks of lignin appear at $1500\text{--}1750\text{cm}^{-1}$. Both of these spectra show that there are obvious characteristic peaks of lignin at $1500\text{--}1750\text{cm}^{-1}$ for lean hemp fibre¹³. Also, the intensity of lignin peak gets weaker for microwave heating method as compared to water bath heating,

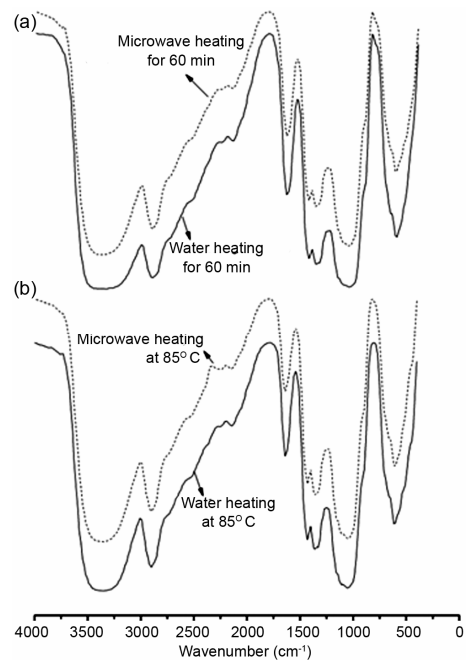


Fig. 2—FTIR spectra of lean hemp fibre degummed (a) for 60 min and (b) at 85°C using different heating methods

which indicates that there is more obvious degumming effect and non-thermal effect exists in the microwave heating.

Conclusion

The results show that the degumming effect of microwave-assisted heating is better than the water bath heating and the gap in gum content between the two methods increases with the increase in time and temperature. Also the longitudinal surface of hemp fibre after microwave-assisted heating is found significantly smoother and clearer than in water bath heating. The FTIR spectrum shows that the intensity of lignin peak gets weaker using microwave heating which is the illustration of more obvious degumming effect and the existence of non-thermal effect in the microwave heating.

Acknowledgement

Authors are thankful for the financial support by Natural Science Foundation of China (No. 51273097, 51306095 and 51403112), Taishan Scholars Construction Engineering of Shandong Province and

Program for Scientific Research Innovation Team in Colleges and Universities of Shandong Province.

References

- 1 Wang J H & Gita N R, *Text Res J*, 73 (2003) 339.
- 2 Akin D E, Dodd R B & Perkins W, *Text Res J*, 72 (2002) 510.
- 3 Qu L J, Zhu S F & Wang S Y, *J Appl Polym Sci*, 97 (2005) 2279.
- 4 Li CY, Qu L J & Guo X Q, *Res J Appl Sci Eng Technol*, 6 (2013) 269.
- 5 Qu L J, Guo X Q & You R H, *J Donghua University*, 27 (2010) 516.
- 6 Camel V, *Analyst*, 126 (2001) 1182.
- 7 Yemis O & Mazza G, *Bioresour Technol*, 102 (2011) 7371.
- 8 Niyaz M M, Fereshteh M & Arami M, *Silk Fibre Polym*, 11 (2010) 234.
- 9 Menéndez J A & Arenillas A, *Fuel Proces Technol*, 9 (2010) 11.
- 10 Bischof V S, Schramm C & Katovic D, *Text Res J*, 73 (2003) 733.
- 11 Fouda M E, Shafei A & Hebeish A, *Carbohydr Polym*, 77 (2009) 651.
- 12 Gupta D, Sen K & Sen S, *Cellul Chem Technol*, 10 (1976) 285.
- 13 Guo J B, Tao Z Y & Luo X G, *Chem J*, 63 (2005) 1536.