A Novel Eco-Friendly Scouring and Bleaching Technique of Flax Rove Using Supercritical Carbon Dioxide Fluid

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ABSTRACT

A novel eco-friendly scouring and bleaching technique for flax rove was developed using supercritical carbon dioxide fluid. Effects of system temperature, pressure, time, and carbon dioxide flow on the scouring and bleaching properties of flax rove were investigated. The results showed that low residual gum content and significant improvements in whiteness of the flax rove were obtained. The residual gum content and the whiteness were affected by the system temperature, pressure, time and fluid flow. An optimized scouring and bleaching procedure for flax rove was found at a temperature of 120°C, a pressure of 28 MPa, a time of 120 min, and a fluid flow of 30 g/min in supercritical carbon dioxide fluid. In addition, surface morphology and breaking strength of processed flax rove were also evaluated and compared to those properties of the original flax rove samples.

INTRODUCTION

Flax (Linum usitatissimum) is a kind of cellulosic fiber widely used for textiles and for technical applications, for example, aerospace, firefighting, and health care because of its low cost, renewable nature, easy availability, improved performance and ease of chemical and mechanical modifications [1, 2]. The chemical composition of flax fiber mainly contains cellulose, hemicellulose, lignin, pectin, protein and wax of which hemicellulose, lignin, pectin are difficult to remove [3]. Flax fiber displays high crystallinity and orientation, affecting its ductility, elasticity, softness, crimp and other physical properties, resulting in difficulties in the spinning and weaving processes [4, 5]. Hence, scouring and bleaching are employed to remove hemicellulose, lignin, and pectins from flax rove before spinning or yarn forming [6-8]. To date, chemical, chemical-biological and bio-enzyme methods have been used industrially to scour and bleach flax rove [9-11]. These methods produce a large amount of wastewater containing sodium chlorite, soda ash, hydrogen peroxide and other chemicals, resulting in serious water pollution. Traditional multiple aqueous rinsing and bleaching processes are complicated, increasing the manufacturing cost. Thus, there is an increasing demand for a novel eco-friendly scouring and bleaching technique which can be applied easily and efficiently to flax rove.

Supercritical carbon dioxide fluid is a promising solvent for textile dyeing, as it is non-toxic, non-flammable, non-polluting, can be inexpensively produced by many industrial processes, and is able to solvate both hydrophobic and hydrophilic substances [12-14]. Moreover, substances can be readily recovered from supercritical carbon dioxide fluid by depressurization. Using supercritical carbon dioxide fluid to replace water offers a water free, non-polluting, energy preserving solution for bleaching and scouring flax rove for cosmetics, environmental and pharmaceutical applications [15, 16]. Supercritical carbon dioxide fluid is characterized by high mass transfer rates, liquid like density and variable selectivity (realized by the variation of system pressure and temperature), making this technique valuable for seed, fruit and vegetable processing and extraction [17-19]. To date, there have been no studies on the scouring and bleaching of flax rove using supercritical carbon dioxide fluid.

The aim of this work was to apply supercritical carbon dioxide fluid to carry out the scouring and bleaching of flax rove. Effects of system temperature, pressure, time and fluid flow on the scouring and bleaching properties were investigated. Surface morphology and breaking strength of flax rove were also tested.

EXPERIMENTAL

Materials

Flax roves were provided by Jiaxing Unbleached Linen Textile CO., LTD. Samples with a fineness of 577 tex were used for the scouring and bleaching study. Carbon dioxide gas (99.9%) used in the experiments was purchased from Zhonghao Guangming Research & Design Institute of Chemical Corporation. The analytical reagent grade sodium hydroxide was purchased from Tianjin Kemiou Chemical Reagent.

Scouring and Bleaching Using Supercritical Carbon Dioxide Fluid

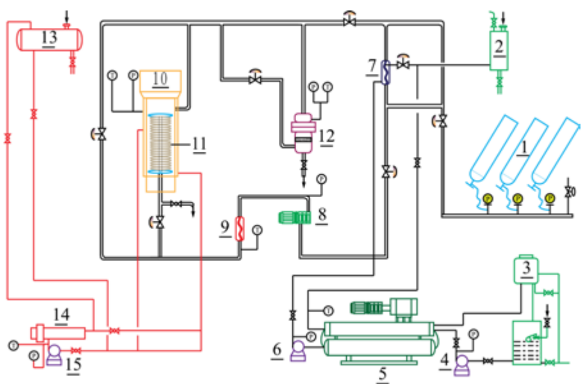

FIGURE 1. Schematic diagram of supercritical carbon dioxide fluid apparatus for scouring and bleaching: (1) carbon dioxide cylinder, (2) ethylene glycol elevated tank, (3) cooling tower, (4) water pump, (5) compressor, (6) ethylene glycol pump, (7) refrigerator, (8) high-pressure pump, (9) heat exchanger, (10) scouring and bleaching vessel, (11) flax rove, (12) separator vessel, (13) conduction oil tank, (14) conduction oil system, (15) oil pump.

Scouring and bleaching of flax rove was conducted in the batch supercritical carbon dioxide fluid system described in *Figure 1*. Before scouring and bleaching, flax rove was placed in a scouring and bleaching vessel and sealed. Carbon dioxide stored in a carbon dioxide cylinder was liquefied using a refrigerator. The liquid carbon dioxide was injected into the scouring and bleaching system, pressurized above the critical pressure (7.38 MPa) using a high-pressure pump, and heated to above the critical temperature (31.10°C) with a heat exchanger. Carbon dioxide in the supercritical state was then introduced to the scouring and bleaching vessel for 30 min to 150 min to extract the non-fiber tissues (i.e. hemicellulose, lignin, pectins) from flax rove at system temperatures, pressures, and fluid flows, ranging from 80°C to 120°C, 16 MPa to 32 Mpa and 10 g/min to 50 g/min, respectively. Supercritical carbon dioxide fluid and the extracts were then separated in a separator vessel where the extracts were preserved in the separator while the depressurized gaseous carbon dioxide was cleaned further with a gas purifier, cooled by the refrigerator, and flowed into the carbon dioxide storage cylinder for reuse. The flax rove was then removed and used for further analysis.

Residual Gum Content Measurement

A flax rove sample (5 g) before and after supercritical carbon dioxide fluid scouring and bleaching was placed into a weighing bottle, and oven dried to a constant weight at 105°C. The flax rove sample was then placed at a dryer for 30 min, and weighed and a dry weight (G_0) was obtained.

The weighed flax rove sample was dipped into a round-bottomed flask which contained 250 ml sodium hydroxide solution at a concentration of 20 g/l. The sample was boiled for 3 h in a vessel equipped with a condenser. After the boiling process, the flax rove sample was rinsed in a sample sieve. In order to obtain the dry weight after residue extraction ($G_0^{'}$), the flax rove was dried to a constant weight at 105°C, and cooled in a dryer for 30 min. Thus, the residual gum content (W_c/%) for flax rove was calculated according to Eq. (1) :

$$W_c = \frac{G_0 - G_0^{'}}{G_0} \times 100 \qquad (1)$$

where G_0 is the dry weight before treatment for flax rove; $G_0^{'}$ is the dry weight after residue extraction for flax rove. Each experiment was carried out three times, and each data point reported is the average of three samples.

Whiteness Measurement

Whiteness, a physical index for optical performance of materials, was determined using a brightness meter (PN-48B, Pnshar, China) with the following settings: illuminant D65, large area view, specular excluded, UV included and CIE 1964 Supplemental Standard Observer (10 observer). The whiteness (WI/%) of the flax rove was calculated according to Eq. (2) :

$$WI = Y + 800(0.3138 - x) + 1700(0.3310 - y) \qquad (2)$$

where, Y, x, y are chromaticity coordinates of the treated flax rove.

Breaking Strength Measurement

The breaking strength measurements were carried out on a universal material testing machine (gauge length, 250 mm; test speed, 500 mm/min; TH-8102S, TopHung, China), and the strength value (σ_b/CN) was calculated according to Eq. (3):

$$\sigma_b = \frac{4F_p}{\pi D^2} \quad (3)$$

where F_p is the maximal tensile fracture force in kg; D is the mean diameter of flax rove in centimeters. Each experiment was carried out ten times, and each reported data point is the average of ten specimens.

RESULTS AND DISCUSSION

The scouring and bleaching properties of flax rove were affected by many factors, including system temperature, pressure, time and fluid flow. To examine the effect of these parameters on the scouring and bleaching properties (residual gum content and whiteness) of flax rove, experiments were carried out at 80°C to 120°C, 16 MPa to 32 MPa, 30 min to 150 min and 10 g/min to 50 g/min, respectively.

Residual gum content and whiteness were measured before supercritical carbon dioxide treatment. *Table I* shows that the initial average residual gum content of the flax rove was 21.76%, and the whiteness was 15.52.

TABLE I. The residual gum content and the whiteness of flax rove before scouring and bleaching.

Sample	Residual gum content (%)	Whiteness
1	21.98	15.63
2	22.3	14.89
3	22.76	15.77
4	21.05	15.09
5	20.71	16.22
Average value	21.76	15.52

Effect of System Temperature

In order to investigate the effect of system temperature on the scouring and bleaching properties of flax rove in supercritical carbon dioxide fluid, flax rove was extracted at temperatures ranging from 80°C to 120°C, with a pressure 28 MPa, a dyeing time 120 min, and a fluid flow 30 g/min. *Figure 2* shows that the residual gum content, an indicator of removal efficiency of non-fiber tissues (i.e. hemicellulose, lignin, pectins) in flax rove, was obtained in supercritical carbon dioxide fluid. It can be seen from *Figure 2* that the residual gum content of the flax rove decreased as the system temperature increased from 80°C to 100°C. An accelerated reduction in the residual gum content was observed at system temperatures higher than 100°C. *Figure 2* also depicts the effect of the system temperature on the whiteness of flax rove in supercritical carbon dioxide fluid. There was an improvement in the whiteness of the flax rove samples as the system temperature increased from 80°C to 100°C. There was also a notable increase as temperature increased from 100°C to 120°C.

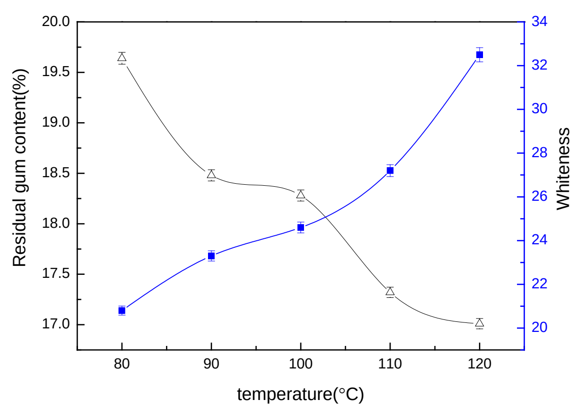

FIGURE 2. Effect of system temperature on the residual gum content and the whiteness of flax rove in supercritical carbon dioxide fluid. (-Δ-) Residual gum content, (-■-) Whiteness.

The above results demonstrate that it is feasible to remove hemicellulose, lignin, pectins, and other non-fiber tissues in flax rove using supercritical carbon dioxide fluid, and the system temperature had a significant effect on the removal efficiency of the non-fiber tissues in the flax rove [20]. In general, supercritical carbon dioxide fluid extractions are defined in terms of variables directly related to the relative solvent strength, which is dependent on the fluid density [21, 22]. In the extraction process, the density of supercritical carbon dioxide fluid is very sensitive to system temperature. This might be the reason that the residual gum content and the whiteness of the flax rove sample changed significantly when the system temperature was increased from 80°C to 90°C. Further, a moderate increase in system temperature from 90°C to 100°C led to a decrease in the density of carbon dioxide fluid, with a consequent reduction in dissolving capacity. However, further increase in temperature can also accelerate the mass transfer of supercritical carbon dioxide fluid, thereby decreasing the residual gum content and improving the whiteness of flax rove [16]. Considering the effect of temperature on the residual gum content and the whiteness of flax rove, a system temperature of 120°C was employed for scouring and bleaching of flax rove in subsequent experiments.

Effect of System Pressure

The effect of system pressure on the scouring and bleaching properties of flax rove in supercritical carbon dioxide fluid was investigated at pressures ranging from 16 MPa to 32 MPa, with a temperature 120°C, a dyeing time 120 min and a fluid flow 30 g/min. As depicted in *Figure 3*, a significant reduction of the residual gum content from 18.10% to 16.09% was achieved with the system pressure increased from 16 MPa to 28 MPa, with no further as pressure increased to 32 MPa.

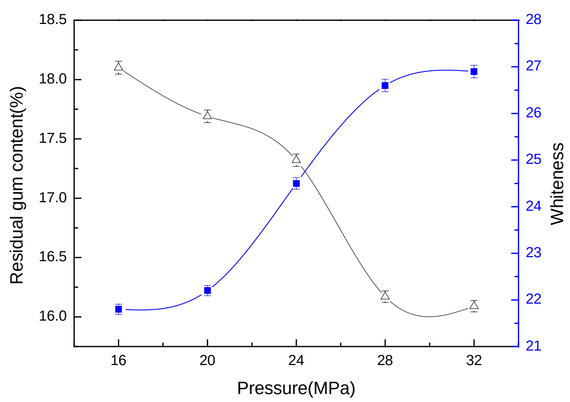

FIGURE 3. Effect of system pressure on the residual gum content and the whiteness of flax rove in supercritical carbon dioxide fluid. (-Δ-) Residual gum content, (-■-) Whiteness.

Figure 3 shows that after supercritical scouring and bleaching, the whiteness of the flax rove increased slightly as system pressure increased from 16 MPa to 20 MPa. A significant linear increase resulted between 20 MPa and 28 MPa, with no further increase as pressure increased to 32 MPa.

Theoretically, an increase of system pressure in a supercritical state can lead to a rise in the dissolving capacity of the carbon dioxide. Higher recovery of volatile fractions and a lower recovery of non-volatile fractions can also be realized under higher pressure conditions. This makes it possible to control the extraction process by adjusting the pressure [23]. For these reasons, the residual gum content was reduced with the increasing of pressure while the whiteness was increased accordingly. Over the range of pressure studied, fluid density increase is presumably the main mechanism resulting in a lower residual gum content and a higher whiteness. Based on the results obtained, a system pressure of 28 MPa was used subsequent experiments.

Effect of System Time

The effect of system time on the scouring and bleaching properties of flax rove in supercritical carbon dioxide fluid was investigated at times ranging from 30 min to 150 min, with a temperature 120°C, a pressure 28 MPa, and fluid flow 30 g/min. The obtained results are shown in *Figure 4*. It can be seen in *Figure 4* that the residual gum content of the flax rove was reduced significantly between 30 and 120 minutes, with little further reduction as time increased to 150 minutes.

Figure 4 also reveals that a moderate enhancement in the whiteness of the flax rove was achieved as the system time was increased from 30 min to 90 min, and then a significant increase was observed as system time increased to 150 min. These indicates that the hemicellulose, lignin, pectins and other non-fiber tissues in the flax rove were degraded and/or removed, thus improving the whiteness of the flax rove. Based on these results, a time of 120 min was used in further experiments for the supercritical scouring and bleaching of flax rove.

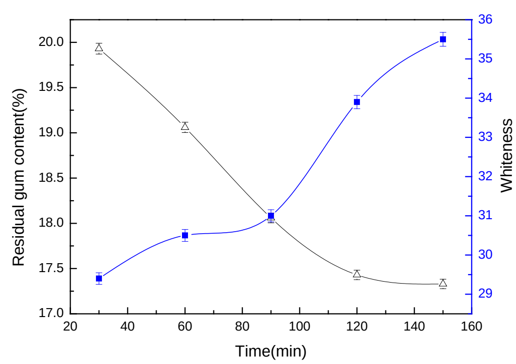

FIGURE 4. Effect of system time on the residual gum content and the whiteness of flax rove in supercritical carbon dioxide fluid. (-Δ-) Residual gum content, (-■-) Whiteness.

Effect of Fluid Flow

The effect of fluid flow on the scouring and bleaching properties of flax rove in supercritical carbon dioxide was investigated at rates ranging from 10 g/min to 50 g/min, with a temperature 120°C, a pressure 28 MPa and of 120 min. *Figure 5* indicates that the residual gum content was decreased was the fluid flow increased from 10 g/min to 20 g/min, and reached the lowest point at 30 g/min. Simultaneously, an prominent improvement for the flax rove whiteness was obtained as fluid flow increased from 10 g/min to 30 g/min. However, it is notable that both residual gum content and whiteness for the extracted flax rove were negatively affected obtained in supercritical carbon dioxide fluid when the fluid flow increased from 30 g/min to 50 g/min.

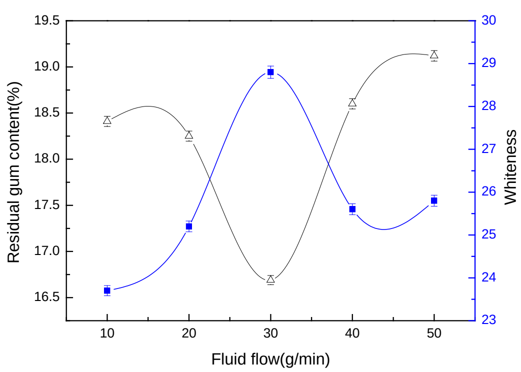

FIGURE 5. Effect of fluid flow on the residual gum content and the whiteness of flax rove in supercritical carbon dioxide fluid. (-Δ-) Residual gum content, (-■-) Whiteness.

Theoretically, a higher fluid flow causes supercritical carbon dioxide fluid to penetrate more easily into the amorphous phase of the flax fibers, leading to swelling of the fibers [24]. Accordingly, the extraction capacity of the non-fiber tissues in the flax rove was increased. However, in some cases very high CO_2 fluid flow actually decreases the removal efficiency due to insufficient contact time between the flax rove and supercritical carbon dioxide fluid [25, 26]. Higher fluid flow promotes an increase in operational and capital costs, and this fact must be considered in industrial situations. Based on the results obtained, a fluid flow of 30 g/min is recommended for supercritical scouring and bleaching of flax rove.

Surface morphology analysis of the flax rove in supercritical carbon dioxide fluid

An investigation of the surface morphology of flax rove before and extraction at a temperature of 120°C, a pressure of 28 MPa, a time of 120 min, as well as a fluid flow of 30 g/min in supercritical carbon dioxide fluid was carried out using SEM.

As shown in *Figure 6(a)*, the original flax rove sample displays a relatively clean and smooth surface. *Figure 6(b)* shows that slight damage of phloem cell on the surface of the flax fiber occur as a result of extraction. More grooves and bulges appeared on the surface of the extracted flax fiber, and there is obvious damage present. The results indicate that the non-fiber tissues between flax fibers can be removed in supercritical carbon dioxide fluid, and the splitting degree of the flax rove is improved, resulting in some changes in the surface morphology of the flax fibers. Thus, hemicellulose, lignin, pectins and other non-fiber tissues in the flax rove can be degraded or removed in supercritical carbon dioxide fluid, which is consistent with the NMR spectroscopy results from previous studies [20].

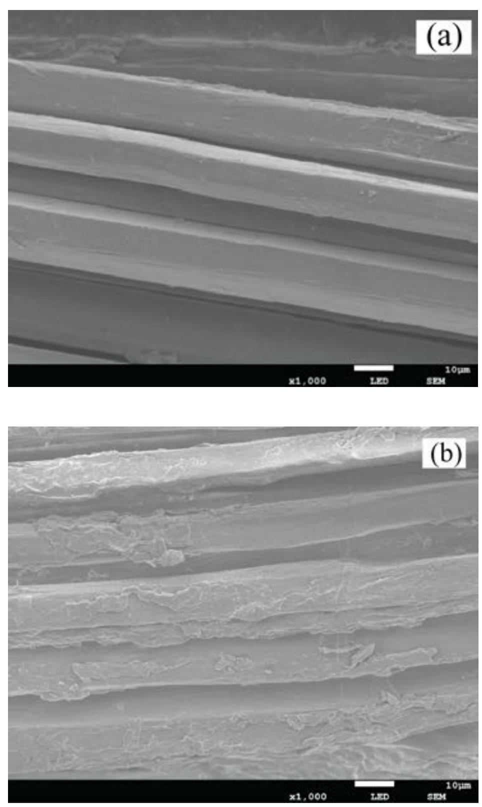

FIGURE 6. SEM images of the flax rove: fiber surface of the original sample (a) treated at a temperature of 120°C (b) in supercritical carbon dioxide fluid.

Effect of Supercritical Carbon Dioxide Fluid on the Breaking Strengths of the Flax Rove

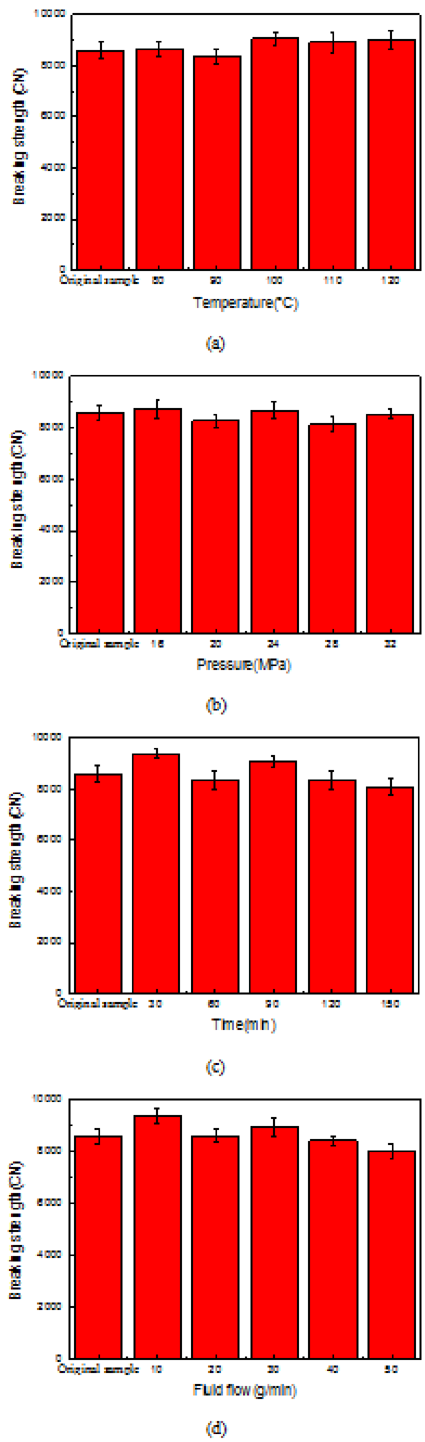

FIGURE 7. Effect of supercritical carbon dioxide fluid on the breaking strengths of the flax rove.

In order to investigate the mechanical properties of the flax rove, the breaking strengths of the flax rove samples before and after supercritical carbon dioxide fluid scouring and bleaching were measured, as given in *Figure 7*. The results show that the breaking strength of the original flax rove sample was 8598.86 CN. After scouring and bleaching in supercritical carbon dioxide fluid, there is no significant change for the flax roves extracted for 30 min to 150 min at system temperatures, pressures and fluid flow, ranging from 80°C to 120°C, 16 MPa to 32 MPa, and 10 g/min to 50 g/min, respectively. Generally, supercritical carbon dioxide fluid had excellent mass transfer and penetration effect on the fibers, which can significantly neaten their macromolecular structure [16]. Therefore, it is obvious that scouring and bleaching of flax rove in supercritical carbon dioxide fluid have little negative influence on the breaking strength of flax rove.

CONCLUSION

A novel and eco-friendly scouring and bleaching method for flax rove using supercritical carbon dioxide fluid instead of a water medium was investigated. The results revealed that the system temperature, pressure, time and fluid flow significantly affected both the residual gum content and the whiteness of flax rove. Optimized scouring and bleaching process conditions for flax rove were determined. These consist of a temperature of 120°C, a pressure of 28 MPa, a time of 120 min and a fluid flow of 30 g/min in supercritical carbon dioxide. Surface morphology analysis proves that the proposed method produces more grooves and bulges, and obvious damage to the surface of the flax fiber. This indicates that non-fiber tissues between flax fibers have been degraded and/or removed by the supercritical carbon dioxide fluid. Furthermore, the scouring and bleaching of flax rove in supercritical carbon dioxide fluid had little or no negative influence on the breaking strength of flax rove. Compared with the traditional method with water-based method, the proposed supercritical scouring and bleaching process conserves more water and energy, and is thus more eco-friendly for the production of flax rove and other materials used in the textile industry.

ACKNOWLEDGEMENT
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