Chemical Composition and Hydrolytic Method of the Waste Bovine Hair from Tannery

Wei-Cai Zeng [1], Wen-Hua Zhang [2], Xue-Pin Liao [2], Bi Shi [1, 2,] *

[1]The Key Laboratory of Leather Chemistry and Engineering of Ministry of Education, Sichuan University, Chengdu 610065, PR China; phone: +86 28 85400356, fax: +86 28 85400356 and e –mail: shibi@scu.edu.cn (Bi Shi), weicaizeng@qq.com (Wei-Cai Zeng)

[2]National Engineering Laboratory of Clean Technology for Leather Manufacture, Sichuan University, Chengdu 610065, PR China; phone: +86 28 85405508, fax: +86 28 85405508 and e –mail: zhangwh@scu.edu.cn (Wen-Hua Zhang), xpliao@scu.edu.cn (Xue-Pin Liao)

Abstract

In the traditional leather industry, bovine hair was commonly dissolved by sodium sulfide and/or sodium hydrosulfide. This so-called hair-destroying unhairing process not only results in a big amount of leftover sulfides in wastewater, but also brings a high organic pollution to wastewater. With the environmental concerns and legislation request, the hair-destroying unhairing technique has being replaced by enzyme-assisting hair-save unhairing method gradually, which can eliminate the dissolution of hair and thus decrease organic pollution and sludge. Although the application of this biochemical technique can effectively control organic pollution, a big amount of bovine hairs generated in the process bring another solid pollution. Therefore, the effective utilizations of keratin in bovine hairs are receiving growing attention. In present study, the hydrolytic method of the waste bovine hair from tannery was investigated and its chemical composition was determined. With the analysis using National Standard of People's Republic of China, the waste bovine hair was observed to be composed by water (11.9%), ash content (6.43%), crude fat (2.56%), protein (85.57%) and metal ions (Na, K, Ca, Mg, 1.78, 0.46, 228.09, 10.28mg/g). Compared with the hydrolysis in acidic condition or under pressure at a high temperature, alkali treatment showed the strongest effect on hydrolysis of the hair, which produced the highest protein content (83.66g/100g) of hydrolysate. Our results suggested that the waste bovine hair was a potential resource to prepare industrial protein.

Key words: Leather making; Bovine hair; Chemical composition; Hydrolysis

1. Introduction

In the traditional leather industry, bovine hair was commonly dissolved by sodium sulfide and/or sodium hydrosulfide. This method was called hair-destroying unhairing process, which brought a big amount of leftover sulfides in wastewater and leaded to a high organic pollution, such as the high value of chemical oxygen demand (COD) and biochemical oxygen demand

(BOD). The usage of this method inhibited the development of leather industry seriously (Shi and Lu 2004). With the environmental concerns and legislation request, the hair-destroying unhairing technique has being replaced by enzyme-assisting hair-save unhairing method gradually, which can eliminate the dissolution of hair and thus decrease organic pollution and sludge (Shi and Wang 2010). However, with the promotion and application of the technology, the tanning process will produce a lot of waste animal hair, which will bring a new solid waste pollution to environment without the effective utilization.

Among the waste animal hairs, wool, camel hair and cony hair could be used as materials in textile industry again for their advantage of long fiber (Li 2005). However, the reuse of waste bovine hair was so difficult, due to its deep color and short fiber. According the previous statistic, the amount of bovine hair from leather industry were 700,000,000 t. Moreover, only 10% of them were reused as materials in animal feed production, and most of them were treated as waste. Bovine hair, mainly composed of keratin, is a superior resource of protein (Teresa and Justyna 2011). The effective and reasonable utilization of waste bovine hair was not only useful for the development of leather industry, but also beneficial for environment and society. In present study, the hydrolytic method of the waste bovine hair from tannery was investigated and its chemical composition was determined for its further application.

2. Materials and methods

2.1. Materials and chemicals

Bovine hairs were collected from a meat factory in Chengdu, China, and were washed, dried at 60 °C for 3 days and finally stored under vacuum.

Ether, ethanol, copper sulfate, potassium sulfate, sulfuric acid, boric acid and sodium hydroxide were purchased from Ke-Long Chemistry (Kelong Co., Ltd., Chengdu, China). The solvents for analysis were of pure water. All reagents used were of analytical grade.

2.2. Determination of the chemical composition of bovine hair (The Ministry of Health of the People's Republic of China 2010a; The Ministry of Health of the People's Republic of China 2003; The China National Standardization Management Committee 2008; The Ministry of Health of the People's Republic of China 2010b)

The chemical composition of the waste bovine hair (water, ash, crude fat and protein content) was measured by the method in the National Standard of People's Republic of China (GB 5009.3-2010, GB 5009.4-2003, GB/T 14772-208, and GB 5009.5-2010, respectively).

According the Chemical Standard of People's Republic of China (HG/T 3941~3942-2007), the metal content of waste bovine hair was determined by Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES) (The People's Republic of China's National Development and Reform Commission 2007).

2.3. Compare the different hydrolytic methods of bovine hair

The waste bovine hair (10 g) was suspended in 200 mL of hydrolytic solution (pure water, 20% of H_2SO_4 and 5% NaOH, respectively), and then stirred in water bath a required temperature (121~126 °C, 95 °C and 95 °C, respectively) for 2 h keeping the different pressure (102.9 KPa, 101.3 KPa and 101.3 KPa, respectively). The homogenate obtained was filtered and centrifuged under 5000 rpm for 20 min. The hydrolysate was prepared by freeze-drying for further determination of protein content by the method in the National Standard of People's Republic of China (GB 5009.5-2010).

2.4. Statistical analysis

The data of all experiments were recorded as means ± standard deviations and were analyzed with SPSS (version 12.0 for Windows, SPSS Inc., CO, USA).

3. Results and discussions

3.1. The chemical composition of bovine hair

By using the standard analysis method, the chemical composition of bovine hair was shown in table 1.

Table 1 Chemical composition of the waste bovine hair from leather industry

Chemical composition	Content
Water (%)	11.19 ± 0.21%
Ash (%)	6.43 ± 1.71%
Crude fat (%)	2.56 ± 0.60%
Protein (%)	85.57 ± 5.61%
Metal	Na, K, Ca, Mg (1.78, 0.46, 228.09, 10.28 mg/g)

A

s shown in table 1, the main composition of bovine hair was protein (86%). The content of water was high, and the content of ash and crude fat was low. Na, K, Ca and Mg were the main kind of metal in bovine hair. Comparing with the previous study (Li 2008), the protein content of bovine hair was the same as wool, and the water, ash and metal content were higher than wool, which might be attributed to the differences of environment, treatment and experiment between them. Being treated with Ca agent in tannin process, the content of Ca was so high in bovine hair. These results suggested that the main chemical composition of bovine hair was protein, and it could be used a potential resource to prepare industrial protein.

3.2. Different hydrolytic methods for bovine hair

3.2.1. Color of different hydrolytic solutions

The color of hydrolysate by using different methods was different. As shown in Fig. 1, the order of color of hydrolytic solutions as: hydrolysis with alkali > hydrolysis with acid > hydrolysis with high pressure and temperature.

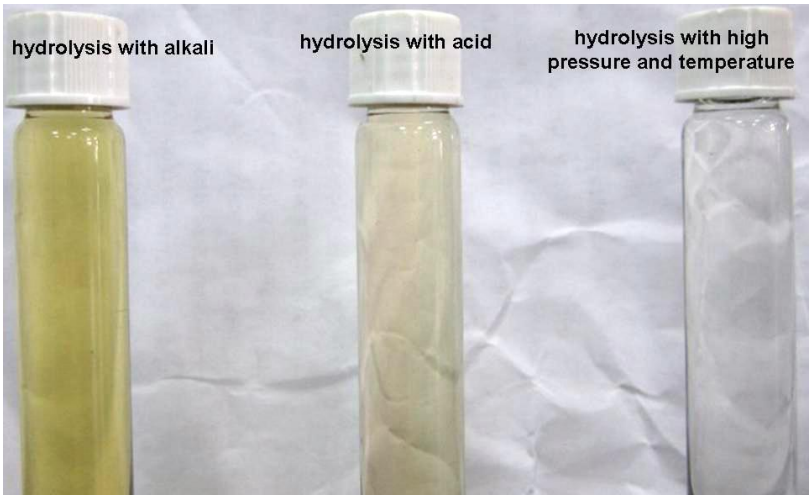

Figure 1 Color of hydrolytic solutions different methods

The color of hydrolytic solution was an effective appearance for the hydrolysis of bovine hair. Commonly, pigment was in the interior of bovine hair (Hill et al. 2010). With the hydrolysis, the bovine hair was damaged and the pigment dissolved in hydrolytic solution. So, the more effective of the hydrolysis, the higher of the color of hydrolytic solution was.

3.2.2. Protein content of different hydrolytic solutions

The protein content of different hydrolytic solutions was determined and the results were shown in table 2.

Table 2 The protein content in different hydrolytic solutions

Hydrolytic methods	Protein content（g/100g）
High pressure and temperature	5.81 ± 1.32
Acid	56.53 ± 3.45
Alkali	83.66 ± 3.94

The results indicated that the hydrolytic solution by using alkali possessed the highest protein content among the methods. The bovine hair was mainly composed by protein (table 1). So, the protein content in hydrolytic solution was the direct evidence of hydrolysis. These differences of hydrolysis were attributed to the physical and chemical characterizations of bovine hair. There was a lot of disulfide linkage in bovine hair, which could not be damaged by using common method but was sensitive to alkali agent (Brebu and Spiridon 2011; Rouse and Dyke 2010). Therefore, with the treatment of alkali, the hydrolysis of bovine hair was effective than others.

With the determination of color and protein content of hydrolytic solution by using different method, alkali was selected to be the better agent for the hydrolysis of bovine hair.

4. Conclusion

By using the alkali hydrolysis, bovine hair could be treated to hydrolytes with high content of protein, which could be 83.66g/100g. There was many Ca in the hydrolytes, and we could use some suitable method to low its content. All the results suggested that the waste bovine hair from leather industry could be used a potential resource to prepare industrial protein.

References

Brebu, M., Spiridon, I., 2011, Thermal degradation of keratin waste, J Analy App Pyroly, 91, 288-295p.

Hill, P., Brantley, H., Dyke, M. V., 2010, Some properties of keratin biomaterials: kerateines. Biomaterials, 31, 585-593p.

Li, W. X., 2008, Research of waste wool, poultry hair keratin degradation and resource utilization, Shanxi normal university, Xian.

Li, W. X., 2005, Pollution iontrol and waste utilization, Chemistry Industry Press, Beijing.

Rouse, J. G., Dyke, M. E. V., 2010, A review of keratin-based biomaterials for biomedical applications, Materials, 3, 999-1014p.

Shi, B., Lu, Z. B., 2004, The clean technology for leather industry, Chemistry Industry Press, Beijing.

Shi, B., Wang, X. C., 2010, Clean technology and mechanism for leather industry, Chemistry Industry Press, Beijing.

Teresa, K. K., Justyna, B., 2011, Biodegradation of keratin waste: theory and practical aspects, Waste Management, 31, 1689-1701.

The Ministry of Health of the People's Republic of China, 2010, Determination of moisture in Food (GB 5009.3-2010), China Standard Press, Beijing.

The Ministry of Health of the People's Republic of China, China National Standardization Management Committee, 2003, Determination of ash in Food (GB / T 5009.4-2003), China Standard Press, Beijing.

The China National Standardization Management Committee, the State Administration of Quality Supervision, Inspection and Quarantine of the People's Republic of China, 2008, Determination of crude fat in Food (GB / T 14772-2008), Standards Press of China, Beijing.

The Ministry of Health of the People's Republic of China, 2010, Determination of protein in Food (GB 5009.5-2010), China Standard Press, Beijing.

The People's Republic of China's National Development and Reform Commission, 2007, Industrial sodium hydroxide metal and non-metallic ion content determination by ICP method (HG / T 3941 ~ 3942-2007), Chemical Industry Press, Beijing.