Extraction and Determination of Total and Soluble Oxalate in Pulping and Papermaking Raw Materials

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Oxalate exists in plant tissue in the form of soluble and insoluble salts. Determination of the oxalate content in a raw material is important for controlling oxalate scaling during the pulping and papermaking processes. In this study, oxalate extraction and determination of the total and soluble oxalate contents in several pulping and papermaking raw materials were investigated. It was found that soluble oxalate can be extracted completely by distilled water at 70 °C within 180 min. Total oxalate can be extracted completely by 2-mol/L hydrochloric acid at 70 °C within 210 min.

Keywords: Total oxalate; Soluble oxalate; Extraction; Pulping and papermaking raw materials

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INTRODUCTION

Oxalic acid is a common, widespread constituent of plants (Andrews and Viser 1951). It occurs as a free acid in the form of soluble salts of potassium and sodium (Baker 1952). It can also be present in precipitated form, mostly with calcium, magnesium, and iron (Buonocore 1955; Noonan and Savage 1999; Yu and Ni 2005). Soluble oxalates (oxalic acid and soluble salts) and insoluble oxalates (predominantly calcium oxalate) can be extracted from a material using hot distilled water and acid solution, respectively (Hönow and Hesse 2002). According to recent studies, the oxalate content in materials varies, mainly depending on the plant family, plant organ, soil quality, and climate (Kasidas and Rose 1980; Siener *et al.* 2006). However, in the pulp and papermaking industry, the duration of storage can also affect the oxalate content because decomposition of microbes produces oxalate (Singh *et al*. 2010).

In addition, it was found that oxalate was formed during the pulping and bleaching processes (He *et al.* 2003; Yu and Ni 2005; Yu and Ni 2007; Li *et al.* 2012). Oxalate in bleaching effluents can combine with a variety of alkaline-earth metals and form salts with low solubility, leading to a series of scaling problems (Yu and Ni 2006; Winestrand *et al.* 2014). Scaling has negative impacts on the operation and the quality of the products alike (Nilvebrant *et al.* 2002). Determining the oxalate content in the raw material is useful in that it can used to adjust the pulping process, potentially limiting scaling.

In previous studies, Zarembski and Hodgkinson observed that the separation of oxalic acid from food by extraction with hot hydrochloric acid can lead to high results oxalate generation from carbohydrates and other compounds (Zarembski and Hodgkinson 1962). However, Libert and Franceschi (1987) observed that dissolution of CaO_x was frequently done using hot acids to avoid incomplete extraction and any oxalate generation due to oxidation of ascorbic acid (Libert and Franceschi 1987; Moßhammer *et al*. 2006).

On the other hand, Hönow and Hesse found that total oxalate was extracted with 2-mol/L hydrochloric acid (Hönow and Hesse 2002). The experiment indicated that D(+) glucose and D(-) fructose could not be converted to oxalate in the presence of hot hydrochloric acid. In the present investigation, the effects of different factors such as temperature and time on oxalate extraction were studied to determine the optimal extraction conditions for soluble and total oxalate. The concentration of oxalate in the extraction liquor was determined by headspace gas chromatography (HS-GC) (Chai *et al.* 2006). The most significant benefit of this work is that it provides reliable extraction conditions for determining the oxalate contents in pulp and papermaking raw materials.

EXPERIMENTAL

Chemicals and Materials

Chemicals (*i.e.*, HCL, H_2SO_4, H_3PO_4, CH_3COOH, glucose, and xylan) used in the experiment were of analytical grade. Raw materials were provided by Guangdong Dingfeng Paper Co. Ltd. (China). The raw materials were then cut into small pieces with a stainless steel knife and ground in a grinder. Solids retained on a 40-mesh screen were considered rejects and those retained on a 60-mesh screen were accepted.

Methods

Extraction experiment

Extraction experiments were carried out in a container with 5.0 g of bamboo (eucalyptus) powder and 500 mL of extraction solution (distilled water, hydrochloric acid, sulfuric acid, acetic acid, or phosphoric acid) immersed in a water bath at constant temperature. During the extraction experiment, a certain volume of extraction solution was taken from the container for analysis. Table 1 provides more detailed information about the conditions of the extraction experiments.

Table 1. Extraction Process Conditions

Parameters	Experiment conditions
Extraction Time (min)	30, 60, 90, 120, 180, 240, 300, 360, 420,600
Temperature (°C)	50, 60, 70, 80, 90
Extraction Medium	H_2O, HCL, H_2SO_4, H_3PO_4, CH_3COOH
HCL Concentration (mol/L)	0.5, 1.0, 1.5, 2.0, 3.0, 4.0
Liquid-to-Solid Ratio	100:1

Oxalate determination

Determination of the oxalate concentration was done using an Automatic Headspace Sampler and a Model HP-6890 capillary gas chromatograph (Agilent Technologies, Palo Alto, CA, USA) using a thermal conductivity detector (Chai *et al.* 2006; Li *et al.* 2008; Li *et al.* 2014).

RESULTS AND DISCUSSION

Extraction and Determination of Soluble Oxalate

Effect of temperature

Oxalate in the raw material exists partly in the form of soluble salts (free oxalate acid) which can be extracted with distilled water at different temperatures. The effect of temperature on the extraction of soluble oxalate of two materials is shown in Fig. 1 (a) and (b) (a: bamboo b: eucalyptus). The date showed the soluble oxalate content in the extraction liquor increased with increasing temperature. As shown in Fig. 1(a) and (b), the extraction at 70 °C was sufficient to completely extract the soluble oxalate under the given conditions. Thus, the temperature of 70 °C was used in subsequent studies.

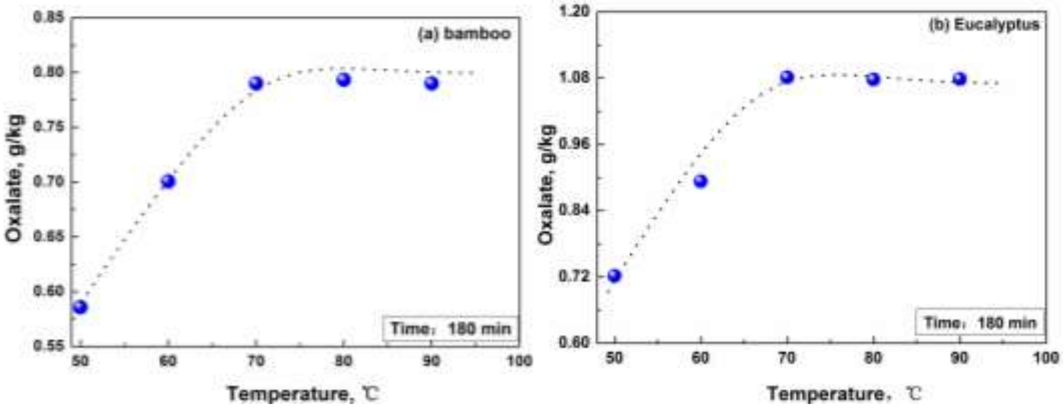

Fig. 1. Effect of temperature on the extraction of soluble oxalate with water (a: bamboo; b: eucalyptus)

Effect of time

As can be seen in Fig. 2 (a), the majority of the soluble oxalate was removed at the beginning of the extraction. After 150 min of extraction, the soluble oxalate content reached a maximum and was maintained at an almost constant value. It was concluded that soluble oxalate was completely extracted. These trends were in agreement with eucalyptus. At this point, the content of soluble oxalate of bamboo and eucalyptus was 0.79 g/kg and 1.09 g/kg, respectively. Therefore, the extraction time of 180 min was chosen.

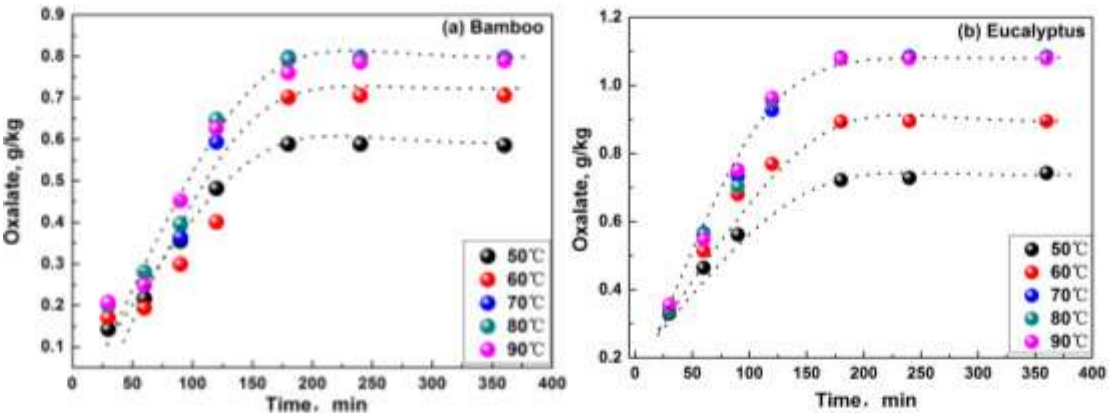

Fig. 2. Effect of time on the extraction of soluble oxalate with water (a: bamboo b: eucalyptus)

Extraction and Determination of Total Oxalate

In order to determine the total oxalate content in plants, different acids (hydrochloric acid, sulfuric acid, acetic acid, and phosphoric acid) were used as extraction media in different experiments. Meanwhile, the effects of other extraction conditions, such as the concentration of the extraction medium, the extraction time, and the temperature, on the degree of extraction are discussed below.

Effect of different acids

Precipitated oxalate is almost always in the form of calcium oxalate in raw materials (Franceschi and Horner 1980). Different acids may have different influences on the dissolution of oxalate. Strong acids (hydrochloric and sulfuric acid) and weak acids (acetic and phosphoric) were used as extraction media to find out which acid would dissolve all oxalates with other conditions kept constant. The change in oxalate concentration using the different acid extraction media is shown in Fig. 3(a) and (b). The oxalate content of bamboo and eucalyptus extracted by hydrochloric acid was about 2.2 g/kg and 2.75 g/kg, which was much higher than that of the other acids, around 1.00 g/kg and 1.30 g/kg. Jadprasong *et al.* found that levels of total oxalate content of 4-cultivated bamboo shoot was more than 1.5 g/kg, and total oxalate was extracted by 2-mol/L hydrochloric acid at 80 °C within 15 min (2006). In addition, the results in Fig. 3(a) and (b) showed that hydrochloric acid functioned better than the other acids. One explanation could be that calcium oxalate dissolves easily in hydrochloric acid and is slightly soluble in dilute acid. Another reason could be that calcium can combine with sulfate ion and form precipitate gypsum species, *e.g.* the hemihydrate or the dihydrate of calcium sulfate with low solubility, and calcium phosphate mineral species are less soluble than the gypsum mineral compounds. In addition, total oxalate extraction increased with extended time. However, the total oxalate content remained unchanged when the time reached 210 min. Therefore, hydrochloric acid was selected as the extraction medium to determine the total oxalate contents of raw materials, and the proper acid extraction duration was 210 min.

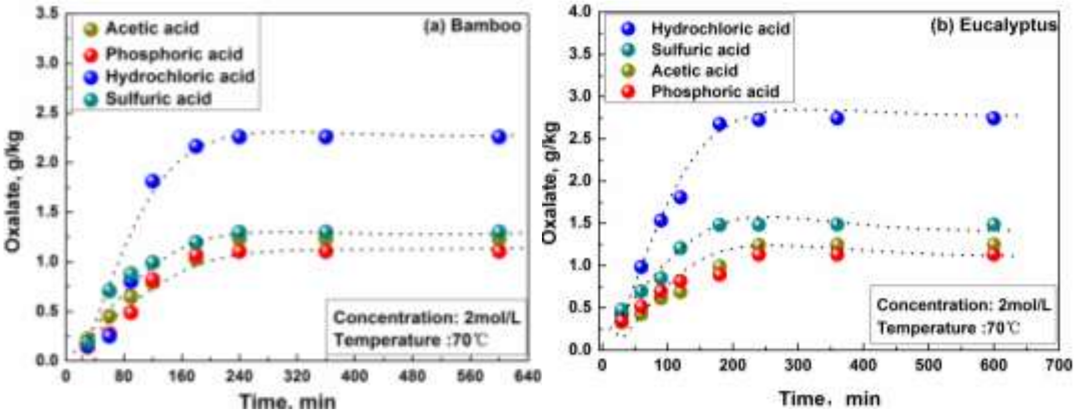

Fig. 3. Effect of different acids on oxalate extraction, concentration of all acids is 2 mol/L (a: bamboo b: eucalyptus)

Effect of hydrochloric acid concentration

The influence of hydrochloric acid concentration on the dissolution of oxalate was studied. As is shown in Fig. 4(a) and (b), oxalate content increased when the hydrochloric acid concentration was increased from 0.5 to 2 mol/L, then leveled off when the acid concentration was further increased from 2 to 4 mol/L. The effect of hydrochloric acid concentration reached a plateau at 2 mol/L. Thus, the proper concentration of hydrochloric acid was judged to be 2 mol/L under the given extraction conditions. These results are in agreement with those of Hönow and Hesse (2002).

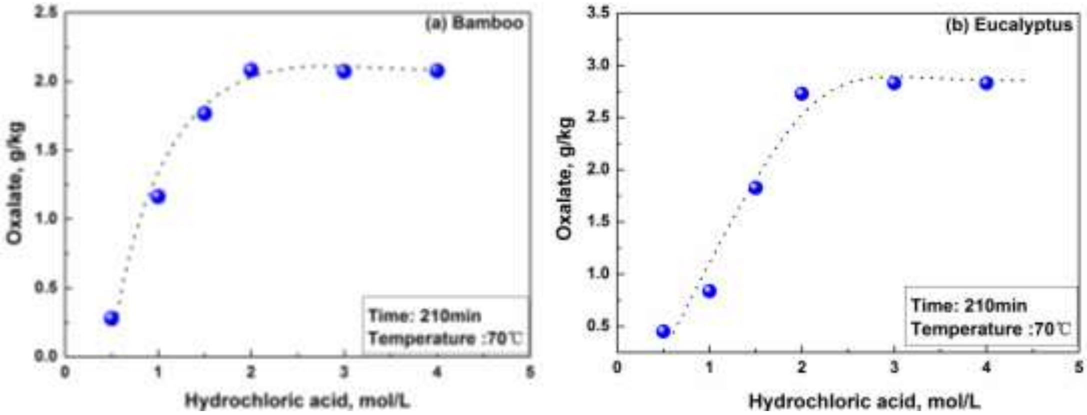

Fig. 4. Effect of hydrochloric acid concentration on oxalate extraction (a: bamboo b: eucalyptus).

Effect of extraction temperature by hydrochloric acids

Temperature was an important parameter during extraction because it affected the dissolution of oxalate. As is shown in Fig. 5 (a) and (b), the oxalate content of two materials in the extract rapidly increased as temperature rose from 50 to 70 °C, then leveled off when the temperature was further increased from 70 to 90 °C. This is because the dissolution reaction absorbs heat from the surrounding environment, making it easy for all oxalate to be dissolved from within the material at increased temperature. The total oxalate content had been completely dissolved from the raw materials when the temperature exceeded 70 °C. In this work, a mild temperature (70 °C) was selected as the extraction temperature. This was in line with the work of Häärä *et al.* (2013), who found that CaC_2O_4 precipitated in pulp can be in soluble form, thus facilitating analysis with 2 mol/L hydrochloric acid at 70 °C for 30 min.

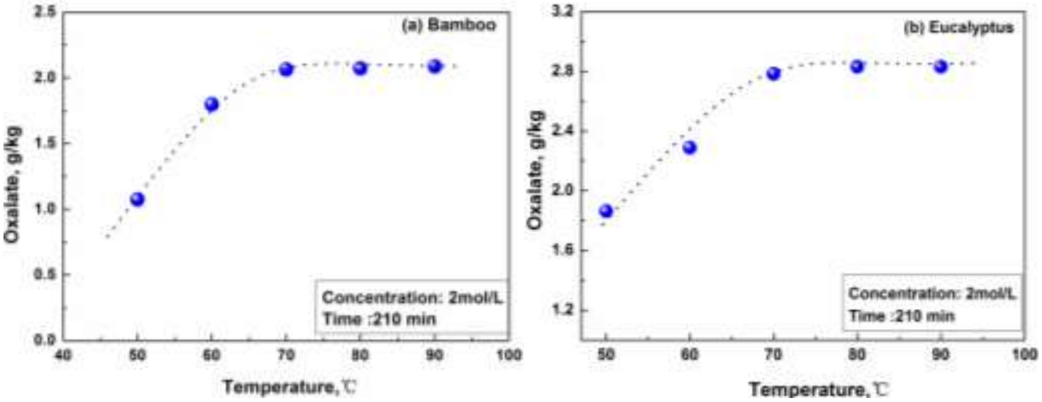

Fig. 5. Effect of temperature on oxalate extraction (a: bamboo power b: eucalyptus power).

Zarembski and Hodgkinson (1962) suggested carbohydrates as a source of oxalate generation by extraction with hot acid. Therefore we tested glucose and xylan at the condition of 2-mol/L hydrochloric acid at 70 °C within 210 min. None of the investigated substances (glucose and xylan) could be the source of the oxalate generation during extraction with 2-mol/L hydrochloric acid at 70 °C within 210 min. The values obtained in this work were in agreement with those of Hönow and Hesse (2002) and indicated that suitable extraction conditions are 25% hydrochloric acid at 100 °C.

Application

The developed method was applied to determine the contents of soluble oxalate and total oxalate in several pulping materials. The results are shown in Table 2.

Table 2. Contents of Total and Soluble Oxalate in Other Pulping and Papermaking Raw Materials*

Material	Total Oxalate (g/kg)	Soluble Oxalate (g/kg)
Acacia	2.3	1.3
Pine	1.4	1.3
Bagasse	2.8	1.4

* Soluble oxalate in materials was extracted in hot distilled water at 70 °C within 180 min, and total oxalate was extracted with 2 mol/L HCl after 210 min at 70 °C

CONCLUSIONS

1. Extraction and determination of the total and soluble oxalate contents in various pulping and papermaking raw materials were achieved.
2. Soluble oxalate in the pulping and papermaking raw materials can be extracted completely in hot distilled water at 70 °C within 180 min, and total oxalate can be extracted completely with 2 mol/L HCl after 210 min at 70 °C.
3. The developed method can be used determine the soluble and total oxalate contents in pulping and papermaking raw materials. It is well-suited for use in the pulp and paper industry.

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REFERENCES CITED

Andrews, J. C., and Viser, E. T. (1951). "The oxalic acid content of some common foods," *Journal of Food Science* 16(1-6), 306-312. DOI: 10.1111/j.1365-2621.1951.tb17384.x

Baker, C. (1952). "The determination of oxalates in fresh plant material," *Analyst* 77(916), 340-344. DOI: 10.1039/an9527700340

Buonocore, M. G. (1955). "A simple method of increasing the adhesion of acrylic filling materials to enamel surfaces," *Journal of Dental Research* 34 (6), 849-853. DOI: 10.1177/00220345550340060801

Chai, X. S., Samp, J., Song, H. N., and Zhu, H. X. (2006). "Novel headspace gas chromatographic method for determination of oxalate in oxygen delignification liquor," *Journal of Chromatography A* 1122(1), 209-214. DOI: 10.1016/j.chroma.2006.04.042

Franceschi, V. R., and Horner, H. T. (1980). "Calcium oxalate crystals in plants," *The Botanical Review* 46(4), 361-427. DOI: 10.1007/BF02860532

Häärä, M., Konn, J., Sundberg, A., and Willfor, S. (2013). "Sample pretreatment for oxalate analysis and the effect of peroxide bleaching parameters on oxalate formation," *Nordic pulp & Paper research journal* 28(1), 42-50. DOI:10.3183/NPPRJ-2013-28-01-p042-050

Hönow, R., and Hesse, A. (2002). "Comparison of extraction methods for the determination of soluble and total oxalate in foods by HPLC-enzyme-reactor," *Food Chemistry* 78(4), 511-521. DOI: 10.1016/S0308-8146(02)00212-1

He, Z., Ni, Y., and Zhang, E. (2003). "Comparison of oxalate formation from spruce TMP: Conventional peroxide bleaching process versus the PM process," *Journal of Pulp and Paper Science* 29(12), 391-394.

Judprasong, K., Charoenkiatkul, S., Sungpuag, P., Vasanachitt, K., and Nakjamanong, Y. (2006). "Total and soluble oxalate contents in Thai vegetables, cereal grains and legume seeds and their changes after cooking," *Journal of Food Composition & Analysis* 19(4), 340-347. DOI:10.1016/j.jfca.2005.04.002

Kasidas, G. P., and Rose, G. A. (1980). "Oxalate content of some common foods: determination by an enzymatic method," *International Journal of Food Sciences and Nutrition* 34(4), 255-266. DOI: 10.3109/09637488009143446

Li, H., Chai, X. S., DeMartini, N., Zhan, H., and Fu, S. (2008). "Determination of oxalate in black liquor by headspace gas chromatography," *Journal of Chromatography A* 1192(2), 208-211. DOI: 10.1016/j.chroma.2008.03.066

Li, H., Chai, X. S., and DeMartini, N. (2012). "Oxalate release and formation during alkaline pulping," *Journal of Wood Chemistry & Technology* 32(3), 187-197. DOI: 10.1515/hf-2013-0123

Li, H., Liu, Y., Zhang, Q., and Zhan, H. (2014). "Determination of the oxalate content in food by headspace gas chromatography," *Analytical Methods* 6(11), 3720-3723. DOI: **10.1039/C4AY00032C**

Libert, B., and Franceschi, V. R. (1987). "Oxalate in crop plants," *Journal of Agricultural and Food Chemistry* 35(6), 926-938. DOI: 10.1021/jf00078a019

Moßhammer, M. R., Stintzing, F. C., and Carle, R. (2006). "Evaluation of different methods for the production of juice concentrates and fruit powders from cactus pear," *Innovative Food Science & Emerging Technologies* 7(4), 275-287. DOI: 10.1016/j.ifset.2006.04.003

Nilvebrant, N. O., Reimann, A., De Sousa, F., Cassland, P., Larsson, S., Hong, F., and Jönsson, L. J. (2002). "Enzymatic degradation of oxalic acid for prevention of scaling," *Progress in Biotechnology* 21, 231-238. DOI: 10.1016/S0921-0423(02)80025-9

Noonan, S. C., and Savage, G. P. (1999). “Oxalate content of foods and its effect on humans,” *Asia Pacific Journal of Clinical Nutrition* 8(1), 64-74. DOI: 10.1046/j.1440-6047.1999.00038.x

Siener, R., Hönow, R., Seidler, A., Voss, S., and Hesse, A. (2006). “Oxalate contents of species of the Polygonaceae, Amaranthaceae and Chenopodiaceae families,” *Food Chemistry* 98(2), 220-224. DOI: 10.1016/j.foodchem.2005.05.059

Singh, P., Sulaiman, O., Hashim, R., Rupani, P. F., and Peng, L. C. (2010). “Biopulping of lignocellulosic material using different fungal species: A review,” *Reviews in Environmental Science and Biotechnology* 9(2), 141-151. DOI: 10.1007/s11157-010-9200-0

Winestrand, S., Sjöde, A., Cassland, P., Hildén, L., Nilvebrant, N. O., and Jönsson, L. J. (2014). “Evaluation of oxalate decarboxylases in industrial bleaching filtrates and in pulp-mill experiments,” *Industrial Biotechnology* 10(2), 126-129. DOI: 10.1089/ind.2014.0001

Yu, L., and Ni, Y. (2005). “Oxalate formation during peroxide bleaching of mechanical pulps,” *Appita Journal* 58(2), 138-143.

Yu, L., and Ni, Y. (2006). “Decreasing calcium oxalate scaling by partial substitution of $Mg(OH)_2$ for NaOH in the peroxide bleaching of mechanical pulps,” *Tappi Journal* 5(2), 9-12.

Yu, L., and Ni, Y. (2007). “Partition of soluble and precipitated oxalate and its implication on decreasing oxalate-related scaling during peroxide bleaching of mechanical pulps,” *Pulp and Paper Canada* 108(1), 39-43.

Zarembski, P. M., and Hodgkinson, A. (1962). “The determination of oxalic acid in food,” *Analyst* 87 (1038), 698-702. DOI**:** 10.1039/AN9628700698

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