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Red algae and their use in papermaking

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ABSTRACT

Gelidialian red algae, that contain rhizoidal filaments, except the family Gelidiellaceae were processed to make bleached pulps, which can be used as raw materials for papermaking. Red algae consist of rhizoidal filaments, cortical cells usually reddish in color, and medullary cells filled with mucilaginous carbohydrates. Red algae pulp consists of mostly rhizoidal filaments. Red algae pulp of high brightness can be produced by extracting mucilaginous carbohydrates after heating the algae in an aqueous medium and subsequently treating the extracted with bleaching chemicals. In this study, we prepared paper samples from bleached pulps obtained from two red algae species (*Gelidium amansii* and *Gelidium corneum*) and compared their properties to those of bleached wood chemical pulps.

1. Introduction

There are over 10,000 described species of red algae (Woelkerling, 1990). Dring (1982) reported that 27.1% of all known species of marine plants are red algae. Although red algae have been consumed by human beings for at least 2800 years, their full agronomic and biotechnological potential has yet to be realized. It has been suggested that red algae can be used in the areas of polyelectrolytes, pharmaceutical products, human nutrition, antimicrobial activity, polysaccharide production, etc. (Kinch et al., 2003).

With regard to chemical composition, red algae consist mostly of polysaccharides, small amounts of proteins, traces of lipids, and inorganic materials. We used red algae for producing raw materials for papermaking to assess their suitability as a replacement for wood pulp. With regard to physical components, the body of red algae contains large amounts of mucilaginous materials such as agar or carrageenan, which can be easily extracted with hot water, and small amounts of solid materials, which are endofibers. After the extraction of the mucilaginous materials, the remaining material mostly consists of endofibers (also known as rhizoidal filaments, rhizine, internal filaments, and hypha Lee et al. (2003)), which are then bleached to make bleached red algae pulp. We believe that bleached red algae pulp can be an alternative source of raw material for papermaking.

We mostly used red algae from the Gelidiaceae family, which contains three genera in Korea: *Gelidium, Pterocladiella,* and *Acanthopeltis*. The shape, growth rate, and amount of endofibers of the members of the Gelidiaceae family can be the criteria for assessing their utilization potential in the pulp and papermaking industries.

There is a long history of the use of mucilaginous carbohydrates extracted from red algae as food additives, and in other applications, but almost no attention has been given to the material that remains after extraction, which consists of mostly rhizoidal filaments or endofibers. Some commercial agar mills in Asia distribute the remaining material to farmers for use as natural fertilizer. In this study, we tried to use these endofibers as a new type of raw material for papermaking, which would be more abundant worldwide than wood fibers. The average growing rate of some red algae in the sea is around 3–10% per day (dry weight) during the growing season (Gel-Or et al., 2004; Ohno et al., 1996; Felicini et al., 1994), and red algae grow under the sea surface worldwide except in the arctic areas. Moreover, global warming and restriction on carbon dioxide emissions make wood cutting more difficult. The price of wood pulp is unstable at present, and will dramatically increase in the long term. We believe that the introduction of red algae pulp from the sea will mitigate the problem of fiber shortage. Actually, there is no quantitative limit on the supply of endofibers or red algae pulp as long as investment for their cultivation in the sea and the necessary processing facilities are available.

2. Methods

2.1. Preparation of red algae pulp

We have previously extracted pulp from red algae species as a preliminary study such as *Gelidium amansii* (J.V. Lamouroux) J.V.

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Lamouroux, *Gelidium asperum* (C. Agardh) Greville, *Gelidium chilense* (Montagne) Santelices and Montalva, *Gelidium robustum* (N.L. Gardner) Hollenberg and I.A. Abbot, *Pterocladiella capillacea* (S.G. Gmelin) Santelices and Hommersand, *Pterocladia lucida* (R. Brown ex Turner) J. Agardh, *Gelidium corneum* (Hudson) J.V. Lamouroux, and *Acanthopeltis longiramulosa* Lee, Y and Kim, B. The shape and the amount of endofibers vary with the species. The quality and amount of mucilaginous carbohydrates, which are mostly in the medullary cells, are different as well. We selected two species (*G. amansii* and *G. corneum*) for further processing after considering their industrial applicability and availability.

We extracted the mucilaginous carbohydrates at either 120 °C or 140 °C (Table 1). No chemicals were used in the extraction process in one series. In another series, 0.5 % sulfuric acid by dry weight of red algae was used to enhance the extraction, and increase the efficiency of the bleaching process. The extraction process is similar to the pulping process used in the manufacture of wood pulp. There is no lignin in red algae, and therefore, there is no need to use strong chemicals to dissolve lignin. The water to red algae (dry weight) ratio was maintained at 10.

In the bleaching process (Table 2), we used two bleaching chemicals: chlorine dioxide in the first stage and hydrogen peroxide in the second stage. In the first stage, we used 5% active chlorine dioxide by dry weight of the material to be bleached at pH 3.5. Temperature, time duration, and initial pH were 80 °C, 60 min, and 3.5, respectively. The pH was controlled by the addition of sulfuric acid. In the second stage, we used 5% active hydrogen peroxide by dry weight of the material. Temperature, time duration, and initial pH were 80 °C, 60 min, and 12, respectively. The pH was controlled by the addition of sodium hydroxide. The second stage was repeated until the brightness of the handsheet was over 80%. We used two red algae species (*G. amansii*, which was collected from Jeju Island in the Republic of Korea; *G. corneum*, which was imported from Morocco in a dried state). Tables 1 and 2 show the extraction and bleaching conditions used in the preparation of the paper samples from these two red algae species.

2.2. Handsheet making and testing

We made 60 g/m^2 handsheets out of the red algae pulp, according to the TAPPI test method (T205 sp-95). To compare the physical properties of red algae pulp to those of market pulp, we used a mixture (50:50) of commercial SwBKP (a mixture of Hemlock, Douglas fir, and Cedar) and HwBKP (a mixture of Aspen and Poplar), both of which are from Canada. The mixture of SwBKP and

Table 1
Extraction conditions of the red algae.

	Chemicals	Temp. (°C)	Term	Solid yield (%)	Extract yield (%)	Washed out (%)[a]	Initial pH	Final pH
Gelidium corneum	No chemicals	120	GC-120	43.93	35.2	20.9	7.0	6.0
		140	GC-140	35.76	51.25	13.0	7.0	5.0
	Sulfuric acid 0.5%	120	GCS-120	40.44	47.66	11.9	5.0	5.8
		140	GCS-140	37.56	46.58	15.9	3.0	4.6
Gelidium amansii	No chemicals	120	GA-120	33.92	31.83	34.3	6.3	6.0
		140	GA-140	33.34	49.36	17.3	6.5	5.2
	Sulfuric acid 0.5%	120	GAS-120	45.31	27.54	27.2	3.5	5.4
		140	GAS-140	33.99	52.21	13.8	3.4	5.0

[a] Washed out (%) = 100 − solid yield − extract yield.

Table 2
Bleaching conditions and solid contents of the red algae.

	Term	Raw material (%)	Yield after extraction (%)	Yield after ClO_2 bleaching (%)	H_2O_2 bleaching replications	Final yield (%)
Gelidium corneum	GC-120	100	43.93	29.86	2	10.43
	GC-140		35.76	32.28	4	9.46
	GCS-120		40.44	29.79	2	9.54
	GCS-140		37.56	30.65	4	8.54
Gelidium amansii	GA-120	100	33.92	25.85	3	10.46
	GA-140		33.34	26.27	4	8.63
	GAS-120		45.31	25.33	2	8.85
	GAS-140		33.99	25.23	4	7.62

Table 3
Comparison of handsheet properties (bleached chemical wood pulp and red algae pulp).

	Term	Caliper (μm)	Basis weight (g/m^2)	Density (g/cm^3)	Breaking length (km)	Stretch (%)	Smoothness[a] W/F (s)	Drainage (s)	Brightness (%)	Opacity (%)
Wood pulp	WP	92.3	60.02	0.65	4.70	2.94	4.2/6.3	6.96	83.68	77.10
G. corneum	GC-120	106.5	61.08	0.57	4.04	2.60	43.5/65.4	14.85	86.59	92.81
	GC-140	113.3	63.28	0.56	3.74	3.02	38.5/82.4	18.41	81.01	96.79
	GCS-120	80.0	53.45	0.67	4.17	2.46	42.3/68.6	18.88	86.03	92.30
	GCS-140	108.3	60.60	0.56	3.41	1.83	38.8/83.2	18.13	83.71	96.08
G. amansii	GA-120	124.3	62.17	0.50	2.89	2.79	52.3/77.8	9.79	82.47	92.85
	GA-140	130.7	60.30	0.46	2.98	3.46	44.3/68.4	10.01	77.97	95.72
	GAS-120	126.8	60.98	0.48	3.25	4.52	53.2/85.3	10.74	86.66	95.51
	GAS-140	141.5	63.73	0.45	2.93	3.47	45.7/74.2	10.73	84.00	95.39

[a] Bekk smoothness in seconds. Wire side/felt side (W/F).