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Red algae and their use in papermaking

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A B S T R A C T

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).

HwBKP was refined by a valley beater to 450 csf and handsheets of 60 g/m^2 were prepared.

Table 3 shows the properties of handsheets derived from these pulps. The density (T410 om-98, T411 om-97), breaking length, which is a measure of tensile strength (T494 om-96), drainage (T221 cm-99), Bekk smoothness (T479 cm-99), brightness (T452 om-98), and opacity (T425 om-96) of the handsheets were measured according to the TAPPI test method.

3. Results and discussion

3.1. Red algae pulp and its handsheet properties

A cross section of dried *G. amansii* is shown in Fig. 1, where small fibers, and large holes can be observed. The small fibers are endofibers, and the large holes are from medullary cells. From Tables 1 and 2, the yield of the red algae pulp decreased as the extraction temperature was increased or as we increased the number of hydrogen peroxide stages. When acid was added during the extraction process, the pulp yield decreased to around 8%. To increase the brightness of the handsheet to over 80%, it seems that the pulp yield of the two red algae species should be 8–11 %. The red algae that we used were harvested from a wild habitat under the sea, and contained mud, dirt, parasitic plants, and strongly attached calcium substances on their surfaces. If red algae were cultivated rather than collected from the wild, higher yields and a higher quality of red algae pulp could be expected. The bleaching process was continued until more than 80% brightness was obtained, and the yield was calculated at the final stage.

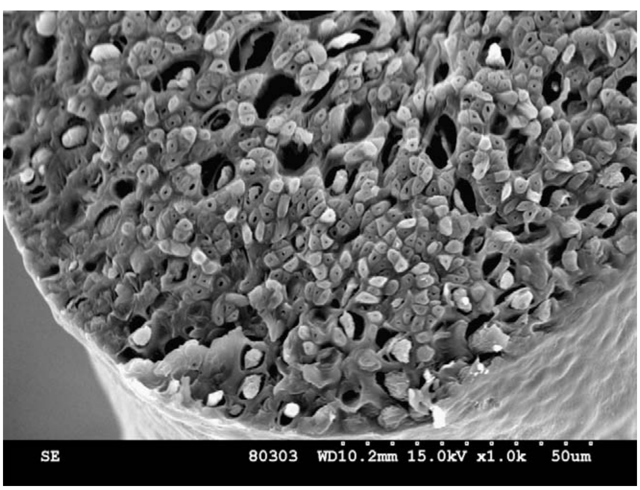

Fig. 1. Cross sectional shape of dried *Gelidium amansii* (J.V. Lamouroux) J.V. Lamouroux.

Table 3 summarizes the test results for the red algae and wood pulp handsheets. We observed that the breaking length of the red algae pulp was lower than that of wood pulp. However, the Bekk smoothness of red algae pulp was exceptionally higher than that of wood pulp. Smoothness is an essential property in printing and red algae pulp is expected to be an excellent source of fiber for high quality printing paper. To increase the smoothness of wood pulp to a level comparable to that of red algae pulp, would require a coating process, which is very expensive in conventional papermaking. The opacity of the red algae pulp handsheet was also considerably higher than that of wood pulp. To obtain over 90% opacity, more than 20% calcium carbonate would have to be added to the wood pulp furnish. The addition of calcium carbonate to wood pulp results in a significant decrease in its breaking length. Red algae handsheet shows high brightness comparable to wood pulp. The CIE L*, A*, and B* values of 'GC-120' in Table 3 were 94.9, −0.36, and 2.16, respectively.

The reasons for the very high smoothness and high opacity of the red algae handsheets can be determined by studying the morphology of the red algae fibers and their handsheets. Figs. 2 and 3 show the surfaces of the handsheets. Red algae handsheets had a highly smooth surface, whereas wood pulp handsheets had a rough one. The specific surface area usually determines the opacity of the paper, and the short and very narrow fibers that can be observed in the red algae handsheet (Fig. 2) produce a very high specific surface area (Scott, 1989). Fig. 4 shows the cross sections of the red algae fibers inside the handsheet at a high magnification, where the endofibers had a very small hole in the middle.

It was found that paper made using red algae pulp had extremely high smoothness, which is a valued property for high quality printing paper, and high opacity, which is very useful for making thin printing paper.

We measured the length and width of typical red algae pulp fibers from *G. amansii*, and they were 500–1000 μm in length, and 3–7 μm in width in the wet state. The width of the dried endofibers was 2–4 μm while that of typical wood fibers 20–40 μm. There was very little difference in the average length and width of the endofibers between *G. amansii* and *G. corneum*. The chemical composi-

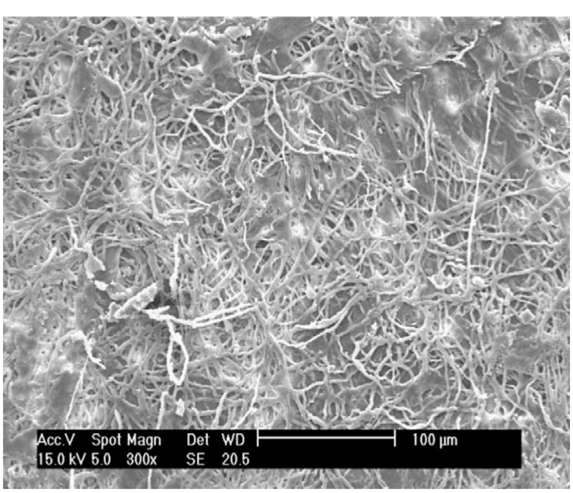

Fig. 2. Shape of red algae pulp fibers in handsheet (300×).

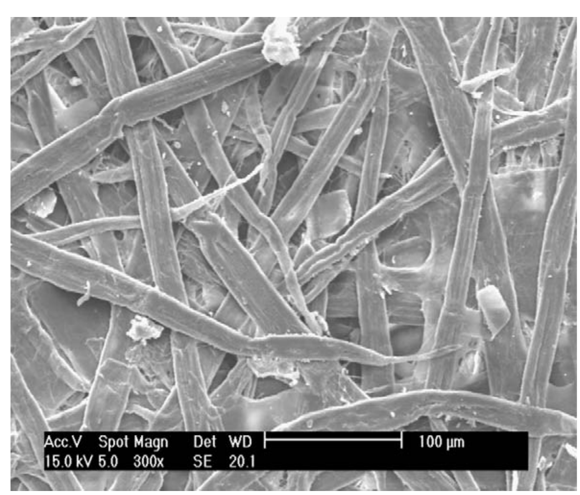

Fig. 3. Wood pulp (mixture of SwBKP and HwBKP) in handsheet (300×).

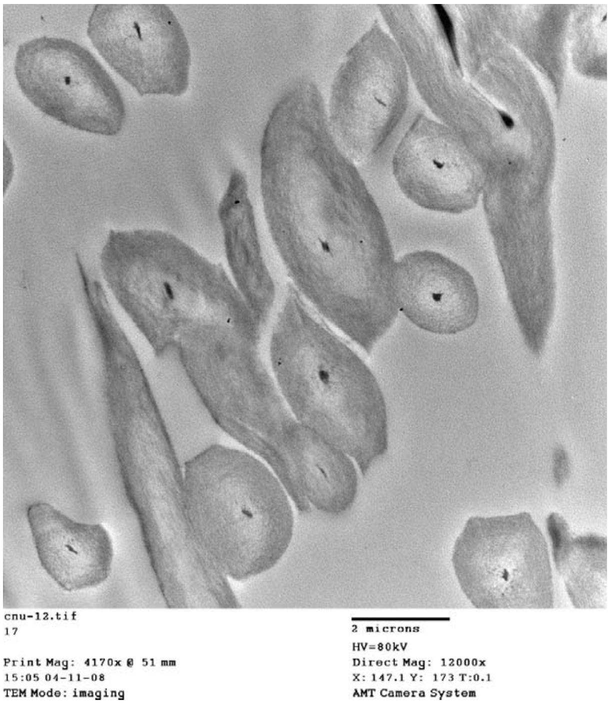

Fig. 4a. View of part of a cut edge of red algae handsheet (space bar is 2 μm).

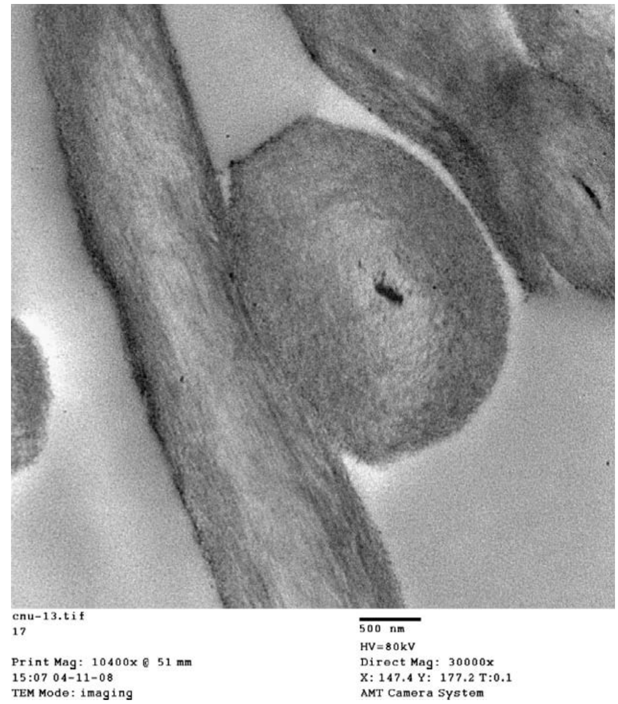

Fig. 4b. View of part of a cut edge of red algae handsheet (space bar is 500 nm).

tion and crystalline structure of the endofibers are currently under investigation.

Drainage, which is related to the productivity and energy consumption of the papermaking process, was slower for red algae pulp than for wood pulp. The short fiber length and high specific surface area of the fibers of red algae pulp result in slow drainage. However, it was observed that extraction process at higher temperature made the drainage of red algae pulp faster, but strengths of their handsheets lower. Further development of the extraction process for improving drainage will be helpful for the wider utilization of red algae pulp.

There were few differences in the breaking length and drainage between *G. corneum* and *G. amansii*. Breaking length was higher for *G. corneum*, but drainage was faster for *G. amansii*. Bleaching of *G. amansii* was not effective when the extraction process was performed at 140 °C in the absence of chemicals (Table 3).

3.2. Pilot trial results of red algae pulp

We conducted a pilot trial using red algae pulp for making printing grade paper (40–50 g/m^2) in a slow papermachine (50–60 m/min), located at the Cheon Yang Paper Co., Jeonju, Republic of Korea. The papermachine was originally designed to use exceptionally long non-wood fibers. The paper width was 1.2 m. One Yankee and three supplemental cylinder dryers were installed. We used a cylinder former to make the trial samples. The wet pick-up from the wet press to the dryer was excellent. There were some difficulties in the drying section due to the high wetness of the red algae furnish, but it was found to be manageable. The properties of the trial samples were compared to those of commercial light weight printing paper, which was made from wood pulp, and was of a premium grade used for the production of Bibles and dictionaries (Table 4).

Red algae paper had a Bekk smoothness value of 150–300 s, whereas commercial premium grade printing paper had a smoothness of 30–150 s (Table 4). The higher the Bekk value is, the smoother the paper. Commercial copy papers usually have a Bekk smoothness value of 15–30 s. Red algae paper had higher opacity and brightness but the tensile strength was not lower at the same basis weight.

The applications of paper made from red algae pulp are widespread – high quality printing paper, filter paper, cigarette paper, the surface layer of multiply paper, security paper, edible paper, medical paper, and food paper.

4. Conclusions

We introduced the potential use and value of red algae pulp as a raw material for papermaking. To be economically feasible, mass cultivation of red algae is essential; this would provide clean cultivated red algae without impurities and result in higher yields. The process of making high brightness pulp from red algae is simpler

Table 4
Comparison of the properties of trial red algae paper to commercial papers.

Sample[a]	Basis weight (g/m^2)	Density (g/cm^3)	Bekk smoothness (s)		Breaking length (km)		Brightness (%)	Opacity (%)	Ash[b] (%)
			Felt	Wire	MD	CD			
Commercial copy paper	75	0.75	33.0	19.9	7.88	2.70	83.2	94.9	16.5
Red algae trial paper	46	0.76	273.0	182.9	5.64	4.39	81.9	93.0	0.42
Commercial light wt. paper A.	42	0.80	55.1	33.8	6.24	4.20	70.5	87.6	18.5
Commercial light wt. paper B	43	0.86	141.7	97.3	6.03	4.06	72.2	90.0	17.3

[a] All the samples were calendered.
[b] Ashes were measured at 450 °C.

than that from wood; no pulping chemicals are used and bleaching process is much simpler.

- The yield of bleached red algae pulp from the selected wild red algae (*G. amansii* and *G. corneum*) was 8–11% , with a brightness over 80%.
- The handsheets produced from red algae pulp had very high Bekk smoothness and opacity, which are essential properties for high-valued printing paper, when compared to those of wood pulp.

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