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Simultaneous production of bio-ethanol and bleached pulp from red algae

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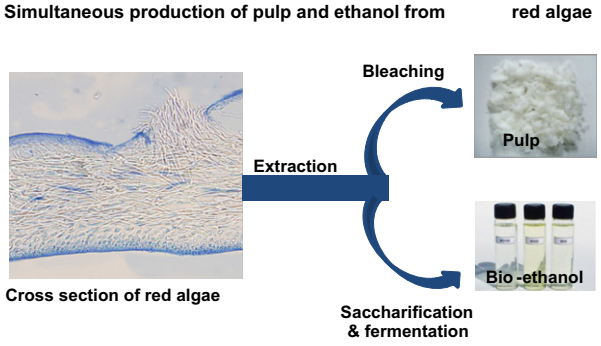
HIGHLIGHTS

- High quality pulp and ethanol were produced simultaneously from red algae.
- Bleached pulp yield was 10–11%, and ethanol 10% (w/w) by dry weight of red algae.
- Sodium thiosulfate was an effective additive in red algae extraction process.
- Commercialization of red algae pulp may enable low cost ethanol production.

GRAPHICAL ABSTRACT



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ABSTRACT

The red algae, *Gelidium corneum*, was used to produce bleached pulp for papermaking and ethanol. Aqueous extracts obtained at 100–140 °C were subjected to saccharification, purification, fermentation, and distillation to produce ethanol. The solid remnants were bleached with chlorine dioxide and peroxide to make pulp. In the extraction process, sulfuric acid and sodium thiosulfate were added to increase the extract yield and to improve de-polymerization of the extracts, as well as to generate high-quality pulp. An extraction process incorporating 5% sodium thiosulfate by dry weight of the algae provided optimal production conditions for the production of both strong pulp and a high ethanol yield. These results suggest that it might be possible to utilize algae instead of trees and starch for pulp and ethanol production, respectively.

1. Introduction

Bleached red algae pulp fibers were first prepared by Seo et al. (2009, 2010) and their performances as papermaking raw materials was shown to be excellent with respect to opacity and smoothness of the handsheet paper. In the process of pulp generation, extracts containing agar are produced, which can be used as a substrate for ethanol production after saccharification, purification, and fermentation (Keating et al., 2004; Dhaliwal et al., 2011). Water-soluble extracts from *Gelidium elegance* contained mostly galactan, and 3,6-anhydrogalactose and D-galactose amounted to over 95% of the dry weight of the extracts (Do et al., 1997). *Gracilaria verrucosa* extracts contained 80–85% of galactan by weight (Do et al., 1997). The authors also determined that total soluble carbohydrates in the extracts from *G. elegance* and *G. verrucosa* amounted to 30–42% of the total algal dry weight.

To produce high-quality pulp more effectively, it is necessary to remove organic compounds (mostly galactan) from the algae effectively during the extraction process so that excessive use of

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bleaching chemicals for treating solid remnants can be avoided. The dry weight of the soluble carbohydrates in the extracts can be increased at elevated extraction temperatures, but temperatures over 140 °C usually cause darkening of the solid remnants and bleaching of the darkened remnants is very difficult, if not impossible by our experimental procedure. To produce ethanol effectively from the extracts, the soluble carbohydrates in the extracts should have a low degree of polymerization (DP) with minimum amounts of impurities such as furfurals and hydroxymethyl furfurals (HMFs). In the present study, *Gelidium corneum*, harvested off the Atlantic coast of south Morocco, was extracted with water in the presence of sulfuric acid or sodium thiosulfate, and the extraction efficiency was compared with that of water alone. Sulfuric acid was selected as an additive in the extraction process to enhance de-polymerization of galactan. Sodium thiosulfate was selected as it was superior to other sulfur-containing chemicals such as sodium bisulfate, sodium hydrosulfite, and sodium metabisulfite in respect of making easy in bleaching, protecting red algae pulp fibers from weakening, and producing large amount of agar extract. Sulfur-containing chemicals usually increase carbohydrate retention and protect cellulosic fiber strength in wood kraft pulping (Casey, 1980). Another important consideration for additive selection was the amount of fermentation inhibitors (e.g., furfurals and HMFs) generated in the extraction process.

2. Methods

2.1. Extraction and paper preparation

G. corneum was imported from Setexam Co., located in Morocco in a dry state. They were washed with water to remove foreign materials such as salt, sand, seashell debris, and mud prior to extraction. The algal material was extracted with water alone at 120 and 140 °C for 3 h (water-1 and water-2 in Table 1, respectively). When the algal material was extracted with additives such as 0.2% of sulfuric acid and 5% of sodium thiosulfate by dry weight of the algae at 120 °C and 140 °C for 3 h, they were denoted as H_2SO_4-1, H_2SO_4-2, $Na_2S_2O_3$-1, and $Na_2S_2O_3$-2, respectively, as shown in Table 1. The solids were separated from the extract by passing through a 200 mesh screen and bleached to make high brightness pulp. In the bleaching process, chlorine dioxide and hydrogen peroxide were used in the first and second stages, respectively. In the first stage, 5% active chlorine dioxide by dry weight was employed at pH 3.5. The temperature, time duration, and initial pH were 80 °C, 60 min, and pH 3.5, respectively. The pH was controlled by the addition of sulfuric acid. In the second stage, 5% active hydrogen peroxide by dry weight of the material was used. The temperature, time duration, and initial pH were 80 °C, 60 min, and pH 12, respectively. The pH was controlled by the addition of sodium hydroxide. The second stage was repeated until the brightness of handsheets was over 80%. It took two and four H_2O_2 bleaching steps after extraction at 120 and 140 °C, respectively.

The bleached pulp was used for the production of handsheets according to the TAPPI standard method (T205 sp-95. Forming handsheets for physical tests of pulp). The physical properties of the handsheets were tested according to TAPPI test methods, i.e., the density (T410 om-98, T411 om-97), the breaking length (a measure of tensile strength; T494 om-96), the drainage (T221 cm-99), the brightness (ISO 2470), and the opacity (ISO 2471). The brightness and the opacity were measured using the Color Touch model manufactured by Technidyne Co. All the data are averages of results from triplicate experiments, unless otherwise indicated.

2.2. Saccharification of Gelidium extracts

G. corneum extracts of 500-ml volume were hydrolyzed in the presence of 0.5–1% oxalic acid at 121 °C for 30 and 60 min, and neutralized by the addition of calcium carbonate. The hydrolysates were centrifuged at 10,000*g* for 10 min, and the supernatants were analyzed to determine the reducing sugars by the DNSA (dinitro salicylic acid) method (Miller, 1959). The total sugar concentration was measured by the phenol-sulfate method (Dubios et al., 1956). After saccharification, the red algae extract was treated by steam stripping to remove furan compounds such as furfural (FUR) and hydroxymethyl furfural (HMF) (Mansilla et al., 1998; Demirbas, 2006; Warner et al., 2006), and used as a substrate for ethanol fermentation (Linden et al., 1992; Maleszka et al., 1982).

2.3. Ethanol production

A galactose-fermenting yeast strain, *Saccharomyces cerevisiae* No. 9, was isolated from sludge of a waste water treatment site of a local mill producing dried agar, Taeryong agar-agar Co., located in Miryang, Kyungsangbuk-Do, Republic of Korea, in 2008 (Kim and Yoon, 2011). It produced ethanol from galactose at 30 °C as shown Fig. 1. The yeast was grown in a 500-mL Erlenmeyer flask containing 100 mL of YP-sugar medium containing 0.2% yeast extract, 1% peptone, 0.15% diammonium hydrogen phosphate, and 3% galactose at 30 °C, pH 5.6 for 20 h with shaking at 120 rpm. Cells were harvested by centrifugation (at 12,000*g*, 15 min, 4 °C), and cell pellets were resuspended in 60 mL of fresh YP-sugar broth and inoculated into 2 L of culture medium (ca. 2.0×10^7 CFU mL^{-1}) in a 5-L fermenter (KF-5L; Kobiotech Co., Incheon, Korea). Ethanol fermentation was carried out in 2 L of YP-sugar medium containing 12.3% reducing sugars obtained from *G. corneum* hydrolysates prepared previously. Ethanol concentration in the fermented broth was determined using a hydrometer after distillation. The yield of ethanol was calculated by comparison with theoretically full glucose conversion to ethanol, using the Gay-Lussac Table, according to which 1 g of glucose can be converted to 0.511 g of ethanol and 0.489 g of carbon dioxide.

The chemical compositions of the soluble carbohydrates in the extracts, solid remnants, and bleached red algae pulp from *G. corneum* were analyzed. The samples were hydrolyzed by

Table 1
Parameters and results for the extraction of the red algae, *G. corneum*.

Sample names	Chemicals	Chemical dosage (%)[a]	Extraction temp. (°C)	Solid yield (%)	Extracts yield (%)	Physical state of extract (20 °C)	Extracts conc. (%)	Initial pH	Final pH
Water–1	–	0.0	120 °C	43.93	35.20	Gel	6.24	7.0	6.0
Water–2	–	0.0	140 °C	35.22	50.84	Solution	6.69	7.0	4.0
$Na_2S_2O_3$–1	$Na_2S_2O_3$	5.0	120 °C	38.50	46.89	Gel	7.09	7.5	7.0
$Na_2S_2O_3$–2	$Na_2S_2O_3$	5.0	140 °C	33.06	55.97	Solution	7.15	6.5	5.0
H_2SO_4–1	H_2SO_4	0.2	120 °C	39.63	40.12	Gel	6.11	6.0	5.5
H_2SO_4–2	H_2SO_4	0.2	140 °C	34.36	51.17	Solution	6.52	6.0	4.0

[a] Chemical weight % based on the algal dry weight (assay. H_2SO_4, 98.0%; $Na_2S_2O_3$, 95.0%).