

Agar production from *Gracilaria* with improved qualities

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ABSTRACT

Agar is manufactured from the red algae *Gelidium*, *Gelidiella* and *Gracilaria*. It is one of the commercially important marine products. The agar produced from *Gelidium* and *Gelidiella* is considered as the first grade agar and fetches high price. The presence of sulphate content in *Gracilaria* agar affects the quality of the agar and it is usually sold at low price. It is used only as food grade agar. The different Indian and foreign technologies for production of *Gracilaria* agar with improved yield and quality are given in this paper.

Introduction

Marine algae are one of the renewable and economically valuable sea wealth. Among various marine products, agar is a phytochemical extracted from red algae. The species of *Gelidium*, *Gelidiella*, *Pterocladia* and *Gracilaria* are commercially exploited and used as raw material for the production of agar (Jensen 1979; Chapman and Chapman 1980; Craige and Wen 1984; Wang *et. al.*, 1984). In India the raw materials for agar production are *Gelidiella acerosa* and *Gracilaria edulis*. About 180 species of *Gracilaria* occur in the world (Kim, 1970). Nearly 25 agar industries are functioning in maritime states of Tamilnadu, Kerala and Karnataka and producing annually 75 tons of agar. Most of the agar industries are using *Gracilaria* spp as raw material and manufacturing food grade agar. During the years from 1978 to 2000, 108 to 982 tons of *Gracilaria edulis*, 2 to 96 tons of *G. crassa*, 3 to 110 tons of *G. foliifera* and 129 to 830 tons

of *G. verrucosa* were utilised per annum by the Indian agar industries (Silas and Kalimuthu 1987; Kaliaperumal and Kalimuthu 1997; Kalimuthu and Kaliaperumal 1991 and 1996; Kaladharan and Kaliaperumal 1999; Ramalingam *et. al.*, 2000; Kaliaperumal and Uthirasivan 2001). It shows that most of the agar industries depend only on *Gracilaria* spp as raw material, not only in India but also in foreign countries (Durairatnam, 1980, 1984, 1987 and 1990; Durairatnam and Santos, 1981; Hurtado Ponce and Umesaki 1987). About 60% of the annual world production of agar is mainly from *Gracilaria* (Matsushashi and Hyashi, 1972; Jensen, 1979; Abbot, 1980; Bird *et. al.*, 1981; Durairatnam and Santos, 1981; Muller and Furneaux 1987). In India the extraction of agar by cottage industry method was developed by Thivy (1960) and the commercial method by Visweswara Rao *et. al.* (1965). Many Indian workers later developed different technologies for agar extraction with some modification (Bose *et. al.*, 1943;

Chakraborty, 1945, Joseph and Mahadevan, 1948; Karunakar *et. al.*, 1948). The agar extracted from *Gelidiella* is found as superior quality when compared with that of *Gracilaria* spp. The presence of sulphate content in the *Gracilaria* agar is responsible for the low gel strength. In countries like China, Japan and Philippines, different technologies are developed for agar extraction from *Gracilaria* spp to improve the quality of agar. Those different methods are summarised in this paper.

Agar production from *Gracilaria* spp. in India

The species of *Gracilaria* are collected from the southeast coast of Tamilnadu in the Gulf of Mannar Islands and in the coastal area between Rameswaram and Sethubavachatram in Palk Bay side; dried in sun on the beach and sent to the agar industries for production of food grade agar. The sundried seaweeds are washed with freshwater to remove the sand and other water soluble impurities in the agitator tank. The washed seaweeds are then treated with hydrochloric acid followed by fresh water washing. The acid free washed seaweeds are boiled and the agar is extracted. The agar gel is cooled at room temperature and then kept in freezing room at -20°C for 24 hrs. After thawing, the agar sheets are bleached. The methods used in India for processing *Gracilaria edulis* and other *Gracilaria* spp for agar production are given in Annexure 1 to 8.

The agar extracted by preacid treatment method usually has low gel strength

74-150 g/cm² (Mathew *et. al.*, 1993; Coppen, 1989; Kaliaperumal and Uthirasivan, 2001). As the yield and gel strength vary from species to species and also according to extraction method (Armisen and Galatas, 1987), it is necessary to develop new processing technology suitable to our *Gracilaria* species for the production of good quality agar.

Alkali treatment techniques

At suitable temperature, by treating *Gracilaria* with dilute alkaline solution containing Calcium, the yield and quality of agar can be improved (Funaki and Kojima, 1951; Durairatnam and Albanisa Maria De Sene, 1993). Treatment with 2% NaOH solution and then with 5% NaOH solution at a higher temperature or under pressure, will be an useful technique, if the yield is very low. The seaweed residues after extraction still remain stiff. In general, the *Gracilaria* weeds are treated with 6-7% NaOH solution for 1-2 hours at 70-90°C and for some species a higher concentration of alkali is needed (Ji Ming Hou, 1990). Using NaOH, Japanese have developed the technology of alkali treatment to improve the gel strength of *Gracilaria* agar. The quality deciding factor is the presence of sulphate content in the agar. NaOH solution remove the sulphate content of the agar ($-SO_3 + NaOH = Na_2SO_4 + H_2O$). The treatment time, temperature and concentration of NaOH vary in the methods followed by research workers of many countries (Ji Ming Hou, 1990) and these details are given below.

Country	Concentration of NaOH (%)	Treating temp. (°C)	Time of treatment (hr)
Argentina	6.0	50-60	1.0
Chile	6.0-7.0	88-90	2.0
Mexico	6.0	90	0.5-1.0
Africa	6.0	70	1.0-1.5
India	20.0	70	1.0
Taiwan	10.0	85-90	1.0
Portugal	4.0-5.0	60	1.0

a) Japanese method

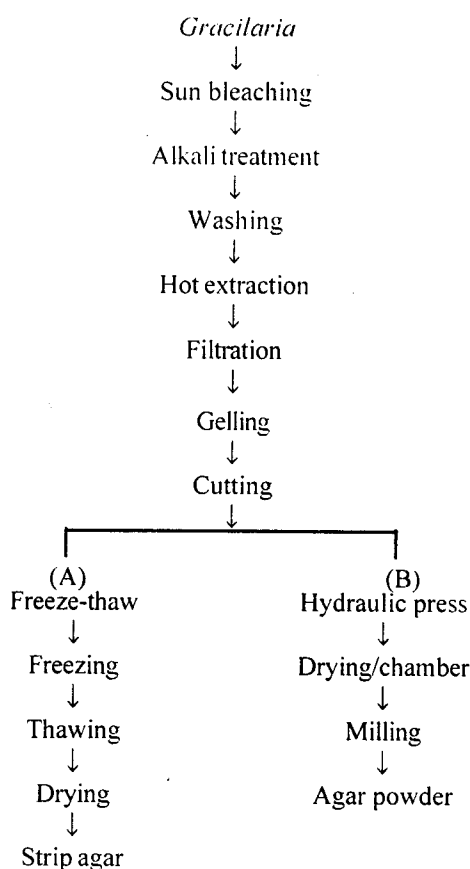
In Japan 140 kg of NaOH is dissolved into 1700 litre of water and 400 kg. of dry *Gracilaria* is treated as follows (Akio Okazaki, 1971).

Grade of <i>Gracilaria</i>	Treating temp. (°C)	Treatment period (hr)
Superior quality	85 - 90	3.0 - 4.0
Middle quality	80 - 82	2.0 - 3.0
Inferior quality	70 - 75	1.5 - 2.0

After alkali treatment, the seaweed is washed thoroughly and boiled at 98-99°C for 3.5 to 4.0 hr. If necessary, to reduce the boiling time from 3.5 to 4.0 hr to 1.5 to 2.0 hr, about 2.5 to 3.0 litres of weak acid like acetic acid is added in the agar extractor, after 30 minutes of cooking. The press extractor is unsuitable as the outer layer of the seaweed *Gracilaria* is very soft.

b) Chinese method

Since the amount of sulphated galactan varies with species, growth season and locality, the alkali treatment process is an extreme important step for *Gracilaria* to improve the quality of agar product (Ji Ming Hou, 1990). The flow sheet of *Gracilaria* agar production in China is given below.



Since 1950, many attempts were made in China to process *Gracilaria* for getting quality agar and high yield. Among the 17 species of *Gracilaria* exploited for the agar production, agar of *Gracilaria asiatica* and *G. tenuistipitata* have higher gel strength of 234 - 1025 g/cm² and 329 - 1035 g/cm² respectively (1% agar gel). The yield and gel strength from these species are mainly dependant on the processing technology using the proper concentration of alkali, treatment time and temperature. The strong prealkaline treatment before extraction cause hydrolysis of sulphate groups and transforms L-galactose 6 - sulphate into 3, 6 - anhydro-L-galactose and improves the gel strength of the

Gracilaria agar. The three methods of alkali treatment used in China (Chen Jia Xin, 1995) are given below and agar processing technologies developed in China is given in Annexure - 4.

i) Treatment with high concentration of NaOH at room temperature

Gracilaria seaweed is submerged in 30-40% of NaOH solution for 5 days or more at room temperature. The volume of NaOH is about 15 to 20 times of the dry raw material. By this method the yield and gel strength of agar are high. The demerits of this method are that it is a long time processing method and it requires large quantities of NaOH and also large size seaweed immersing tanks. This method is suitable for delicate *Gracilaria* plants.

ii) Treatment with medium concentration of NaOH at tepid (moderate) temperature

In this method usually 15-20% concentration of NaOH is used at 60-85°C treating temperature for 16-20 hr. This is suitable to almost all the species of *Gracilaria*. This method also improves the yield and gel strength of the agar to a maximum level.

iii) Treatment with lower concentration of NaOH at high temperature

Usually a low concentration of NaOH (2-6%) is used at a higher temperature (90-95°C) for 1-3 hr. The concentration of NaOH and temperature are dependant on the quality and texture of *Gracilaria* species. For seaweeds with hard texture and large quantities of seaweeds, this method is used.

c) Methods followed in other countries

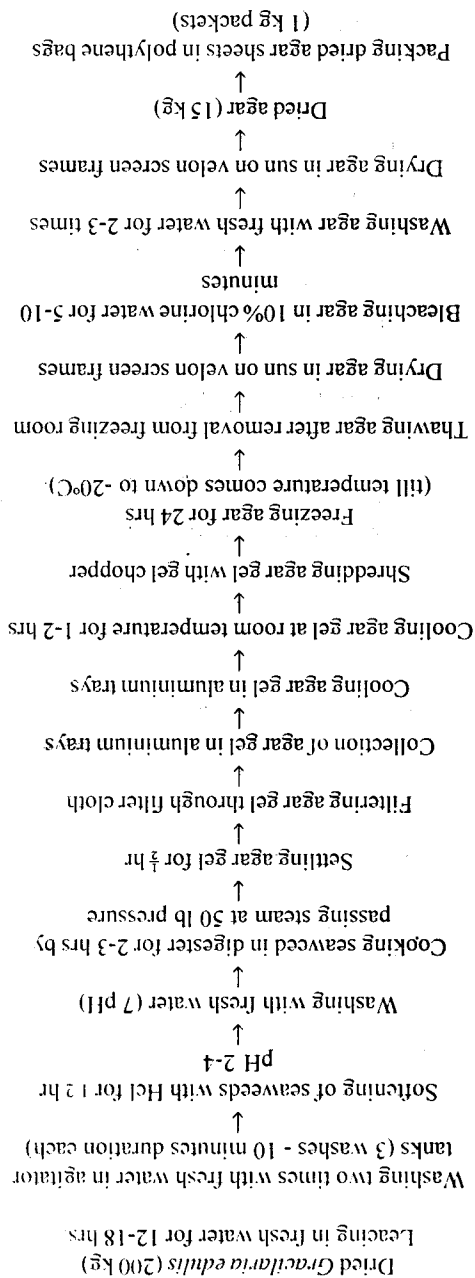
The various methods used for agar processing in China, Philippines, Myanmar, Vietnam and Thailand (Anon, 1996) together with the methods developed in India are given in the Annexures 1 to 8. Details regarding the concentration of NaOH and treatment time, temperature, neutralising agents and other

chemicals added at the boiling stage are given in the flow charts (Annexures 4 to 8). Neutralising the seaweeds after alkali treatment is an important step and the seaweeds should be thoroughly washed free of alkali. Generally in China, India and Myanmar, the seaweeds after thorough washing with fresh water, they are neutralised with hydrochloric acid. But in Philippines and Thailand, acetic acid is used to maintain the pH at 5.6 to 6.0. At the time of extraction of agar, Sodium metaphosphate and Barium perchlorate are used in China whereas Disodium tetraborate ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) solution and acetic acid are used in Vietnam (Annexure - 7). The concentration of bleaching agents such as bleaching powder and Sodium hypochlorite and also the bleaching time should be strictly followed. After this washing, reduction should be carried out using the reducing agents such as Sodium thiosulphate (Ji Ming Hou, 1995).

Finally the agar sheets should be dried at 60°C to prevent depolymerisation of the product. The alkaline treatment causes hydrolysis of sulphate group and so it is otherwise called as "Sulphate alkaline hydrolyse" method. The yield and gel strength from some species are mainly dependent on the processing methods. Although the alkali treatment with a higher concentration (30-40%) of NaOH at room temperature is beneficial to the quality and the yield of agar, the consumption of NaOH is too high. A rational condition with medium concentration (8-10%) of NaOH at 80-85°C is recommended for commercial production of agar from *Gracilaria*. The yield of agar obtained by alkali treatment method varies from 10 to 15% whereas the yield is only 10% in other methods with acid treatment. The Indian agar industries must follow or develop the suitable processing technologies (Annexure 4 to 8) for production of good quality food grade agar from the *Gracilaria* species occurring in our waters.

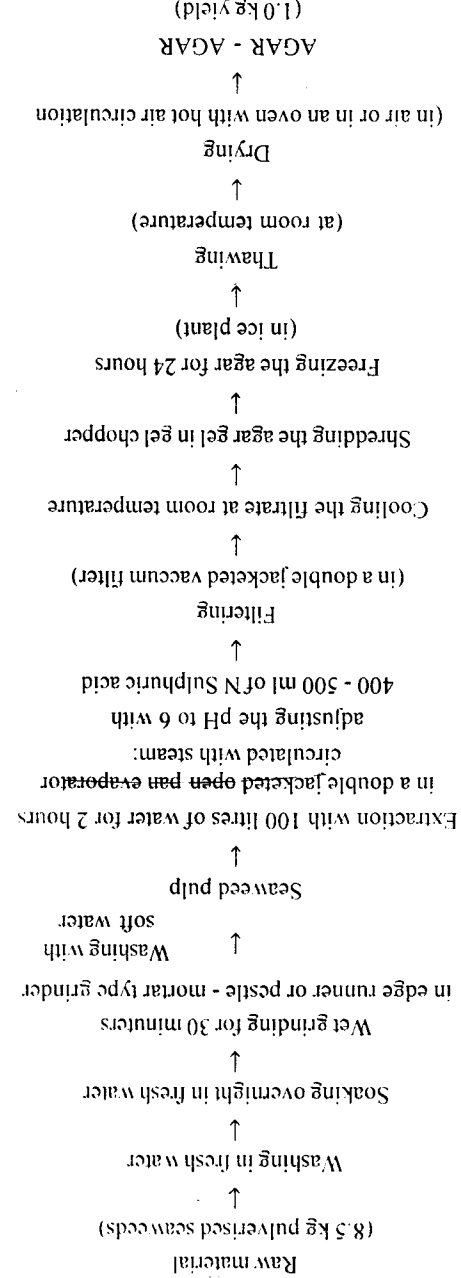
Annexure 1

Production of agar on commercial scale in India (Kaliaperumal and Uthirastavan, 2001)



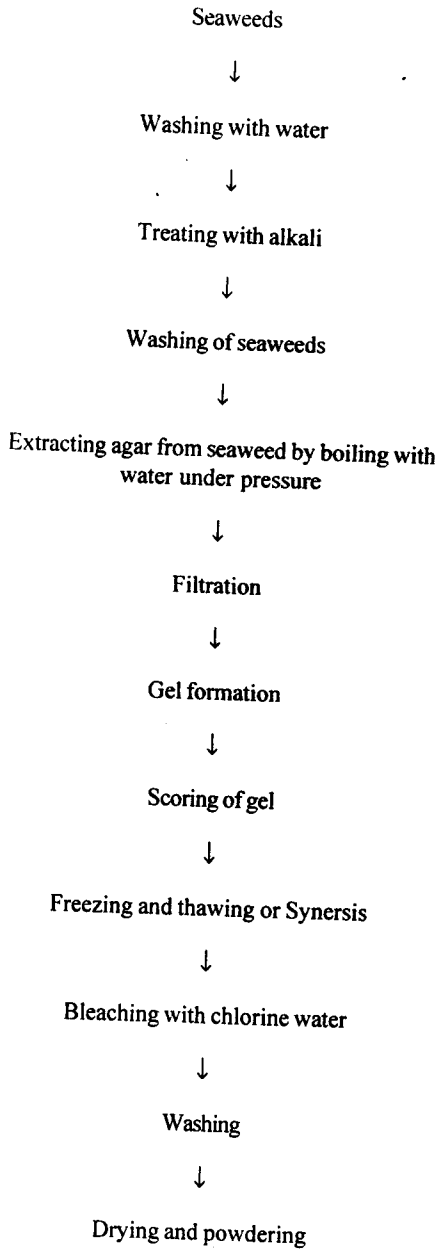
Method for agar manufacture on a commercial scale in India (Visweswara Rao et al., 1965)

Annexure 2



Annexure 3

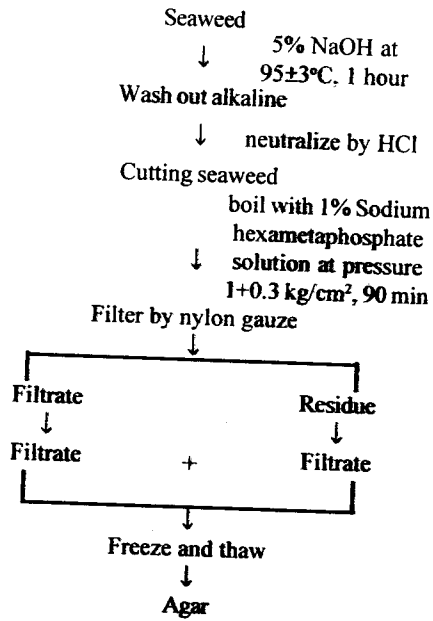
**Agar production in small scale in India
(Mathew, 1999)**



Annexure 4

**Processing Technology for agar in China
(Gracilaria tenuistipitata)**

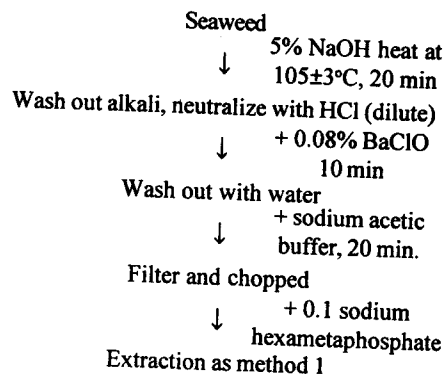
First Method of Extration



Second Method of Extration

25% NaOH treatment, the rest same as 1st method

Third Method of Extration



Processing Technology for agar in Philippines

Annexure 5

Dried *Gracilaria*
 (*Gracilaria fastigiata*, *G. salicornia*, *G. changii*
 and *Gracilaria* spp)

↑
 5% NaOH at
 90°C, for 3 hours

↑
 Wash out alkaline

↑
 adjust the pH to 5.6-
 6.0 by acetic acid

↑
 Extraction with water

↑
 2 hours at 85-90°C

↑
 Add filter aid
 (Diatomaceous earth)

↑
 Filtration under pressure at 60-80 psi

↑
 Agar gel setting at room temperature

↑
 Freezing and thawing

↑
 Drying

Agar

Processing Technology for agar in Myanmar

Annexure 6

Sun bleached *Gracilaria*

(*Gracilaria verrucosa*, *G. edulis*, *G. crassa*,
G. foliifera, *G. millardetii* and *G. textorii*)

↑
 Treatment with 2-6%
 NaOH solution at
 90°C for 1½ hours

↑
 Wash out alkali

↑
 neutralization with
 HCl

↑
 Extraction with water
 (at 100°C for 2 hours)

↑
 Filtration

↑
 Gel setting at room temperature

↑
 Cutting the gel

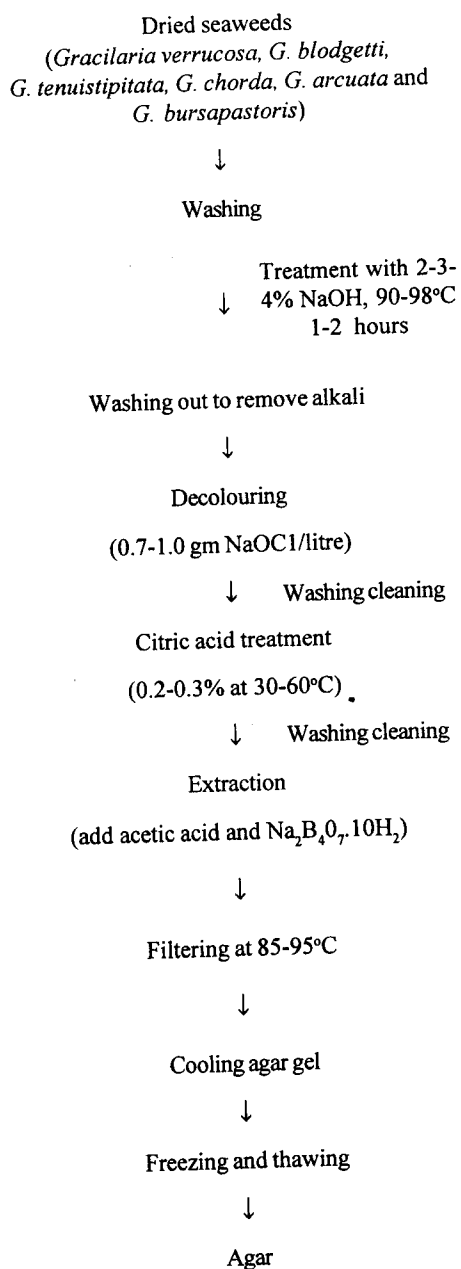
↑
 Freezing and thawing

↑
 Sun drying

Agar

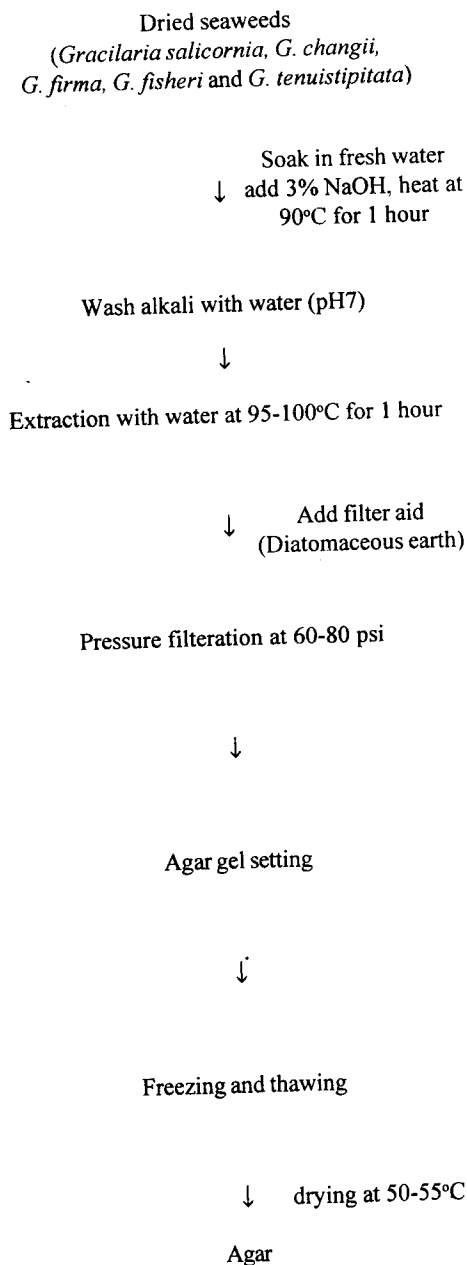
Annexure 7

Processing Technology for agar in Vietnam



Annexure 8

Processing Technology for agar in Thailand



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