STUDIES ON PHYSICO-CHEMICAL CHARACTERISTICS OF IOTA-CARRAGEENAN EXTRACTED BY ULTRASONIC METHOD

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UNIVERSITI MALAYSIA SABAH
2006

BORANG PENGESAHAN STATUS TESIS

JUDUL : **STUDIES ON PHYSICO-CHEMICAL CHARACTERISTICS OF IOTA- CARRAGEENAN EXTRACTED BY ULTRASONIC METHOD**

IJAZAH : DOKTOR FALSAFAH
SESI PENGAJIAN : 2003-2006

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D.M.REDDY PRASAD
PS2003-008-014 (A)
30th JUNE 2006

ACKNOWLEDGMENT

Thank you GOD.

I would like to express my sincere and profound gratitude to the Vice Chancellor, Universiti Malaysia Sabah, and Dean, School of Engineering and Information Technology for giving an opportunity and also for providing scholarship for me during my entire research work.

I would like to express my unlimited appreciation to Prof. Madya. Dr. Awang Bono and Prof. Madya. Dr. Duduku Krishnaiah for their valuable supervision, guidance in the research and preparation of this thesis. They encouraged me to go in depth study in the areas of Chemical and Sono Chemical Engineering. Their consistent motivation and encouragement allowed me to perform better and unleashed my capabilities in many areas, especially in the field related to this thesis.

I would like to express my sincere gratitude Prof. Dr. Sazali Yaccob and Dr. Paulraj M Pandiyan for helping in neural network application in my research, Prof. Dr. Kamatam Krishnaiah, who assisted me in mass transfer modeling and special thanks to Associate Prof. Dr. A. Prabhakar, for his valuable suggestions in the text preparation.

I would like to express my thanks to the Lab Assistants, Miss. Noridah Abas, Miss. Noor Aemi Dawalih, Mr. Abdullah Tarikim, Mr. Panjiman Saidin who did the maintenance of equipment during my research work.

I would also like to extend my sincere thanks to my students, Mr. Srinath (Dalhousie University) Canada, Ms. Varalakshmi(Ohio University) Athens, Mr. Prabhu Kumar(University of Wisconsin)USA, Mr. Madhavan and Mr. Anandh Kumar(National University) Singapore, my colleague Mr.C. Karthikayan and others whom are not mentioned here for their support and cooperation through out this research work.

Finally, I am also grateful to my Grandmother Mrs. Yarraka, parents Sri. D. Mogilappa Chetty and Smt. Parvathi, my sisters Mrs. D.M. Reddy Prasuna and Mrs. D.M. Reddy Prameela for their love, continuous support and encouragement in completing this research work.

ABSTRAK

KAJIAN SIFAT PSIKO-KEMIKAL IOTA-KARRAGEENAN YANG DIEKSTRAK MELALUI KAEDAH ULTRASONIK

Karrageenan adalah gam semulajadi yang boleh larut dalam air dan boleh dijumpai dalam beberapa spesis rumpai laut. Ia merupakan sejenis bio-polimer tersulfat semulajadi yang terbentuk daripada unit-unit galaktosa. Kebanyakan kepelbagaian rumpai laut yang terdapat di Laut China Selatan adalah *Caulerpa, Ulva, Sargassum, Euchema, Gracilaria, Gelidiella*, dan *Kappaphycus*. Pengekstrakan haba i-karrageenan daripada rumpai laut tidak memberi hasil yang tinggi, malah memakan masa. Pengekstrakan terbantu ultrasonik telah dicadangkan sebagai kaedah alternative. 20kHz ultrasonik berkeamatan tinggi telah digunakan dalam pengekstrakan i-karrageenan daripada *Euchema Denticalatum* dengan air sebagai pelarut. Hasil i-karrageenan telah meningkat sebanyak 50.0 hingga 57.2%. Korelasi matematik mudah untuk menganggar pekali pemindahan jisim pepejal – cecair telah diterbitkan berdasarkan keadaan pengoperasian iaitu VIZ., amplitud, saiz zarah, dan suhu bagi pengekstrakan untrasonik i-karrageenan. Tambahan lagi, kaedah penganggaran konvensional i-karrageenan dalam larutan akuas memerlukan penyah-polimeran and tempoh yang lebih lama. Kaedah spektroskopi ultrasonik dengan rangkaian neural juga telah dibangun sebagai kaedah alternatif. Beberapa model rangkaian neural buatan telah diguna seperti, *Back propagation (BP), Radial basis function (RBF)* dan *modified functional link neural network* (FLNN). Kaedah RBF mendapati masa penganggaran yang rendah iaitu 26 saat. Pengubahsuaian i-karrageenan dengan kehadiran Ag^+ menghasilkan sifat gel yang lebih baik. Ia lebih berguna kepada industri farmaseutikal. Sifat psiko-kemikal seperti resapan pasif, kekuatan gel, histerisis dan struktur mikro gel i-karrageenan terubah telah diuji. Didapati bahawa kehilangan berat gel melalui resapan pasif adalah dalam julat 0.7-1.2% dan pada tempoh 240 jam. Gel menunjukkan kekuatan yang semakin tinggi apabila kepekatan Ag^+ meningkat, manakala tahap keelastikan pula semakin menurun. Masa penenangan maksimum yang dicapai adalah pada kepekatan 70mM Ag^+, manakala pada kepekatan yang lebih tinggi, gel menjadi semakin tepu. Histerisis bagi gel terubah dapat diperhatikan di antara suhu gelatin (T_g) dan penyerakkan (T_f), dan ianya sangat bergantung kepada kepekatan Ag^+. Imej SEM bagi filem campuran menunjukkan ketidakrataan permukaan gel berkadar songsang dengan peratusan i-karrageenan. Keputusan daripada kaedah baru dan korelasi yang ditemui daripada kajian ini menawarkan pengaplikasian untuk penghasilan produk baru dalam industri proses yang berasaskan i-karrageenan.

ABSTRACT

STUDIES ON PHYSICO-CHEMICAL CHARACTERISTICS OF IOTA- CARRAGEENAN EXTRACTED BY ULTRASONIC METHOD

Carrageenans are water-soluble natural gums, which occur in certain species of seaweeds. They are sulfated natural biopolymers made up of galactose units. The major varieties of seaweeds are available from South China Sea at Sabah are Caulerpa, Ulva, Sargassum, Eucheuma, Gracilaria, Gelidiella *and* Kappaphycus*. The thermal extraction of i-carrageenan from seaweed does not give high yield and time consuming. Ultrasonic assisted extraction was proposed as an alternative method. The 20 kHz high intensity ultrasound was used in the extraction of i-Carrageenan from Eucheum denticulatum by using water as solvent. i-carrageenan yield increased from 50 to 57.2%. A simple mathematical correlation for the estimation of the solid-liquid mass transfer coefficient was derived in terms of operating conditions VIZ., amplitude, particle size and temperature for ultrasonic extraction of i-Carrageenan. The diffusion coefficient of i-Carrageenan in water was estimated from the mass transfer coefficient.Further more the conventional estimation methods of i-carrageenan in aqueous solutions need depolymerization and longer duration. The ultrasonic spectroscopy technique coupled with neural network has been developed as a alternative. In that the artificial neural network models such as Back Propagation (BP), Radial Basis Function (RBF) and modified Functional Link Neural Network (FLNN) were used. As the RBF method showed the low estimation time of 26 sec.The modification of i-carrageenan in presence of Ag^{+} produced better gel characteristics. It could be more useful in pharmaceuticals industries. The physico-chemical properties like passive diffusion, gel strength, hysterisis and micro structure of modified i-Carrageenan gels were tested. The weight loss of the gels in passive diffusion was found to be in the range 0.7-1.2% at 240 h. The gels exhibited high firmness as the Ag^{+} concentration increased while decrease in the elasticity was observed. The relaxation time reached maximum at 70 mM of Ag^{+} and at higher concentration the gels exhibited saturation. The hysterisis of the modified gels was observed between gelation (T_g) and dissolution (T_f) temperatures and it was strongly dependent on Ag^{+} concentration. The SEM images of the blended films showed that the roughness varies inversely with the percentage of i-Carrageenan. The results of new methods and correlations developed offer unprecedented scope of applications for developing new i-Carrageenan based products in the process industries.*

ABBREVIATION

BP	Back Propagation Procedure
DSP	Digital Signal Processing
EBP	Error Back Propagation Procedure
FLNN	Functional Link Neural Network
LMS	Least Mean Square
NMSE	Normalized Mean Square Error
RBF	Radial Basis Function
SEM	Scanning Electron Microscope

SYMBOLS

A	Amplitude (m)
a	Interfacial area (mm^2)
C_A	i-Carrageenan concentration (kg/m^3)
C_A^*	i-Carrageenan equilibrium concentration (kg/ m^3)
D_p	Diameter of the particle (mm)
D_{AB}	Diffusion coefficient of i-carrageenan in water (m^2/s)
f	Frequency (Hz)
I	Sound wave intensity (W/m^2)
K_L	Solid-liquid mass transfer coefficient (m/s)
r	Constant
s	Constant
T	Temperature (^oC)
t_e	Extraction time (s)
V	Volume of the reactor (ml)

Greek Letters

δ	AC boundary layer thickness (m)
μ	Dynamic viscosity (kg/m-s)
γ	Kinematic viscosity (m^2/s)
ρ	Density of liquid (kg/m^3)
ω	Angular frequency (rad /s)
ψ, β	Constants

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CHAPTER 1

INTRODUCTION

1.1 General introduction

For several hundred years, carrageenan has been used as a thickening and stabilizing agent in food in Europe and the Far East. In Ireland the use of carrageenan started more than six hundred years ago. In the village of Carraghen on the south Irish coast, flans were made by cooking the so-called Irish moss (red seaweed species *Chondrus crispus*) in milk. The name carrageenin, the old name for carrageenan, was first used in 1862 for the extract from *C. crispus* and dedicated to this village [Tani. M *et al.* 2003]. From the 19th century Irish moss was also used for industrial beer clarification and textile sizing. The commercial production began late in 1930's in the US. During that time, the trading shifted from dried seaweed meal to refined carrageenan [Therkelsen 1993].

After the Second World War, a general increase in the standard of living forced an increase in carrageenan production. Fractionation of crude carrageenan extracts started in the early 1950's, resulting in the characterization of the different carrageenan types. The Greek prefixes kappa, iota and lambda were introduced to identify the different carrageenans. In the same period the molecular structure of carrageenans was determined [Vreeman *et al.* 2004]. The structure of 3,6-anhydro-D-galactose in k-Carrageenan as well as the type of linkages between galactose and anhydrogalactose-rings was determined. Today, the industrial manufacture of carrageenan is no longer limited to the extraction from Irish moss, but numerous red seaweed species are used. Traditionally these seaweeds have been harvested from naturally occurring populations. Farming of seaweed to increase the production started almost 200 years ago in Japan. Scientific information about the seaweed life cycles, allowed artificial seeding in the 1950's. Today, nearly a dozen seaweeds are commercially cultivated and, thus, lowering the pressure on naturally occurring populations.

2 Background

Malaysia especially Sabah is a maritime state with more than three quarters of its boundaries abutting the sea. Seaweeds are Algae, which are classified by their pigment. These are non-flowering plants with neither roots nor leaves. Moreover, these are obviously found attached to a fixed structure by means of a holdfast. They come in a variety of forms, from microscopic single-cells to filamentous shape and large bushy growths.

Most of the seaweeds are growing from intertidal zone until a depth of 30 – 40 meter. Normally 75% - 90% weight of fresh seaweeds is contained water [Philip Sze. 1986]. The dry weight is included 75% organic and 25% heavy metal such as potassium, sodium, magnesium and ion calcium [Robledo and Delegrin. 1997]. Seaweeds are classified into four main groups based on the presence of the main photosynthetic pigments: the green (division *Clorophyta*), red (division *Rhodophyta)*, brown (division *Phyaeophyta)* and blue-green algae (Fig. 1.1) [Ridzam Hashim. 1993, In A. Steinbüchel *et al.* 2002, De Velde *et al.* 2002].

The majority seaweeds around the ocean of Malaysia are of division *Rhodophyta* which consists of 45 species. Besides that, division *Chlophyta* has 41 species and division *Phyaeophyta* has 24 species. The seaweeds which are found off the Sabah coasts are commonly *Eucheuma (Rhodophyta), Gracilaria (Rhodophyta), Sargaassum (Phyaeophyta), Caulerpa (Cyanophyta), Turbinaria (Phaeophyta), Dictyota (Phaeophyta), and Padina (Phyaeophyta)* [De Ruiter *et al.* 2002].

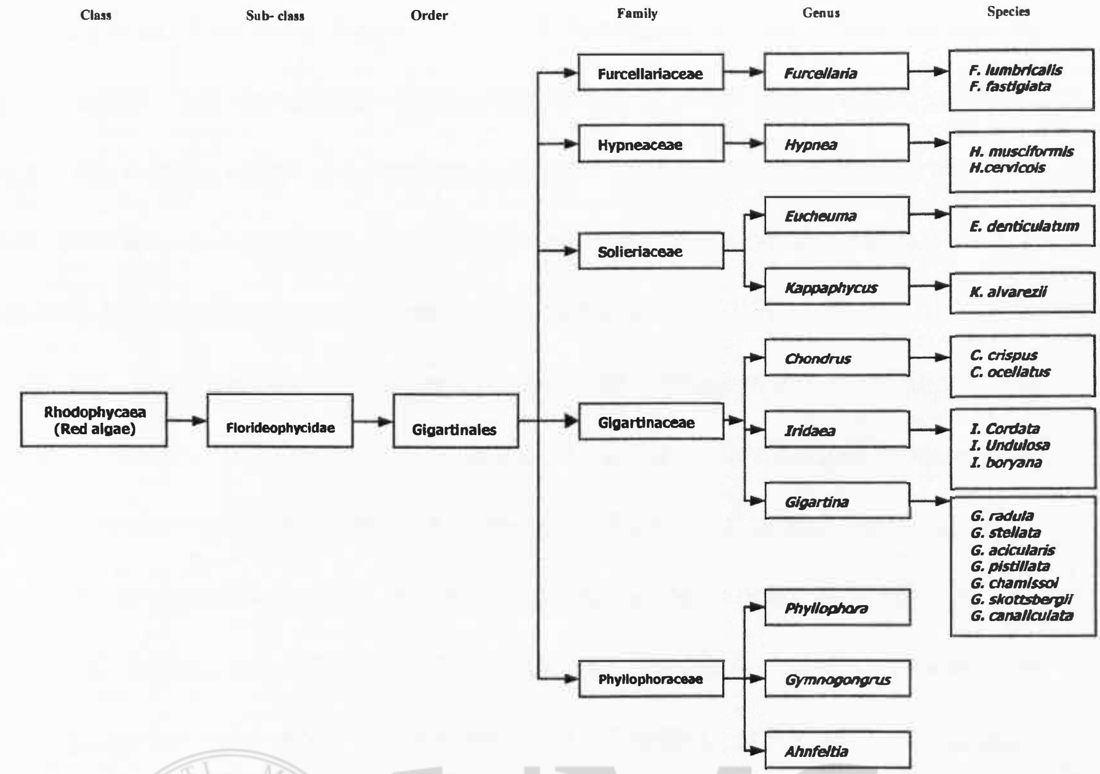

Figure 1.1: Taxonomical tree of carrageenan-bearing seaweeds

Seaweeds, which may surprise the common man, have many economic uses. They are traditionally used in the country as food, animal feed, fertilizer, and in the preparation of traditional medicine. Each type of seaweed has their use. For example the red algae, Eucheuma sp (Fig 1.2) consists of carrageenan and is cultured on reef flats in Sabah.

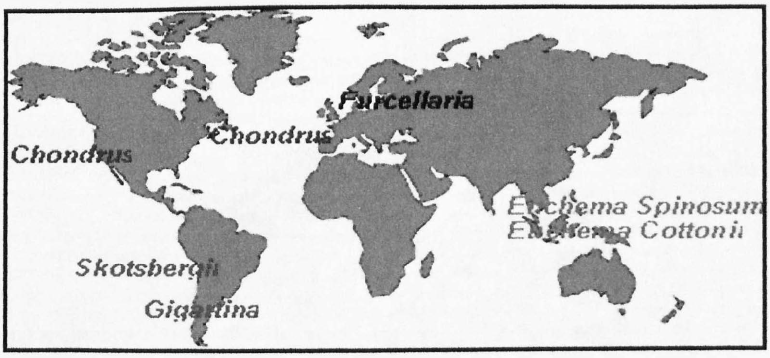

Figure1.2: Distribution of the seaweed species in the world

Nowadays, in the world about 70 to 80% Carrageenan are extracted by using two main species of which are *Eucheuma cottonii* and *Eucheuma spinosum* from

Divisi *Rhodophyta.* The main factor to extract carrageenan from these species is, easy plantation in sea. Besides that, by using different ways of extraction different structure can result, which accompany with the variety physical properties and chemical properties. k-Carrageenanis obtained from *Eucheuma cottonii* and i-Carrageenan from *Eucheuma spinosum* [Baker 1984, Anna 1980].

In the last few years, the requirement of carrageenan applications are increasing constantly by at least 5 -7 percent per annum. The reason of increasing requirement of carrageenans is its unique ability to form an almost infinite variety of gels at room temperature, rigid or compliant, tough or tender with high or low melting point. Despite the similarity of its molecular structures, the gels have very different properties. Carrageenan solutions will thicken, suspend and stabilize particulates as well as colloidal dispersions and water/oil emulsions. Therefore, the Carrageenan solution will give the good performance in rheological properties [Anna 1980].

Carrageenan is a natural marine colloidal gum, which is a jelly-like substance. It is an anionic polysaccharide extracted from marine red algae and exists in the voids within the (Fig 1.3) cellulose structure of Red seaweed [Luning 1990].

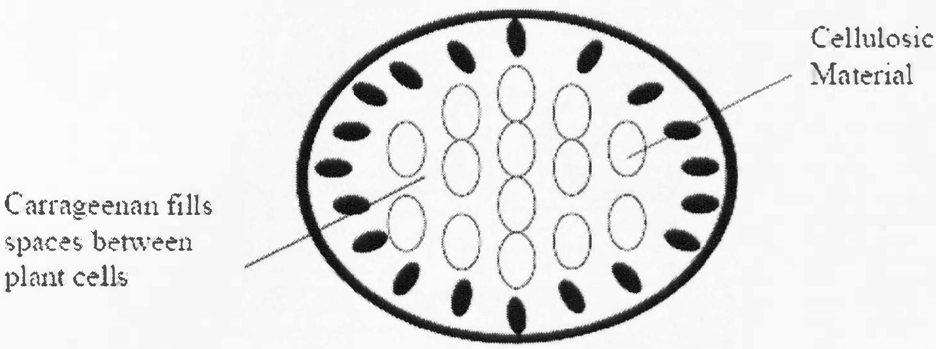

Figure 1.3: Cross-section of seaweed