

**SYNTHESIS AND CHARACTERIZATION OF
PHOTOPROTECTIVE HYDROXYAPATITE EMULSION FROM
TAMBAN BONE (*SARDINIELLA FIMBRATA*)**

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Synthesis and characterization of photoprotective hydroxyapatite
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Helmi Rozaini.

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MOHD ZUL HELMI ROZAINI

**Thesis submitted in fulfillment of the requirement for the degree of
doctor of philosophy in the Institute of Marine Biotechnology**

Universiti Malaysia Terengganu

May 2017

DEDICATION

.....Dedicated to my lovely wife Mrs Armiza Ahmad

My beloved children, Arianna Zureen, Aryan Zachary, Ardit Zayyan, Ardhiya Zandra, Arya Zafra and Ara Zawra

My respectful parents, Hj Rozaini Adnan and Hjh Rohaya Musa

“Thank you for your everlasting love, passion, support and unstoppable Du’a. I know how hard and painful along this journey and thank you for your understanding and always stay strong besides me”

ABSTRACT

Abstract of thesis presented to the Senate of Universiti Malaysia Terengganu in fulfillment of the requirement for the degree of Doctor of Philosophy

SYNTHESIS AND CHARACTERIZATION OF PHOTOPROTECTIVE HYDROXYAPATITE EMULSION FROM TAMBAN BONE (*SARDINIELLA FIMBRATA*)

MOHD ZUL HELMI ROZAINI

May 2017

Main Supervisor : Professor Mohd Effendy Abd Wahid, Ph.D.

School/Institute : Institute of Marine Biotechnology

Development in the fish processing industry has led a large amount of waste every year around the world. Fish waste including, fish head, scales, bones and guts. Certain fish bones have an attractive added value which contain hydroxyapatite (HAp), $(Ca_{10}(PO_4)_6(OH)_2)$ that can potentially be used as UV absorbance (unmodified HAp). Thus, with the additional of manganese and ferum, new hybrid sunscreen materials have been initiated i.e modified HAp-Fe and modified HAp-Mn. Therefore, *Sardinella fimbriata* bone have been discovered and synthesized to be utilized as sunscreen in cosmeceuticals. This work was divided into five stages. The first was the preparation of pure HAp by extracting the fish bone waste and calcinations process. The percentage yields obtained from the extraction consist of 41.2 ± 0.66 % (w/w) which was almost half of the dry weight of 100 g samples. The second part of the work were discussed on the preparation of sunscreen emulsion via microhedral emulsion stabilized by the nonionic surfactants and olive oil as co-surfactant. The rheology of the microhedral samples was governed by oil droplets size and oil volume fraction. Flow curves and the viscosity-shear rate profile showed that the samples displayed shear thinning behaviour. The third part of this study basically an extended study of previous topic including the preparation, development and the morphological studies of porous calcium phosphates or HAp in microhedral emulsion. Highly porous calcium phosphate or HAp crystals with unique morphologies had been successfully synthesized using olive oil-water microhedral as a convenient reaction medium to regulate nucleation and crystals

growth. The fourth part of this work have been carried out to determine the sun protection factor (SPF) of sunscreen emulsion contained of unmodified HAp, modified HAp and commercially available samples of sunscreen emulsions of various manufactures by UV spectroscopy method. The unmodified HAp recorded with SPF 20 and modified HAp-Mn measured with SPF 25. Modified HAp-Fe microhedral emulsions were recorded with SPF 50 and the highest SPF value compared to the commercial sunscreen product. The fifth part of this work was discussed on the application of the modified HAp-Fe as potential sunscreen agents. Prior to direct application on skin, cytotoxicity test was carried out in vitro to ensure that the crystals in microhedral formulation pose no hazard to cells. As a result, all microhedral emulsion samples with IC_{50} value more than 30 $\mu\text{g/mL}$ were considered as non-toxic on RAW264.7 cell lines. Thus, the four formulation samples were safe to be further used in the next examination on human skin analysis. The skin analysis was evaluated by using the Dermalab[®] (Cortex Technology) equipment which recorded the positive outcomes in all parameter including hydration (moisture), transepidermal water loss (TEWL), elasticity, skin color (melanin) and also high resolution ultrasound skin imaging.

ABSTRAK

Abstrak tesis yang dikemukakan kepada Senat Universiti Malaysia Terengganu sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

SINTESIS DAN PENCIRIAN EMULSI FOTOPELINDUNG HIDROKSIAPETIT DARIPADA TULANG IKAN TAMBAN (*SARDINIELLA FIMBRATA*)

MOHD ZUL HELMI ROZAINI

Mei 2017

Penyelia Utama : Professor Mohd Effendy Abd Wahid, Ph.D.

Sekolah/Institut : Institut Bioteknologi Marin

Pembangunan dalam industri pemprosesan ikan telah menghasilkan sejumlah besar sisa setiap tahun di seluruh dunia. Sisa ikan termasuk, kepala ikan, sisik, tulang dan isi ikan. Tulang ikan tertentu mengandungi hydroxyapatite (HAp), $(\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2)$ yang berpotensi untuk digunakan sebagai bahan penyerap UV (tulang tidak diubahsuai). Dengan penambahan mangan dan ferum, bahan pelindung UV hybrid telah dihasilkan i.e HAp-Fe diubahsuai dan HAp-Mn diubahsuai. Ini membuktikan bahawa tulang ikan Tamban (*Sardiniella fimbriata*) sangat berpotensi untuk digunakan sebagai pelindung UV dalam kosmeseutikal. Penyelidikan ini dibahagikan kepada lima bahagian. Bahagian pertama adalah penyediaan HAp tulen dengan mengekstrak sisa tulang ikan Tamban dan pengkalsinan. Kadar hasil peratusan HAp yang diperolehi daripada pengekstrakan adalah $41.2 \pm 0.66\%$ (w/w) iaitu hampir separuh daripada berat kering 100 g sampel. Bahagian kedua telah membincangkan penyediaan emulsi pelindung UV melalui emulsi mikrohedral yang distabilkan oleh surfaktan tak ionik. Reologi emulsi mikrohedral mempengaruhi saiz titisan minyak dan jumlah pecahan minyak emulsi. Keluk dan profil kadar kelikatan ricih aliran ini menunjukkan bahawa sampel menunjukkan sifat penipisan ricih. Bahagian ketiga kajian ini adalah kajian lanjutan topik sebelumnya termasuk penyediaan, pembangunan dan kajian morfologi kalsium fosfat berliang atau HAp dalam emulsi mikrohedral. Kristal kalsium fosfat berliang atau HAp dengan morfologi unik telah berjaya disintesis menggunakan minyak zaitun dan air dalam emulsi mikrohedral yang merupakan medium tindak balas yang mudah untuk mengawal penukleusan dan pertumbuhan kristal. Bahagian keempat kajian ini telah

dijalankan untuk menentukan nilai faktor perlindungan matahari (SPF) bagi emulsi mikrohedral yang terkandung dalam HAp tidak diubahsuai dan HAp diubahsuai dan juga perbandingan dengan sampel penyerap UV komersial dengan kaedah spektroskopi UV. HAp tulen (tidak diubahsuai) mencatatkan nilai SPF 20 dan HAp-Mn diubahsuai diukur dengan SPF 25. Emulsi mikrohedral HAp-Fe diubahsuai pula mencatatkan nilai SPF 50 yang merupakan nilai paling tinggi berbanding produk pelindung matahari komersial. Bahagian kelima kajian ini telah membincangkan aplikasi mikrohedral HAp-Fe diubahsuai sebagai agen pelindung matahari yang berpotensi. Ujian ketoksikan telah dijalankan secara *in vitro* untuk memastikan bahawa kristal dalam penggubalan mikrohedral tidak menimbulkan bahaya kepada sel. Hasilnya, semua sampel emulsi mikrohedral dengan nilai IC50 lebih daripada 30 µg / mL dianggap sebagai tidak toksik pada sel RAW264.7. Ujian analisis kulit secara bersepadu juga turut dijalankan dengan menggunakan peralatan Dermalab® (Cortex Teknologi) yang memberikan keputusan positif bagi kesemua parameter yang dikaji termasuk kelembapan, kehilangan air tranepidermis (TEWL), kekenyalan, melanin and dan imej ultrasound kulit.