

# PREPARATION AND PHYSICOCHEMICAL EVALUATION OF BIODEGRADABLE MAGNETIC *K*-CARRAGEENAN BEADS AND APPLICATION FOR CHROMIUM IONS PRE-CONCENTRATION

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(Received: March 7, 2011 - Accepted: July 11, 2011)

## ABSTRACT

This study aims to examine the ability of magnetic *K*-carrageenan beads as an adsorbent in solid phase extraction towards chromium ions from aqueous solution. In this study, *K*-carrageenan magnetic gel-beads were obtained via interphase technique. The beads were kept in 0.3 M KCl to maintain gel strength. Physicochemical of the resulting materials were characterized by Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and magnetometer. FTIR results have confirmed the presence of functional groups such as sulphate esters groups. The diameter of carrageenan beads was about ~764 µm where SEM micrographs showed the spherical formed shape of carrageenan beads and a rough surface with pores. The saturation magnetization value,  $M_s$ , of carrageenan beads in this study was 18.78 EMU/g. The magnetic function of carrageenan beads is to facilitate bead collection and to get the Cr<sup>6+</sup> ion that adsorbed onto the beads. The adsorption of chromium ions by magnetic carrageenan beads are through an ion exchange mechanism and formation of metal-ligand complex. Optimal timing for adsorption of chromium ions was at 60th minute. The optimal operation conditions can be achieved on pH value~1 and concentration of 100 ppm. Langmuir adsorption isotherm curve for Cr<sup>6+</sup> is similar to Langmuir adsorption isotherm types III (unfavorable).

**Keywords:** magnetic *K*-carrageenan beads, interphase technique, ion exchange mechanism, saturation magnetization and Langmuir adsorption isotherm

## INTRODUCTION

Increase in environmental pollution due to industrial development is a challenge to be faced by the community. Heavy metals such as chromium, cadmium, lead, and copper are a result of discharge from various industries may cause serious environmental problems and also health hazards. Nowadays, various methods have been introduced to overcome this problem, such as chemical precipitation, evaporation, ion-exchange, adsorption, cementation electrolysis, and reverse osmosis [1-3]. One of the most effective methods is the use of carrageenan that resulted from magnetic carrier technology for magnetic separation methods, where the purification procedure can be performed in just a test tube or in a container and does not incur expensive costs. Application of this technique has been carried out in the field of molecular biology (in the separation of nucleic acids) and microbiology for the separation of cells [4]. In biology, the adsorbent used are biopolymers which contain the binding sites carboxylate, amines, phosphate, sulphate, and hydroxyl.

Hydrogels from natural biopolymers including alginate, carrageenan, agar, and chitosan are intriguing because of their distinctive biological and physicochemical properties. Along with these natural biopolymers, carrageenan has a wide potential and is effectively used as an adsorbent in solid phase extraction of metal ions. Carrageenan (magnetic) are used in the process of separation (adsorption) for their low cost, their ability in reducing metal content in waste water (sewage), and they cause no toxic effects. The mechanism of metal cations involves formation of complex metal with metal ions and functional groups that are located on the surface or carrageenan pores [5]. In addition, carrageenan has shown that it is a good transport system and can facilitate in controlling pollution by heavy metals such as Pb, Cd, and Cr [6]. Commercial use in pollution control could present with potential opportunities for research and development. Carrageenan is a hydrocolloid extracted from marine red seaweed (*Eucheuma Cottoni* species) based natural polysaccharide. All types of carrageenan have a high degree of polymerization [7-8] and consist of  $\beta$ -(1, 3) sulphated D-galactose and  $\alpha$ -(1, 4)-3, 6-anhydro-D-galactose.

*K*-carrageenan is one type of carrageenan that differs only in the number of ester sulphate groups per disaccharide with the other forms of carrageenan, iota (*ι*-) and lambda (*λ*-). *K*-carrageenan has the lowest level of ester sulphates so it has the properties of a strong gel and is more rigid compared to iota (*ι*-) and lambda (*λ*-) carrageenans. A higher level of ester sulphate means a lower solubility temperature and lower gel strength [9]. Hydro gels from carrageenan can be in the form of beads whereby the gelling processes start

with the presence of metal ions, amine, amino acid derivatives, and organic solvents [10]. With increasing sulphate content, negatively charged ions in the helix structure require the presence of K<sup>+</sup> or Ca<sup>2+</sup> and combine to form macro molecules after which gelation occurs [11].

It is rather important for us to eliminate the chromium cations from industrial waste. Therefore we want to develop new efficient methods to separate polluting heavy metal ions from industrial processes, without consuming much energy and materials for separation. In this manuscript, we have used interphase technique for preparing magnetic *k*-carrageenan spherical beads and investigated its adsorption ability to chromium cations.

## MATERIALS AND METHOD

### Materials

The following materials were obtained from the indicated suppliers and used as received: *K*-carrageenan (Fluka Chemie), iron (III) oxide and hydrochloric acid 99.8% (System), potassium chloride (BDH Chemicals), sodium dichromate (Hamburg) and sodium hydroxide 99.8% (Merck). All reagents were of analytical grade purity. All solutions were prepared using distilled water.

### Preparation of the carrageenan magnetic solution.

2 grams of carrageenan were dissolved in 90 ml distilled water and heated at 60°C ± 5°C. Heating process was continued until the solution became concentrated followed by cooling the hot solution at the temperature range 50-55°C ± 5°C. The solution will form gel at this range of temperature. Fe<sub>3</sub>O<sub>4</sub> were added and mixed to the solution at 2:1 weight ratio of carrageenan to iron oxide and stirred homogeneously.

### Preparation of the carrageenan magnetic beads.

Bead production process was carried out using interphase technique [12]. A mixture containing carrageenan and Fe<sub>3</sub>O<sub>4</sub> were dropped through a syringe into the beaker containing oil and aqueous phase (0.3 M KCl). Beads will be through the oil layer and collected in the aqueous phase. The resulting spherical beads were left in the aqueous phase for an hour. Ice was placed around the beaker to assist in the formation of beads. The solutions were maintained at 10°C for 5 hours to let the beads hardened. After gelation process, the beads were filtered, rinsed with water, to remove excess potassium ion and dried in an oven at 60°C for 24 hours.

**Characterization**

The resultant beads were characterized using scanning electron microscope (SEM) (Model JEOL JSM-6400 SEM), Fourier Transform Infrared Spectroscopy (FTIR) (Model Spectrum BX), and Magnetometer (Model 19500 Microprocessor Controlled).

**Chromium Ion Adsorption by K-Carrageenan Magnetic Beads**

*Determination of optimal timing for adsorption of chromium metal*

The resulting beads were included in a 5 ppm solution of chromium metal in a volume of 50 ml. 1 millilitre of sample solution was taken every 10 minutes for 240 minutes to obtain equilibrium adsorption. The samples taken were diluted five-folds using distilled water for analysis by Atomic Absorption Spectroscopy (AAS) (Model AAnalyst 800). Experiments were performed at room temperature and in a pH close to neutral.

*Determination of optimal pH for adsorption of chromium metal*

In order to determine the optimal pH, 0.10 g of beads of similar size is inserted into each of four beakers containing 50 ml solution of 5 ppm of chromium concentration with a pH of 1, 3, 5 and 7. 0.1M HCl and NaOH solution was used to obtain the appropriate pH. Adsorption was carried out at optimal time and 1 ml samples were taken and diluted five-fold with distilled water for analysis by AAS.

*Determination of optimal concentration for adsorption of chromium metal*

Carrageenan beads with a weight of 0.1 g were put in separate 50 ml chromium solutions with concentrations of 10 ppm, 20 ppm, 30 ppm, 50 ppm, and 100 ppm. Adsorption was carried out at optimal pH and time. Different concentrations of the chromium solution were prepared from a stock solution of 100 ppm and diluted with distilled water. 1 ml of samples was taken and the dilution is done to determine the optimal concentration. The maximum adsorption for metals at a particular concentration was recorded.

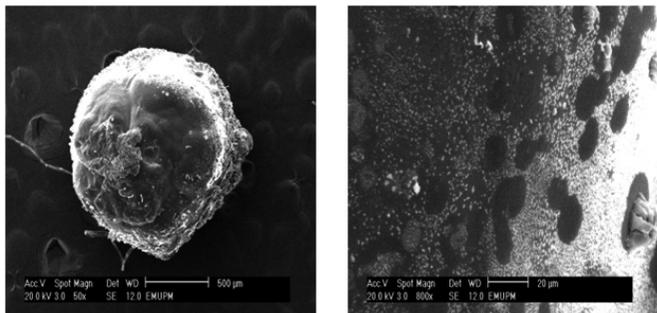
**RESULTS AND DISCUSSION**

In this study, interphase technique has been choosing over ionotropic gelation technique due to difficulties to obtain a polymer gel bead of equal size in ionotropic gelation technique (Lopez et al. 1997). Moreover, interphase technique composed of an aqueous phase (KCl) and oily phase (sunflower oil) which is inexpensive, non-toxic and easily obtainable.

**Characterization of Magnetic K-Carrageenan Beads**

*Scanning electron microscope (SEM)*

Sizes of the beads were depending on the syringe used and we managed to obtain the beads in the equal size. SEM micrographs of magnetic microsphere K-carrageenan beads are presented in Figure 1 (a) and (b). It was observed that samples produced display spherical form, regular shape of carrageenan beads, and rough surfaces due to the formation of pores with a size of about 1 mm.



(a) (b)

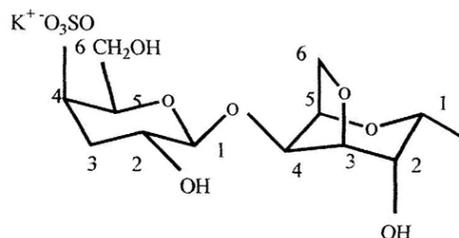
**Figure 1(a) and (b)** Scanning electron microscope (SEM) micrograph of carrageenan microsphere beads.

**K-Carrageenan FTIR Analysis**

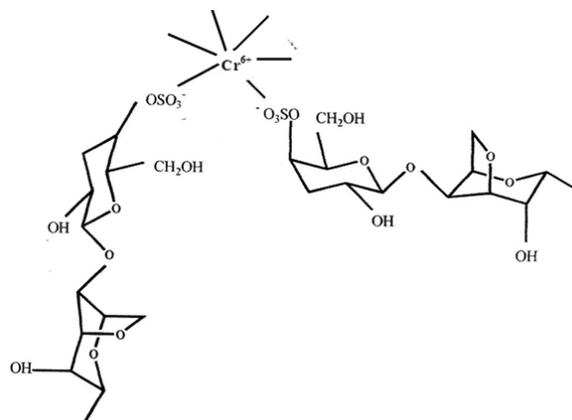
FTIR analysis for commercial K-carrageenan powder (sample A) and magnetic carrageenan after adsorption of chromium ion (sample B), in the range 2000 - 650 cm<sup>-1</sup> are presented in Figure 2. The characteristic broad band

of sulphate esters was observed between 1210-1260 cm<sup>-1</sup> for sample A. Sample A showed characteristic band at 845 cm<sup>-1</sup> that corresponded to galactose-4-sulphate [13], and at 701 cm<sup>-1</sup> which showed the presence of sulphate at pyranose agreed with the previous study done by other researcher [11].

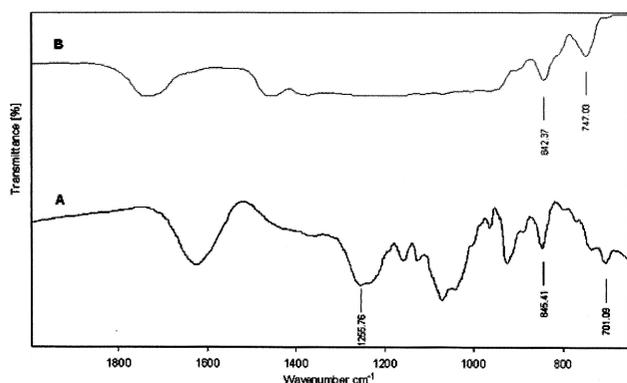
The most remarkable difference observed between sample A and B is the characteristic broad band of sulphate esters was not observed in the range of 1210-1260 cm<sup>-1</sup> in sample B. However, sample B showed a band at 842 cm<sup>-1</sup> that corresponded to galactose-4-sulphate which is slightly shifted compared to sample A. We believed that this is due to the metal ligand formation between carrageenan structures with chromium ion. Scheme 1 shows a structure that may be formed when carrageenan beads bind with stimulants of potassium cation (K<sup>+</sup>). Based on the structure, it appears that a negatively charged sulfate group becomes the binding site in metal adsorption. An ionic exchange reaction takes place as Cr<sup>6+</sup> ions replace K<sup>+</sup> ions and bind to the negatively charged sulfate groups. Six units of repeated carrageenan are required to adsorb Cr<sup>6+</sup> ions as adsorption of chromium metals requires six sites based on six charged ions. Scheme 2 shows the structure that may be formed as carrageenan beads react with chromium metal ions. The carrageenan beads produced have pores on them which allow K<sup>+</sup> ions out easily and enable transferring Cr<sup>6+</sup> ions into the carrageenan beads. Surface area and pore size distribution of adsorbents affect the rate of metal ion adsorption.



**Scheme 1.** K-carrageenan structure formed when reacts with the solution of potassium chloride (K<sup>+</sup> cation stimulating gel)



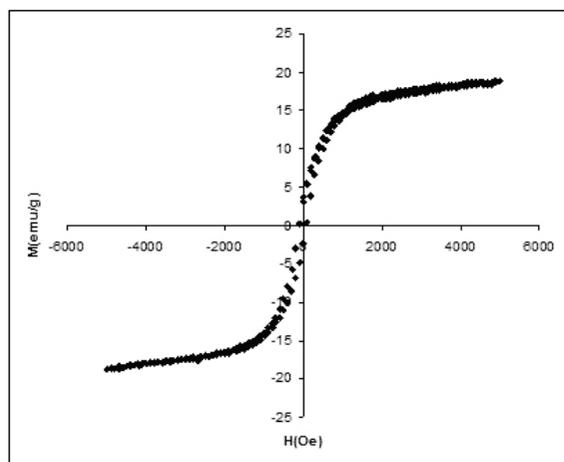
**Scheme 2.** Combination of structural K-carrageenan bound by Cr<sup>6+</sup> ions at a negatively charged sulfate groups.



**Fig. 2** FTIR analysis of K-Carrageenan powder (sample A) and magnetic carrageenan after adsorption of chromium ion (sample B).

#### Analysing Nature of K-Carrageenan Magnetic Beads

The relationship between the magnetic field strength ( $H$ ) and the magnetization per unit mass, ( $M$ ) for carrageenan beads can be observed by plotting the plot of magnetization per unit mass, ( $M$ ) against the magnetic field strength ( $H$ ) as shown in Figure 3. From the observation, it shows that carrageenan beads in this study were behaved as superparamagnetic where it has a permanent magnetic moment. The saturation magnetization,  $M_c$  of carrageenan beads in this study has a value of 18.78 EMU/g, while the  $M_c$  of  $Fe_3O_4$  is 63 EMU/g. Based on the differences in magnetization between  $Fe_3O_4$  and the carrageenan beads magnetic material, the results show that there may have been  $Fe_3O_4$  diamagnetic contribution from the bonds formed in carrageenan beads. From Figure 3, coersivity,  $H_c$  of the beads is 90.82 Oe and it shows that when the magnetic field is zero, magnetization is also zero. Data obtained from the magnetometer analysis of magnetic K-carrageenan beads are shown in Table 2.



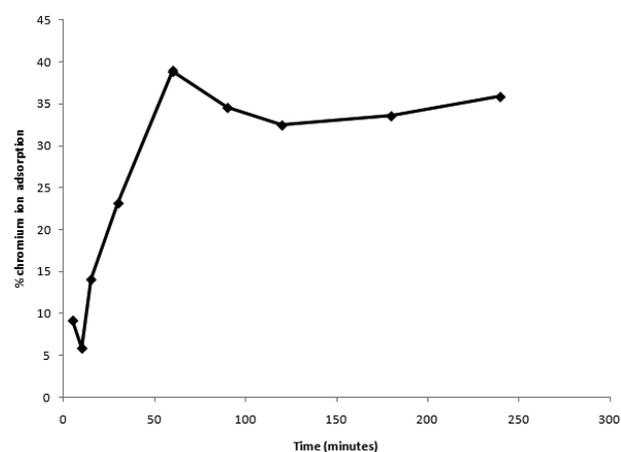
**Fig. 3** Magnetic field strength graph, ( $H$ ) for K-Carrageenan magnetic beads versus magnetization per unit mass, ( $M$ ).

#### Chromium ion Adsorption

##### Adsorption at Different Time Intervals

From the time-adsorption experiment (5–240 minutes), optimal timing for adsorption of chromium ions by the carrageenan beads was obtained. A graph of the concentration of  $Cr^{6+}$  ions adsorbed was plotted against time, as shown in Figure 4. In general, it was found that the adsorption of  $Cr^{6+}$  ions by carrageenan beads occurred immediately and increased gradually at the beginning of the reaction (Table 3). The adsorption time was recorded as early as the 5th minute of the experiment, with an adsorption percentage of 9.2%. Optimal adsorption occurred at the 60th minute. However, percentage of adsorption started to decrease after reaching the optimal time where the percentage of adsorption decreased from 38.9% to 34.6% in the 90th minute. Carrageenan beads started to dehydrate in chromium ion solution after more

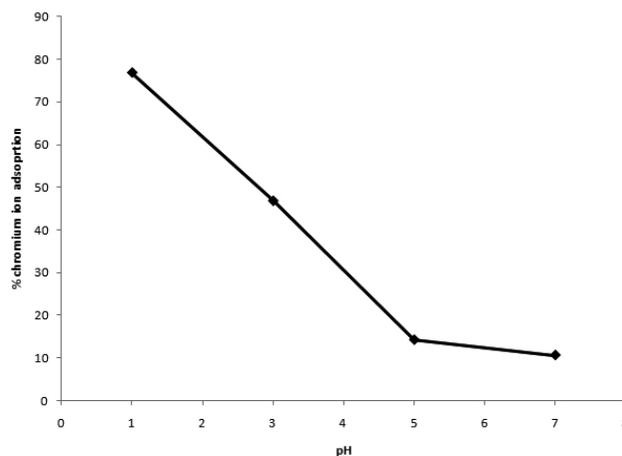
than 60 minutes. This is due to diminish the stimulant gel cation in the reaction mixture causing carrageenan beads to dissolve.



**Fig. 4** Percentage Chromium Metal Ion Adsorption against Time

##### Adsorption at Different pH

Adsorption at various pH values was carried out to obtain optimal pH value for adsorption. Carrageenan beads are capable of ionization under certain pH conditions. Hence, pH solution plays a crucial role that affects the adsorption of metal ions. Carrageenan beads exist as an ionic species. It has a sulphate ion group bound to its polysaccharide. From the graph plotted using adsorption percentage against pH (Figure 5) it is clear that maximum adsorption occurs in strongly acidic media (pH 1), where adsorption percentage was 76.9% (Table 4).



**Fig. 5** Percentage of Chromium Adsorption against pH

The number of negative charges on the surface of carrageenan beads increases with increase in pH. This is due to the deprotonation that occurred in areas where metal was bound hence raising the rate of metal adsorption. At pH higher than pH 7, heavy metal ions will hydroxidize, resulting in the presence of ions that would interfere with the adsorption process. This will lead to failure in obtaining optimal adsorption. Therefore, pH of the solutions was varied with pH ranging between pH 1 to pH 7.

##### Adsorption at different concentrations

Figure 6 shows a graph of the  $Cr^{6+}$  metal ion adsorption percentage against the initial concentrations of  $Cr^{6+}$  metal ions. The concentration was varied from 10–100ppm in order to attain optimal concentration. It was found that, overall, the percentage of metal ion adsorption increases as the concentration of  $Cr^{6+}$  increased. The results show that at the concentration of 100 ppm, the maximum adsorption obtained was 62.95%. Adsorption at the beginning of the

reaction was, however, unstable. This may be due to incomplete reaction of the carrageenan beads in the solution.

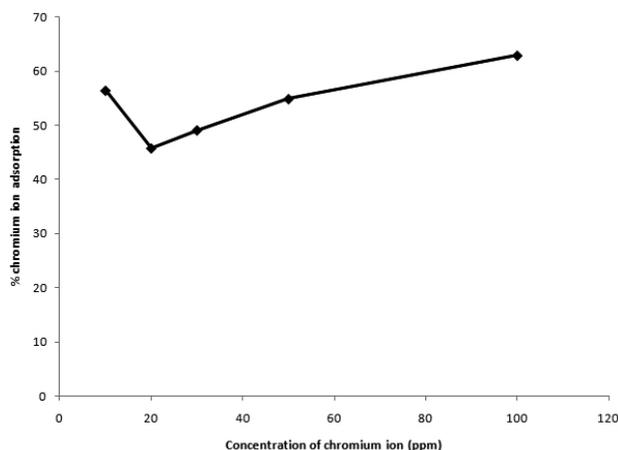


Fig. 6 Graph Percentage of Chromium Metal Ion Adsorption against Initial Concentration Chromium Metal Ions (ppm).

**The intake of metal ions (q values) for Cr<sup>6+</sup> ion**

From the previous study done by other researcher [5], the intake of metals, q, isothermally is stated in the following equation below:

$$q = \frac{V(C_i - C_f)}{1000M}$$

where,

- q = intake of metal ions (metal ions mg / K-carrageenan beads g)
- V = volume of metal solution
- C<sub>i</sub> = initial concentration of metal solution ( mg/l )
- C<sub>f</sub> = final concentration of metal solution ( mg/l )
- M = the mass of the K-carrageenan beads

The shape of the graph in Figure 7 is found to be similar to the Langmuir adsorption isotherm type III (unfavorable). The Langmuir adsorption model was used to predict ion adsorption properties of Cr<sup>6+</sup> by carrageenan beads. It also reflects the adsorption of metal ions occurring on the surface of the adsorbent bead. Based on these graphs, it can be seen that the adsorption of Cr<sup>6+</sup> ion occurs minimally at low ion concentrations. When the concentration of Cr<sup>6+</sup> increased, the adsorption of chromium metal by carrageenan beads also reached a maximum level. The Langmuir model for graphs of unfavorable types described that the adsorption of chromium metal ions occurs in a single layer (monolayer).

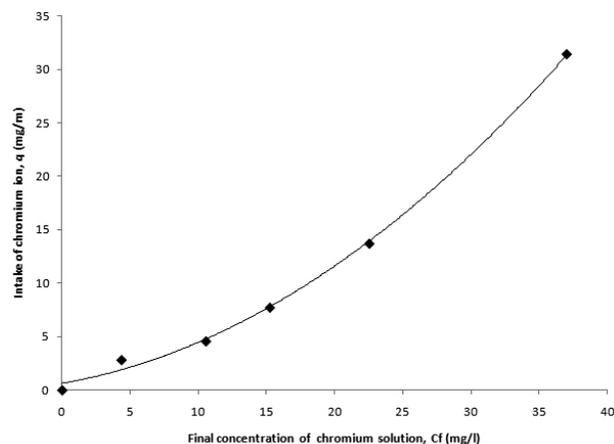


Fig. 7 Graph q values against final concentration, Cf of Cr<sup>6+</sup> ions

**CONCLUSION**

In conclusion, the magnetic K-carrageenan beads were successfully generated via interphase technique. The strength of carrageenan gel is stimulated in the presence of K<sup>+</sup> ions that react as cations from 0.3 M KCl solution, and managed to maintain physical conditions of the sphere beads when added with the metal ion solution. FTIR results confirmed the presence of functional groups such as sulphate esters groups. SEM micrographs showed the regular spherical formed shape of carrageenan beads and a rough surface with pores with the diameter of carrageenan beads was about 1 mm. The saturation magnetization of carrageenan beads in this study has a value of 18.78 EMU/g. K-carrageenan beads adsorb Cr<sup>6+</sup> ions through the mechanism of ion exchange, chelating formation, and adsorption. This studied showed the abilities of magnetic carrageenan beads as adsorbent in solid phase extraction towards chromium ion from aqueous solution. The magnetic function in K-carrageenan beads is to facilitate the collection of beads without having to filter to get rid of the Cr<sup>6+</sup> ion content adsorbed onto the beads. In addition, several metals individually interact with the magnet because the metals have their own magnetic features. Optimal timing for adsorption of chromium ions by the carrageenan beads occurred at the 60th minute while maximum adsorption occurs in strongly acidic media (pH~1) and at the concentration of 100 ppm, the maximum adsorption was obtained. Adsorption of Cr<sup>6+</sup> ions by carrageenan beads has the form of the Langmuir isotherm type III (unfavorable).

**ACKNOWLEDGEMENTS**

The authors are thankful to Research University Grant Scheme (RUGS) and Laboratory of Marine Biotechnology, Institute of Bioscience, Universiti Putra Malaysia for providing the facilities.

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