**UNIVERSITI PUTRA MALAYSIA**

# *PREPARATION AND CHARACTERIZATION OF CORE-SHELL COPPER NANOPARTICLES STABILIZED BY KAPPA CARRAGENAN AND SODIUM ALGINATE*

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By

**HAJAR KHANEHZAEI**

**Thesis Submitted to the School of Graduate Studies Universiti Putra Malaysia, in Fulfillment of the Requirement for the degree of Master of Science**

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**DEDICATION**

*To God, who gave me life and strength*

*To my family*

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Master of Science

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**Chairman: Professor Mansor B. Ahmad, PhD**
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Among metal nanoparticles, copper nanoparticles (Cu-NPs) have recently attracted increased attention because of their low cost (in contrast to Au and Ag) and their usable properties. Rate of resistance of microorganisms to antibiotics is alarming. Pathogenic bacteria are becoming much resistant to antibiotics. Copper nanoparticles synthesis particularly in bio-based stabilizers can act as antimicrobial agents, which in turn could resist pathogenic microorganisms. In this work, synthesis and characterization of Cu-NPs and Cu@$Cu_2O$ core shell nanoparticles (CSNPs) were carried out in the presence of two different marine polymers as stabilizers *Kappaphycus alvarezii* (*K. alvarezii*) and sodium alginate (SA) by two varied methods; chemical reduction and gamma irradiation. The aim of this research is to synthesize, characterize and test the antimicrobial activity of Cu and $Cu_2O$ nanoparticles. The Cu@$Cu_2O$-CSNPs were synthesized by using chemical reduction method in *K. alvarezii* media. Also Cu-NPs and Cu@$Cu_2O$ -CSNPs were prepared in sodium alginate by using same method. The synthesis carried out using aqueous medium in presence of hydrazinium hydroxide as reducing agent, $CuSO_4.5H_2O$ as copper precursor and sodium hydroxide as pH moderator.

The effects of the concentration of *K. alvarezii* and sodium alginate as stabilizer were studied. Formation of nanoparticles was determined by UV–vis spectroscopy where surface plasmon absorption maxima can be observed at 390-600 nm from the UV–vis spectrum. The synthesized nanostructures were also characterized by X-ray diffraction (XRD). In addition; the morphology and structure of the nanoparticles were investigated by Transmission Electron Microscopy (TEM), emission scanning electron microscopy (FESEM) and Energy-dispersive X-ray spectroscopy (EDX). TEM results showed a gradual decrease of particle size from low concentration of *K. alvarezii* and sodium alginate to high concentration. The study clearly

showed that using various amounts of *K. alvarezii* and sodium alginate led to produce Cu@$Cu_2O$-CSNPs with different sizes and ratios of Cu:$Cu_2O$. For the *K. alvarezii*/Cu@$Cu_2O$-CSNPs, the Cu-NPs increased and the $Cu_2O$ decreased with increasing the concentration of *K. alvarezii* until 0.2 wt.% in the Cu@$Cu_2O$-CSNPs. At the highest concentration of *K. alvarezii*, Cu decreased compare to $Cu_2O$. Moreover for the Cu@$Cu_2O$-CSNPs synthesized in sodium alginate with increasing the media concentration, the Cu increased and at the highest concentration of media (1.0 wt.%) only copper nanoparticles were produced. The size of the nanoparticles decreased as the amount of *K. alvarezii* and sodium alginate was increased.

Moreover the *K. alvarezii*/Cu@$Cu_2O$-CSNPs and SA/Cu-NPs were synthesized by using gamma irradiation method. The synthesis was done through γ-irradiation reduction of copper ions. The suspension was irradiated under γ-irradiation source $^{60}Co$ with doses of 5, 20, 40, 80, 100 and 120 kGy at room temperature. The effect of irradiation dosage was investigated. The UV-Vis spectroscopy results obtained for samples indicated that only the samples which were irradiated by 80, 100 and 120 kGy showed surface plasmon resonance (SPR) peaks in the range of 350-600 nm. It was due to the formation of *K. alvarezii*/Cu@$Cu_2O$-CSNPs and SA/Cu-NPs for these doses. TEM analysis indicated size and distribution of the nanoparticles varied in different doses of gamma irradiation. When the absorbed dose increased from 80 to 120 kGy the nanoparticle size decreased. Following synthesis of the nanoparticles, antibacterial analysis of the synthesized particles was investigated. Antimicrobial analysis conducted on the synthesized nanoparticles showed activity against all tested microorganisms.

Abstrak tesis yang dikemukakan kepada senate Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

**PENYEDIAAN DAN PENCIRIAN NANOPARTIKEL KUPRUM TERAS CANGKERANG YANG DISTABILKAN OLEH KAPPA CARRAGENAN DAN NATRIUM ALGINAT**

Oleh

**HAJAR KHANEHZAEI**

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Antara nanopartikel logam, nanopartikel tembaga (Cu-NPs) baru-baru ini telah menarik banyak perhatian kerana kos yang rendah (berbanding Au dan Ag) dan sifat-sifat bermanfaat mereka. Kadar rintangan mikroorganisma terhadap antibiotik adalah membimbangkan. Bakteria patogenik menjadi lebih tahan terhadap antibiotik. Nanopartikel tembaga sintesis terutamanya dalam penstabil berasaskan bio boleh bertindak sebagai agen anti-mikrob, yang seterusnya dapat menahan mikroorganisma patogenik.

Dalam kerja ini, sintesis dan pencirian nanopartikel Cu dan nanopartikel teras petala (CSNPs) Cu@$Cu_2O$ telah dijalankan dengan menggunakan dua polimer marin yang berbeza sebagai penstabil, *Kappaphycus alvarezii* (*K. alvarezii*) dan natrium alginat (SA) oleh dua kaedah iaitu penurunan kimia dan radiasi gamma. Tujuan kajian ini adalah untuk mensintesis, mencirikan nanopartikel Cu dan $Cu_2O$ dan menguji aktiviti antimikrobia nanopartikel.
CSNPs Cu@$Cu_2O$ telah disintesis dengan menggunakan kaedah penurunan kimia dalam media *K. alvarezii*. Cu-NPs dan nanopartikel teras petala Cu@$Cu_2O$ juga telah disediakan dalam natrium alginat dengan menggunakan kaedah yang sama. Sintesis dijalankan dalam medium akueus dengan meggunakan hidrazinium hidroksida sebagai agen penurunan, $CuSO_4.5H_2O$ sebagai prekursor tembaga dan natrium hidroksida sebagai pengawal pH.

Kesan kepekatan *K. alvarezii* dan natrium alginat sebagai penstabil telah dikaji. Pembentukan nanopartikel telah ditentukan oleh spektroskopi UV-nampak di mana penyerapan plasmon permukaan maksimum dapat dilihat pada 390-600 nm dari spektrum UV-nampak. Nanostruktur yang disintesis juga dicirikan dengan pembelauan sinar-X (XRD). Sebagai tambahan,

morfologi dan struktur nanopartikel telah disiasat dengan Mikroskopi transimisi electron (TEM), mikroskopi pengimbasan electron FESEM dan Tenaga-serakan sinar-x (EDX). Keputusan TEM menunjukkan saiz zarah berkurangan secara sedikit demi sedikit daripada kepekatan *K. alvarezii* dan natrium alginat rendah kepada kepekatan tinggi. Kajian ini jelas menunjukkan bahawa dengan memvariasikan jumlah *K. alvarezii* dan natrium alginat membawa kepada penghasilan CSNPs Cu@$Cu_2O$ dengan saiz dan nisbah Cu:$Cu_2O$ yang berbeza. Untuk CSNPs *K. alvarezii*/Cu@$Cu_2O$, Cu-NPs bertambah dan $Cu_2O$ berkurang dengan peningkatan kepekatan *K. alvarezii* sehingga berat 0.2% dalam nanopartikel Cu@$Cu_2O$. Pada kepekatan tertinggi *K. alvarezii*, Cu menurun berbanding $Cu_2O$. Tambahan pula nanopartikel Cu@$Cu_2O$ yang disintesis dalam natrium alginat dengan peningkatan kepekatan media, Cu meningkat dan pada kepekatan tertinggi media (berat 1.0%) hanya nanopartikel tembaga dihasilkan. Saiz nanopartikel berkurang sebagaimana jumlah *K. alvarezii* dan natrium alginat meningkat.

Selain itu, *K. alvarezii*/Cu@$Cu_2O$-CSNPs dan SA/Cu-NPs telah disintesis dengan menggunakan kaedah radiasi gamma. Sintesis itu dilakukan melalui penurunan ion tembaga oleh sinar-γ. Koloid itu telah diradiasi di bawah sinar-γ bersumberkan $^{60}Co$ dengan penyerapan dos daripada 5, 20, 40, 80, 100 dan 120 kGy pada suhu bilik. Keputusan spektroskopi UV-nampak diperolehi menunjukkan bahawa hanya sampel yang telah diradiasi sebanyak 80, 100 dan 120 kGy menunjukkan puncak plasmon permukaan resonans (SPR) dalam julat 350-600 nm. Ia adalah disebabkan oleh pembentukan *K. alvarezii*/Cu@$Cu_2O$-CSNPs dan SA/Cu-NPs bagi dos-dos tersebut. Analisis TEM menunjukkan saiz dan taburan nanopartikel berubah dalam dos radiasi gamma berbeza. Apabila dos yang diserap meningkat dari 80 kepada 120 kGy, saiz nanopartikel berkurangan.

Selepas mensintesis nanopartikel, analisis antibakteria zarah yang disintesis telah dikaji. Analisis antimikrobia dijalankan ke atas nanopartikel yang disintesis dan ianya menunjukkan aktiviti terhadap semua mikroorganisma yang diuji.

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I certify that a Thesis Examination Committee has met on 25 May 2015 to conduct the final examination of Hajar Khaneh Zaei on her thesis entitled "Preparation and Characterization of Core-Shell Copper Nanoparticles Stabilized by Kappa Carragenan and Sodium Alginate" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Master of Science.

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This thesis submitted to the Senate of Universiti Putra Malaysia has been accepted as fulfillment for the degree of Doctor of Philosophy.

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| | |
|---|---|
| CSNPs | Core shell nanoparticles |
| *K. alvarezii* | *Kappaphycus alvarezii* |
| SA | Sodium alginate |
| NPs | Nanoparticles |
| SPR | Surface Plasmon Resonance |
| XRD | X-ray Diffraction |
| TEM | Transmission Electron Microscopy |
| FESEM | Field Emission Scanning Electron Microscopy |
| SEM | Scanning Electron Microscopy |
| EDX | Energy Dispersive X-ray |
| FT-IR | Fourier Transfer Infrared Spectroscopy |
| DIZ | Diameters of inhibition zone |
| MRSA | *Methicillin Resistant Staphylococcus aureus* |

# CHAPTER 1

# INTRODUCTION

## 1.1 Background

Nanotechnology is one area which offers insight into materials at a nano levels. Nanotechnology deals with technology at atomic, molecular as well as macromolecular level which is in nano-scale. It also gives the basic knowledge of nanoparticles and their effect in association with their application and size (Roco, 2001). Nanoparticle sizes are specifically on interest in nanotechnology studies, as the sizes affect most of their special properties. The special properties of nanoparticles have varying results in various nanotechnology applications. There are different nanoparticle types for different applications such as metallic, non-metallic, carbon nano tubes as well as oxide nanoparticles (Yun *et al.*, 2008). Metallic nanoparticles have special properties which are because of a combination of big proportion of high energy surface atoms as compared with bulk solid as well as to the nanometer scale mean free path of electrons in any metal (~ 10–100 nm for most metals at room temperature). These are useful in different applications including catalysis, optoelectronics, magnetic, biology as well as micro-electronics (Lijie Zhang and Webster, 2009).

At present, among metallic nanoparticles, synthesis of copper (both oxide and metallic) nanoparticles has gained the attention of scholars because of their usable properties and inexpensiveness.

Copper being one of the inexpensive materials, has gained the attention of researchers via its nanoparticle synthesis due to the similarity in terms of properties with silver and gold, which are expensive (Chattopadhyay and Patel, 2012). Copper is in fact regarded as an alternative for gold, silver as well as platinum in the areas of thermal conducting as well as micro-electronics. Also it has been reported in studies of antimicrobial susceptibility studies, that copper nanoparticles were shown to have increased antibacterial activity than its counterparts in silver (Valodkar *et al.*, 2012). This aids copper nanoparticles synthesis one major area of research in nanotechnology. Copper nanoparticles synthesis of various compositions with preferred sizes as well as shapes is crucial for exploring their applications in the field of nanotechnology (Wen *et al.*, 2011). Areas such as catalysis (Hoover *et al.*, 2006), micro-electronics and sensors (Yun *et al.*, 2008) greatly depend on the size and shapes of nanoparticles.

## 1.2 Problem statement

In the current environmental pollution being a challenging situation, using environment friendly materials is adamant in research work. Natural sources are being used to get biopolymers which are bio-degradable. They are non-toxic, easily available and also renewable which make them environmentally-friendly. Rate of resistance of microorganisms to antibiotics is surprising. Pathogenic bacteria are becoming much resistant to antibiotics, which are produced on a continuous basis for combating microorganism. At present, antibiotics are resisted by every single pathogenic organism, which makes the fight much challenging (Raffi *et al.*, 2010).

Nanotechnology is a crucial area for research in future with immense potential in terms of nano-medicine. Nanoparticles and their properties such as antimicrobial and smaller size make them able for application in various areas such as medicine and biology. They show an extensive range of properties such as biological properties which varies from their bulk materials. As such synthesis of copper nanoparticles varies from their bulk materials. As such, copper nanoparticles synthesis particularly in bio-based stabilizers can act as antimicrobial agents, which in turn could resist pathogenic microorganisms. For synthesis of copper nanoparticles the stabilization of nanoparticles is one of the major problems to applications and the production of copper nanoparticles is much more challenging than noble metals because copper nanoparticles are totally sensitive to aqueous solutions, and air is stable at these conditions. To avoid oxidation of copper nanoparticles during synthesis an inert environment, such as argon or nitrogen is used.

Stabilization of nanoparticles is difficult due to the high surface area to volume ratio and surface energy of nanoparticles. To obtain copper nanoparticles with high stability, Surfactants and polymers widely used as stabilizers. Many of these commonly used stabilization agents, such as Polyethylene glycol (PEG) and poly vinyl pyrrolidone (PVP) are organic chemicals which are probably toxic.

## 1.3 Objectives

Synthesis of copper (both oxide and metallic) nanoparticles is beneficial because of its applicability in various industries. Its similarity in terms of properties with noble and expensive metals such as platinum, silver and gold makes it a good alternative to these metals, mainly because of the ready availability as well as its inexpensive nature. Even though there are different Cu and Cu@$Cu_2O$ nanoparticles synthesis approach, this study intends to explore the synthesis and characterization of Cu and Cu@$Cu_2O$ core shell nanoparticles in the sodium alginate and *Kappaphycus alvarezii* (*K. alvarezii*) as stabilizer via using two varying physical (γ-irradiation) as well as chemical approaches.

The specific objectives are:

1. To prepared *(K. alvarezii)* and sodium alginate stabilized Cu-NPs and Cu@ $Cu_2O$-CNSPs by chemical reduction and γ-irradiation methods.
2. To characterize Cu-NPs and Cu@$Cu_2O$-CSNPs using some of the different spectroscopy techniques.
3. To evaluate the antibacterial capability of the produced nanoparticles.

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