PREPARATION AND APPLICATIONS OF SOME CHITOSAN DERIVATIVES

By

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(B.Sc. in Chemistry, 2003)

For

The Partial Fulfillment of the Master Degree

Cairo University
Faculty of Science
Department of Chemistry

2009 - 2010

تحضير وتطبيقات لبعض مشتقات الكيتوزان

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(بكالوريوس العلوم - قسم الكيمياء، ٢٠٠٣)

للحصول على

درجة الماچستير فى العلوم (كيمياء فيزيائية)

كلية العلوم - جامعة القاهرة

2010 - ٢٠٠٩

ABSTRACT

Name: **Mohamed Abdel Tawab Sayed Hassanin**

Title of thesis: **Preparation and Applications of Some Chitosan Derivatives**

Degree: **M.Sc., Faculty of science, Cairo University, 2009.**

ChitoCin and ChitoThioCin polymer ligands were synthesized by the reaction of chitosan with cinnamoyl chloride and/or cinnamoyl isothiocyanate. ChitoCin acts as monobasic monodentate ligand which coordinates through oxygen site of the NH-C=O moiety of each monomer unit while ChitoThioCin acts as monobasic bidentate polymer ligand which coordinates through oxygen and sulfur sites of the NH-CO-NH-C=S moiety. From elemental and spectral data (Ft-IR, ESR and electronic spectra), it was found that, all the prepared metal complexes have octahedral geometrical structures. Thermodynamic parameters of the metal complexes were calculated. At lower pH, ChitoCin and ChitoThioCin polymer ligands have highest capacity for Fe(III), while at higher pH, they have highest capacity for Cu(II). The two polymeric chitosan derivatives prefer Cu(II) ions in chelation while Ni(II) ions are the less favorable with different mixtures of metal ions. Langmuir and Freundlich isotherm for the adsorption of Cu(II), Cr(III) and Fe(III) onto ChitoCin and ChitoThioCin were studied.

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Acknowledgment

I would like to express my deep sense of gratitude to my supervisor ***Prof. Dr. Maher Z. Elsabee*** *for his advice, support and encouragement during the course of this work. I am grateful to him for his patience and understanding during the writing of this dissertation.*

I would like to express my sincere grateful thanks to my supervisor ***Dr. Adel Emara*** *for his constructive comments and his valuable suggestions and considerable discussions he always, and continued to help out whenever possible.*

I would like to express my thanks to all the members and fellows in prof. Dr. Elsabee lab for their kindness and help.

M. Abdel Tawab

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Aim of the work

In this study, the reaction of chitosan with either cinnamoyl chloride or ammonium thiocyanate/cinnamoyl chloride to afford two polymeric chitosan derivatives having [-NH-(C=O)-] and [-NH-(C=S)-NH-C=O)] moieties has been investigated.

The obtained polymers have different chelating sites which might be more effective for the metal uptake and could be used to remove Cu(II), Ni(II), Co(II), Cr(III) and Fe(III) from their solutions. The chelating behavior will be investigated under several conditions; different isotherm models will be studied. .

Different physicochemical and spectroscopic studies will be used to identify the chemical and geometrical structure around each metal centre. Also, the kinetic parameters of the thermal decomposition of the prepared polymers and their metal complexes will be calculated based on Coats-Redfern method from the thermograms of the TGA analysis**.**

Chapter I

Introduction and Literature Survey

1.1. What is Chitin-Chitosan?

Chitin is an abundant organic material found mostly in crustaceans, mollusks and insects where it forms a constituent of the exoskeleton. It is also represented in fungal cell walls [1]. Chitin can be obtained from fungi, insect, lobster, shrimp and krill. Crabs obtained from seafood processing waste are an important commercial source [2]. According to some reports, 5000-8000 tons of crab shell material is disposed off by the seafood industry annually. Chitosan is derived from chitin, by a deacetylation reaction using an alkali. Chitosan is therefore a copolymer of glucosamine and N-acetyl glucosamine [3]. It is composed of β-(1 → 4)-2-amino-2-deoxy-D-glucopyranose (glucosamine units) and β-(1 → 4)-2-acetamido-2-deoxy-D-glucopyranose (acetylglucosamine units) [4]. The term "chitosan" refers to chitin that has been deacetylated to greater than 50%. Chitosan has many properties that have generated interest in its use such as biodegradability, biocompatibility and its nontoxic nature [5].

1.2. Chitin-Chitosan Timeline [6, 7]

- 4000 years ago: Crab shell was listed as a medicine in the legendary agricultural textbook of China.
- 14th–17th Century: Crab shell was listed as a medicine in the Ming Dynasty herb list.
- 16th Century: Crab & lobster shell tea was used as a folk remedy for maintaining or recovering health in various parts of the world.
- 1811: French history Professor Braconot isolated chitin from a mushroom and named it fungin.

- 1823: French scientist, Ogier, discovered that chitin could be used to create external skin and named it chitin, which means envelope in Greek.
- 1859: Rouge found chitosan.
- 1894: Hoppe-Seyler named “chitosan.”
- 1950: USSR Medical Academy & Lichtenstein researched chitin-chitosan for military purposes.
- 1965: Applications to agriculture and industry were made by the US & China to use chitin-chitosan.
- 1977: The first international conference on chitin-chitosan was held in Boston, USA.
- 1982 (April): Japanese Ministry of Agriculture and Fishery began a ten-year project of developing “Unused Biomass.”
- 1982 (July): The second international conference on chitin-chitosan was held in Sapporo, Japan.
- 1984: Japan-American Seminar “The New Function of Chitin-Chitosan” was held at Delaware University, USA.
- 1985: Japanese Ministry of Education gave scientific research grants to 13 Universities for “New Developments of Basic and Applied Researchers on chitin-chitosan and Their Related Enzymes”
- 1985: The third international conference on chitin-chitosan was held in Ancona, Italy.
- 1987: The first popular chitin-chitosan book in Japanese Crab Revolution by Kesao Kaneko was published.
- 1991: The fifth international conference on chitin-chitosan was held at Princeton University, USA.