PREPARATION AND CHARACTERIZATION OF ACRYLIC ACID-GRAFTED-CARBOXYMETHYL SAGO STARCH FOR REMOVAL OF CADMIUM(II) AND CHROMIUM(III) FROM AQUEAUS SOLUTION

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FS 2013 45

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By

SABARIAH BINTI KAMARUDIN

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia in Fulfilment of the Requirements for the Degree of Master of Science

December 2013

DEDICATION

To God,
Who gave me the life, strength and the guidance
and
To My Beloved Family,
Mama, Abah, Abang and Kakak
With grateful appreciation for their encouragement and love

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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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December 2013

Chairman :**Professor Mansor B. Ahmad, Ph.D.**

Faculty :**Science**

Polysaccharides such as starch and cellulose play important role in the polymer research because they are from natural resources and biodegradable. Their use in non-food applications depends on unique special properties they provide, often at costs below those of synthetic polymer. Chemically modified starches with improved properties are gaining increasing importance in industry not only because they are low in cost, but mainly because the polysaccharide portion of the product is biodegradable. In this study, carboxymethyl sago starch (CMSS) was grafted with acrylic acid monomer by radical polymerization technique, using electron beam irradiation. Effect of monomer absorption, degree of substitution (DS) of CMSS, radiation condition and irradiation dose during irradiation grafting process were investigated. Percentage of grafting was determined by thermogravimetry method using thermal gravimetic analysis (TGA). Thermogram of the combustion shows 3 steps of decomposition. Study showed that optimum grafting was 121.7% was achieved for CMSS with DS 1.0, 15 kGy irradiation doses. The grafted CMSS was characterized using TGA, Fourier transformed infrared spectroscopy (FTIR) and scanning electron micrography (SEM). The swelling of grafted CMSS is up to 7927% for grafted CMSS DS 1.0 and 4869% for grafted CMSS DS 1.2. Grafted CMSS was then applied for removal of Cr(III), and Cd(II) ions from aqueous solution by using adsorption method. Analysis of the metal adsorption was quantified using inductively coupled plasma optical emission spectroscopy (ICP-OES). The influences of various parameters such as degree of substitution of CMSS, pH and adsorption temperature were investigated. Cadmium was the highest adsorbed metal on grafted

CMSS with maximum percentage of adsorption 97% while for chromium, the maximum percentage of adsorption was 48% using grafted CMSS DS 1.0. Results showed that grafted CMSS DS 1.0 gave higher adsorption of metal ion compare to grafted CMSS DS 1.2

The results showed that carboxymethyl sago starch grafted acrylic acid could be an effective and economical adsorbent for removal of heavy metals ions from industrial wastewater.

Abstrak thesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

PENYEDIAAN DAN PENCIRIAN ASID AKRILIK-CANGKUKKAN-KARBOKSIMETIL KANJI SAGU UNTUK PENYINGKIRAN KADMIUM(II) DAN KROMIUM(III) DARIPADA LARUTAN AKUES

Oleh
SABARIAH BINTI KAMARUDIN

Pengerusi : Profesor Mansor B. Ahmad, Ph. D.

Faculti : Sains

Polisakarida seperti kanji dan selulosa memainkan peranan penting dalam penyelidikan polimer kerana ia terhasil daripada sumber semula jadi dan mesra alam. Kegunaan polisakarida dalam aplikasi bukan makanan bergantung kepada ciri-ciri khas unik yang terdapat padanya, ditambah pula dengan kos penghasilan yang lebih rendah berbanding polimer sintetik. Struktur kimia kanji yang diubahsuai dengan ciri-ciri yang lebih baik semakin penting dalam industri bukan sahaja kerana pembuatannya hanya memerlukan kos yang rendah, tetapi yang lebih utama kerana bahagian polisakarida di dalam produk adalah mesra alam. Dalam kajian ini, karboksimetil kanji sagu (CMSS) telah dicangkuk dengan monomer asid akrilik dengan teknik pempolimeran radikal, menggunakan sinaran alur elektron. Kesan penyerapan monomer, darjah penukargantian (DS) CMSS, keadaan sinaran dan dos radiasi ketika proses mencangkuk telah dikaji. Peratusan cangkukan ditentukan oleh kaedah termogravimetri menggunakan analisis termal gravimetri (TGA). Kajian ini menunjukkan bahawa cangkukan optimum sebanyak 121.7% telah dicapai untuk CMSS dengan DS 1.0, menggunakan dos radiasi sebanyak 15 kGy. Pencirian dilakukan dengan menggunakan TGA, spektroskopi inframerah transformasi Fourier (FTIR) dan analisis permukaan menggunakan mikroskopi pengimbasan elektron (SEM). Pengembangan CMSS tercangkuk didalam air adalah sebanyak 7927% untuk CMSS tercangkuk DS 1.0 dan 4869% untuk CMSS tercangkuk DS 1.2. CMSS tercangkuk itu kemudiannya digunakan untuk penyerapan ion Cr(III) dan ion Cd(II) daripada larutan ion tersebut dengan menggunakan kaedah penjerapan. Analisis penjerapan logam telah diukur menggunakan Spektrometri pemancaran optik plasma berganding aruh (ICP-OES). Pengaruh pelbagai parameter seperti darjah penukargantian CMSS, pH dan suhu penjerapan telah dikaji. Kadmium merupakan logam yang

paling tinggi terjerap pada CMSS tercangkuk dengan peratusan maksimum penyerapan sebanyak 97% sementara penjerapan maksimum bagi kromium adalah sebanyak 48% menggunakan CMSS tercangkuk DS 1.0. Keputusan menunjukkan CMSS tercangkuk DS 1.0 memberikan peratusan penjerapan yang lebih tinggi untuk menjerap ion logam berbanding CMSS tercangkuk DS 1.2.

Hasil kajian menunjukkan bahawa karboksimetil kanji sagu dicangkuk dengan asid akrilik boleh menjadi penjerap berkesan dan ekonomi untuk aplikasi penyingkiran logam dari air sisa industri.

ACKNOWLEDGEMENTS

In the name of Allah, The Most merciful and The Most Gracious.

First and foremost, I wish to express my deepest gratitude and appreciation to my supervisor, Professor Dr Mansor bin Ahmad for his quidance, supervision and encouragement throughout the course of this study. His inspiration and his great effort to help me in every difficulties will always remain in my mind.

Appreciation also extended to Dr Kamaruddin bin Hashim who continuously helped me throughout this project. His enthusiasm on explaining alot of good ideas contribute a large difference on how i think throughout this course.I also owe my deepest gratitude to Dr Nohazlin binti Zainuddin for her good teaching, good company and constant support through the research.

Special thanks are forwarded to all Malaysian Nuclear Agency staff for their kindness, help and support. I am gratefull to the dean of faculty, the administrators, staff, lecturers, and secretaries in the Chemistry department of Faculty of Science, Universiti Putra Malaysia, for their help and assistance in many different ways.

Last but not least, my warmest gratitude is dedicated to all those who supported me in any respect during the completion of the project.

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LIST OF ABBREVIATIONS

AGU	Anhydroglucose unit
CMS	Carboxymethyl starch
CMSS	Carboxymethyl sago starch
DS	Degree of substitution
FTIR	Fourier transform infrared analysis
SEM	Scanning Electron Microscope
TGA	Thermogravimetry Analysis
MCA	Monochloroacetic acid

CHAPTER 1

INTRODUCTION

1.1 Background of The Study

Polymer modifications are one of the most interesting segments in polymer technology. Natural polymer or synthetic polymer are modified to improve some properties such as biocompatibility, absorbing efficiency, fire retardancy or to provide specific functional group for ion exchange or other application. There are several techniques polymer can be modified such as grafting, cross linking, oxidation and end-capping (Joel, 2003).

Polysaccharides such as starch and cellulose play important role in the polymer research because they are from natural renewable resource and biodegradable. Both of these natural products deserve a special position among the industrially used as raw materials. Polysaccharides are used in the food industry because they are widely available, usually at low cost and non toxic. Their use in non-food applications depends on unique special properties they provide, often at costs below those of synthetic polymer (Bruice, 2004).

Chemically modified starches with improved properties are gaining an importance in industry not only because some of them are low in cost, but mostly because of the polysaccharide structure of the modified starch is biodegradable. Because of these properties, the modified starch become prominent polymer materials in the fields of metal adsorption, dehydration, water preservation and water absorption (Cao *et al.,* 2002).

Superabsorbent is a hydrophilic polymers that can adsorb and retain aqueous fluids in large quantities and with the absorb water are hardly removed even under pressure. Most of the super absorbent based on synthetic polymer are poor in degradability property. Extensive studies have been done to graft or crosslink monomers and polymers onto natural polymer to form superabsorbent natural polymer. Natural polymers like polysaccharides are fairly shear resistant, biodegradable and cause flocculation. However their shelf life was short due to the severe drawback of biodegradation. Synthetic polymers on the other hand are easily tailorable but have poor shear resistant properties. To combine natural and synthetic polymer properties various efforts have been taken (Singh, 1995).

Sago (*Metroxylon sagu)* is obtained from sago palm trees which are abundant in some region with swampy area in Malaysia, Indonesia and Papua New Guinea. In Malaysia, Sarawak is the only producer of sago starch. Sago palm contain of dry basis around 36-59% of

starch and remaining of non starch component such as fibers, hemicelluloses, other cell structural materials, soluble solids and also unidentified traces of other substances. (Sun, *et al*., 1999 and Manan *et al*., 2001).

Carboxymethyl sago starch (CMSS) is a water soluble derivative of sago starch. It is produced through etherification process. This process was carried out by substitution of monochloroacetic acid with hydroxyl group of starch in the presence of strong alkali such as sodium hydroxide. This process is eco friendly and using cost effective materials.

There are various methods in surface modification of polymer. Radiation-induced graft polymerization is one of the methods, leading to materials with new properties (Kabanov & Kudryavtsev, 2003). Grafting has proven to be an effective technique for modifying several properties of synthetic as well as polymers of natural origin. Modifications of several natural polymers like guar gum (GG), starch, cellulose and its derivatives by conventional redox grafting method were reported. Grafting using high-energy radiation offers several advantages over conventional redox grafting method. Grafting via ionization radiation by gamma and electron beam irradiation through the formation of radicals is more environmentally friendly than chemical process. It has been extensively used for grafting of various monomers on different type of polymers. The yield is higher and easier to manipulate than chemical process (Biswal *et al.,* 2007).

Heavy metals are very toxic elements and are not biologically degraded like many organic pollutants. Industrial uses of metal or other domestic waste, which is come in many forms such as wastewater, sludge, solid waste, chemical waste and many others have introduced amounts of toxic heavy metal into environment. The most common hazardous metals found in wastewater are copper, lead, nickel, chromium and zinc (Harrison, 1999). Various methods of removal heavy metal from wastewater such as chemical oxidation, precipitation, coagulation, ion exchange, reverse osmosis, reduction, flocculation, membrane separation, filtration, solvent extraction, evaporation and adsorption have been used to remove toxic from industrial effluents. Natural renewable polysaccharides have been reported to be efficient metal ion sorption. CMSS, as an example has proved to give large amount of water swelling (Norhazlin, 2003). Modification of this polymer via simple derivation, grafting or network formation improves these properties.

1.2 Problem Statement

Many researches have been reported on producing grafting polymer using natural material such as chitosan, cellulose and other material. But none has so far been conducted in producing grafting polymer

using modification of carboxymethyl sago starch. Sago itself has very unique properties towards water as is known, the sago growth in fresh water swamp. Naturally, sago has a strong resistance to water absorption and desorption. This specialty is very appropriate that it would be used in the treatment of water. However, sago starch has to be heated to gel form to increase its absorption capability. Modifications of sago starch by carboxymethylation process will improve its properties from insoluble to water soluble (Norhazlin, 2003). By the addition of other functional groups into carboxymethyl sago starch, it will enhance its properties which will enable carboxymethyl sago starch predominantly used in any environment conditions. Since acrylic acid is a simple monomer which compatible with water, so in theory, it is very suitable for carboxymethyl sago starch to be grafted with acrylic acid to produce a greater absorbent with excellent properties.

1.3 Objectives of The Study

1. To prepare carboxymethyl sago starch with two different DS values for use in the grafting irradiation.
2. To optimize the grafting condition as a function of monomer ratio, irradiation dose, DS of CMSSS and vacuum condition for acrylic acid grafted carboxymethyl sago starch using electron beam irradiation.
3. To characterize the grafted CMSS carried out by Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), scanning electron microscopy (SEM) and swelling behavior.
4. To determine capability of the grafted CMSS to adsorb chromium Cr(III) and cadmium Cd(II) ions.

REFERENCES

Abdel-Halim, E.S. & Al-Deyaba, S.S. 2011. Hydrogel from crosslinked polyacrylamide/guar gum graft copolymer for sorption of hexavalent chromium ion. *Carbohydrate Polymers.* **86.** 1306-1312.

Abd El-Rehim, H.A. & Diaa, D.A. 2012. Radiation-induced eco-compatible sulfonated starch/acrylic acid graft copolymers for sucrose hydrolysis *Carbohydrate Polymers.* **87.** 1905– 1912

Ajmal, M., Hussain K. A., Ahmad, S. & Ahmad, A.1998. Role Of Sawdust In The Removal Of Copper and Nickel Ion From Industrial Wastes. *Water Research*. **32**. 3085-3091.

Annemarie, M.L.H., Desse, M., Budtova, T., Franssen, M.C.R., Visser, G.M., Boeriu, C.G. & Sudhö lter, E.J.R. 2008. Physicochemical properties of etherified maize starches. *Carbohydrate Polymers.* **74.** 170-184

Bagheri, R., Naimian, F. & Sheikh, N.1997. Radiation grafting of acrylamide onto starch-filled low density polyethylene. *Radiation Physics. and Chemistry.* **49.** 497-501.

Bardajee, G. R., Pourjavadi, A., Sheikh, N. Amini-Fazla, M.S. 2008. Grafting of acrylamide onto kappa-carrageenan via g-irradiation: Optimization and swelling behavior. *Radiation Physics and Chemistry.* **77.** 131-137.

Behari K., Pandey P.K., Kumar, R. & Taunk, K. 2001. Graft copolymerization of acrylamide onto xanthan gum. *Carbohydrate Polymer* **46**. 185-189.

Benamer, S., Mahlous, M., Tahtat, D., Nacer-Khodja, A., Arabi, M., Lounici, H. & Mameri, N. 2011. Radiation synthesis of chitosan beads grafted with acrylic acid for metal ions sorption. *Radiation Physics and Chemistry.* **80.** 1391-1397

Benke, N., Taka´ csa, E., Wojna´ rovitsa, L. & Borsab, J. 2007. Pre-irradiation grafting of cellulose and slightly carboxymethylated cellulose (CMC) fibres. *Radiation Physics and Chemistry.* **76.** 1355-1359.

Bhattacharyya, A. 2000. Radiation and Industrial Polymers. *Progress in Polymer Science.* **25.** 371-401.

Bhattacharyya, A., Misra, B.N., 2004. Grafting: a versatile means to modify polymers techniques, factors and applications. *Progress in Polymer Science*. **29.** 767-814.

Bhattacharyya, D., Singhal, R.S. & Kulkarni P.R. 1996. Carboxymethyl starch: an extrusion aid. *Carbohydrate Polymers.* **31.** 79-82.

Biswal, J., Kumar, V., Bhardwaj, Y.K., Goel, N.K., Dubey, K.A., Chaudari, C.V. & Sabharwal, S. 2007. Radiation-induced grafting of acrylamide onto guar-gum in aqueous medium: Synthesis and characterization of grafted polymer guar-g-acrylamide. *Radiation Physics and Chemistry.* **76.** 1624-1630

Bruice, P. Y. 2004. Organic chemistry. *Prentice Hall*

Buchholz, F.L. & Graham, A.T. 1997. Absorbency and superabsorbency in modern superabsorbent polymer technology. *John Wiley & Sons.* 4-6.

Cao, Y.M., Qing, X.S., Sun, J., Zhou, F.M. & Lin, S. 2002. Graft copolymerization of acrylamide onto carboxymethyl starch. *European Polymer Journal.* **38**. 1921-1924.

Chapiro, A. 1962. Interscience. Radiation Chemistry of Polymeric Systems. New York.

Chen, J., Nho, Y.C., Kwon, O.H. & Hoffman, A.S. 1999 Grafting copolymerization of acrylamides onto preirradiated PP Films. *Radiation Physics and Chemistry.* **55.** 87-92.

Cotton, F.A. & Wilkinson, G. 1972 Advanced inorganic chemistry, Interscience Publisher

Deng, B., Li, J., Hou, Z., Yao, S., Shi, L., Liang, G. & Sheng, K. 2008 Microfiltration membranes prepared from polyethersulfone powder grafted with acrylic acid by simultaneous irradiation and their pH dependence *Radiation Physics and Chemistry.* **77.** 898-906.

Elchinger, P., Montplaisir, D. & Zerrouki, R. 2012 Starch/cellulose crosslinking towards a new material *Carbohydrate Polymers.* **87.** 1886-1890

Fang, J.M., Fowler, P.A., Tomkinson, J. & Hill, C.A.S. 2002. The preparation and characterization of a series of chemically modified potato Starches. *Carbohydrate Polymers*. **47**. 245-252

Fitt, L.E. & Snyder, E.M. 1984. Photomicrographs of Starches In Starch : Chemistry and Technology, ed. R.L. Whistler, J.N. BeMiller, and E.F. Paschall, pp: 675-689. Orlando, Florida: Academic Press.

Francis , S., Dhanawade. B.R., Mitra, D., Varshney, L. &Sabharwal, S. 2009. Radiation induced grafting of diallyldimethylammonium

chloride onto acrylic acid grafted poluethylene. *Radiation physics and chemistry*. **78**. 42-47.

Fu, F. & Wang, Q. 2011. Removal of heavy metal ions from wastewaters: A review. *Journal of Environmental Management.* **92.** 407-418.

Gao, W., Lin, X., Lin, X., Ding, J., Huang, X. & Wu, H 2011. Preparation of nano-sized flake carboxymethyl cassava starch under ultrasonic irradiation *Carbohydrate Polymers.* **84.** 1413–1418.

Garnett, J.L., 1979. Radiation Physic Chemistry. **14.** 79–99.

Garnett, J.L., Jankiewicz, S.V. & Sangster, D.F. 1990. Mechanistic aspects of the acid and salt effect in radiation grafting. *Radiation Physics and Chemistry.* **36**. 571–9.

Goyal, P., Kumar, V. & Sharma, P. 2007. Carboxymethylation of Tamarind kernel powder. *Carbohydrate Polymers*. 69. 251-255.

Grasselli, M. & Betz, N. 200.5 Electron-beam induced RAFT-graft polymerization of poly(acrylic acid) onto PVDF. *Nuclear Instruments and Methods in Physics Research*. **236.** 201-207.

Gurgel, L.V.A., Gil, L.F., 2009. Adsorption of Cu(II), Cd(II), and Pb(II) from aqueous single metal solutions by succinylated twice-mercerized sugarcane bagasse functionalized with triethylenetetramine. *Water Research.* **43.** 4479-4488

Harrison, R.M. 1999. Understanding environment an introduction to environment chemistry pollution. *The Royal Society of Chemistry.*

Hashim, K. 1996. Compatibilization of poly vinylidene fluoride/nylon 6 Blends by Intermolecular association. PhD Thesis. Loughborouh University.

Hebeish, A., and Khalil, M.I. 1988. Chemical Factors Affecting Preparation of Carboxymethyl Starch. *Starke.* **40** .147-150.

Heinze, T., Pfeiffer, K., Liebert, T., and Heinze, U. 1999b. Effective Approaches for Estimating the Functionalization Pattern of Carboxymethyl Starch of Different Origin. Starke. 51. 11-16.

Hien, N.G., Phu, D.V., Duy, N.N. & Huy, H.T. 2005. Radiation grafting of acrylic acid onto partially deacetylated chitin for metal ion adsorbent *Nuclear Instruments and Methods in Physics Research.* **236.** 606-610

Huang, Y., Lu, J. & Xiao, C. 2007. Thermal and mechanical properties of cationic guar gum/poly(acrylic acid) hydrogel membranes Polymer Degradation and Stability. 92. 1072-1081.

Joel, R.F. Polymer Science and Technology. 2003. Prentice Hall

Kabanov, V.Y. & Kudryavtsev, V.N., 2003. *High Energy Chem*. **37.** 1–5.

Karadağ, E., Barıs_ Üzüm, Ö., Saraydin, D. & Güven, O. 2005. Swelling characterization of gamma-radiation induced crosslinked acrylamide/maleic acid hydrogels in urea solutions *Materials and Design*. **27.** 576-584

Karim, A. Pei-Lang Tie, Manan, D.M.A. & Zaidul, I.S.M. 2008. Starch from the Sago (*Metroxylon sagu*) PalmTree - Properties,Prospects, and Challenges as a New Industrial Source for Food and Other Uses . *Comprehensif review on Food science and food safety.* **7.** 215-228.

Kim, B.S. & Lim, S.T. 1999. Removal of heavy metal ions from water by cross-linked carboxymethyl corn starch. *Carbohydrate Polymers.* **39.** 217-223.

Kwon, K., Auh, J.H., Park, H.P., Park, C.H. & Ko. J.C. 1997. Physiochemical Properties and Functionality of Highly carboxymethylated starch. *Starch.* **49**. 499-505.

Lagarrigue, S., Alvarez , G., Cuvelier, G. & Flick, D. 2008. Swelling kinetics of waxy maize and maize starches at high temperatures and heating rates. *Carbohydrate Polymers.* **73.** 148-155.

Lanthong, P., Nuisin, R. & Kaitkamjornwong, S. 2006. Graft copolymerization, characterization and degradation of cassava starch-g-acrylamide/itaconic acid superabsorbent *Carbohydrate polymers* **66.** 229-245.

Lawal, O. S., Adebowale, K. O., Ogunsanwo, B. M., Barba, L. L., & Llo, N. S. 2004. Oxidized and acid thinned starch derivatives of hybrid maize: Functional characteristics, wide-angle X-ray diffractometry and thermal properties. *International Journal Biological Macromolecules.* **35**. 71–79.

Lawal, O. S., Lechner, M. D., & Kulicke, W. M. (2008a). Single and multi-step carboxymethylation of water yam (Dioscorea alata) starch: Synthesis and characterization. International Journal of Biological Macromolecules. **42**. 429–435

Liu, T., DeSimone, J.M. & Roberts, G.W. 2006. Cross-linking polymerization of acrylic acid in supercritical carbon dioxide. *Polymer*. **47.** 427-428.

Manan, D.M.A., Islam, M.N. & Mohd Azemi, B.M.N. 2001. Enzymic extraction of native sago starch from sago (*Metroxylon sagu*) waste residue. *Starch/Starke*. **53**:639.43.

McClatchey, W., Manner, H. I. & Elevitch C. R. 2006. *Metroxylon amicarum*, *M*. *paulcoxii*, *M. sagu*, *M. salomonense*, *M*. *vitiense*, and *M*. *warburgii* (sago palm) Arecaceae (palm family) www.traditionaltree.org

Mishra, S., Usha Rani, G. & Sen, G. 2012. Microwave initiated synthesis and application of polyacrylic acid grafted carboxymethyl cellulose. *Carbohydrate Polymers.* **87** . 2255-2262.

Nagasawa, N., Yagi,N., Kume, T., & Yoshii, F. 2004 Radiation crosslinking of carboxymethyl starch. *Carbohydrate Polymers.* **58**.109-113.

Nasef, M.M. & Hegazy, E.S.A., 2004. Preparation and applications of ion exchange membranes by radiation-induced graft copolymerization of polar monomers onto non-polar films. *Progress in Polymer Science*. **29**. 499–561.

Niu, C., Wu,W., Wang, Z., Li, S., & Wang, J. 2007. Adsorption of heavy metal ions from aqueous solution by crosslinked carboxymethyl konjac glucomannan. *Journal of Hazardous Materials.* **141.** 209–214.

Norhazlin, Z. 2003. Carboxymethylation of Sago Starch and Sago Waste
and the Formation of Carboxymethyl Starch-Hydrogel Via Irradiation Technique. MSc Thesis. Universiti Putra Malaysia. 135p

Nurmi, L., Holappa, S., Mikkonen, H. & Seppälä, J. 2007. Controlled grafting of acetylated starch by atom transfer radical polymerization of MMA *European Polymer Journal.* **43.** 1372-1382.

Pengfei, L., Maolin, Z. & Jilan, W. 2001. Study on radiation-induced grafting of styrene onto chitin and chitosan. *Radiation Physics and Chemistry.* **61.** 149-153.

Pourjavadi, A., Eftekhar Jahromi, P., Seidi, F. & Salimi, H. 2010. Synthesis and swelling behavior of acrylatedstarch-g-poly (acrylic acid) and acrylatedstarch-g-poly (acrylamide) hydrogels. *Carbohydrate Polymers.* **79** 933-940.

Pushpamalar,V., Langford S.J., Ahmad,M., Lim, Y.Y. 2006. Optimization of reaction conditions for preparing carboxymethyl cellulose from sago waste, *Carbohydrate Polymers.* **64.** 312-318.

Raimunda de Abreu, F. & Campana-Filho, S.P. 2009. Characteristics and properties of carboxymethyl chitosan. *Carbohydrate Polymers.* **75.** 214-221

Ratnayake, W.S. & Jackson, D.S. 2009. Starch gelatinization. Department of Food Science and Technology, University of Nebraska-Lincoln. *Advanced in food and nutrition research.* **55.** 221-68.

Reddy, B.R., Mirghaffari, N. & Gaballah, I. 1997. Removal and recycling of copper from aqueous solutions using treated Indian barks. *Resources, Conservation and Recycling***. 21.** 227-245.

Rogueda, C., Polton, A., Tardi, M. & Sigwal, P. 1989. Homopolymerization and copolymerization of methyl methacrylate in the presence of complexing agents -V. influence of the nature of the solvent. *European Polymer Journal*. **25.** 1259-1267.

Sharma, R. K., & Lalita, S. 2011. Synthesis and characterization of graft copolymers of N-vinyl-2-pyrrolidone onto guar gum for sorption of Fe2+ and Cr6+ ions. *Carbohydrate Polymers.* **83.**1929-1936.

Singh, J., Kaur, L. & McCarthy, O.J. 2007. Factors influencing the physico-chemical, morphological, thermal and rheological properties of some chemically modified starches for food applications - A review *Food Hydrocolloids* **21.** 1–22

Singh, R.P., 1995. Advanced turbulent drag reducing and flocculating materials based on polysaccharides. In: Polymers and Others Advanced Materials: Emerging Technologies and Business Opportunities. Plenum Press, New York, 227–244

Staroszczyk, H., Tomasik, P., Janas, P. & Poreda, A. 2007. Esterification of starch with sodium selenite and selenate *Carbohydrate Polymers.* **69.** 299-304

Sun, R., Jones, G.L., Tomkinson, J., & Bolton, J. 1999. Fractional isolation and partial characterization of non-starch polysaccharides and lignin from sago pith*. Industrial Crops and Products.* **19.** 211-220.

Takigami, M., Amada, H., Nagasawa, N., Yagi, T., Kasahara, T., Takigami, S. &Tamada, M. 2007. Preparation and properties of CMC gel. *Transaction Of The Material Research Society Of Japan***. 32**. 713-716

Takigami, M., Hiroki, A., Nagasawa, N., Kasahara, T., Takigami, S. & Tamada, M. 2008. Novels gels derived from carboxymethylcellulose. JAEA publication.

Tanodekaew, S., Prasitsilp, M., Swasdison, S., Thavornyutikarn. B., Pothsree. T. & Pateepasen. R. 2004. Preparation of acrylic grafted chitin for wound dressing application. *Biomaterials*. **25.** 1453-60.

Teramoto, N., Motoyama, T., Yosomiya, R. & Shibata, M. 2003. Synthesis, thermal properties, and biodegradability of propyl-etherified starch. European Polymer Journal **39.** 255-261

Turmanova, S., Trifonov, A., Kalaijiev, O. & Kostov, G.1997. Radiation grafting of acrylic acid onto polytetrafluoroethylene films for glucose oxidase immobilization and its application in membrane biosensor *Journal of Membrane Science.* **127.** 1-7

Villaescusa, I., Fiol, N., Martınez, M., Miralles, N., Poch, J. & Serarols, J. 2004. Removal of copper and nickel ions from aqueous solutions by grape stalks wastes. *Water Research.* **38.** 992-1002.

Wach, R.A., Mitomo, H., Nagasawa, N. & Yoshii, F. 2003. Radiation crosslinking of carboxymethylcellulose of various degree of substitution at high concentration in aqueous solutions of natural pH. *Radiation Physics and Chemistry.* **68.** 771-779

Wang WJ, Powell AD, Oates CG. 1995. Pattern of enzyme hydrolysis in raw sago starch:effects of processing history. Carbohydrate Polym 26:91–7.

Wang, L.F., Pan, SY., Hu, H., Miao, WH. & Xu, XY. 2010. Synthesis and properties of carboxymethyl kudzu root starch. *Carbohydrate Polymers***. 80** 174–179.

Wang, X.S., Tang, Y.P. & Tao, S.R. 2009. Kinetics, equilibrium and thermodynamic study on removal Cr (IV) from aquaeous solution using low cost adsorbent Alligator weed. *Chemical Engineering Journal* **148.** 217-225.

Witono, J.R., Noordergraaf, I.W., Heeres, H.J.&. Janssen, L.P.B.M. 2012. Graft copolymerization of acrylic acid to cassava starch-Evaluation of the influences of process parameters by an experimental design method *Carbohydrate Polymers.* **90**. 1522-1529.

Xie, G., Shang, X., Liu, R., Hu, J. & Liao, S. 2011. Synthesis and characterization of a novel amino modified starch and its adsorption properties for Cd(II) ions from aqueous solution. *Carbohydrate Polymers.* **84.** 430-438.

Yaacob, B., Mohd Amin, M.C.I., Hashim, K. & Abu Bakar, B. 2011 Optimization of Reaction Conditions for Carboxymethylated Sago Starch *Iranian Polymer Journal*. **20**. 1-14.

Yanli, W., Wenyuan, G. & Xia, L. 2009. Carboxymethyl Chinese yam starch: synthesis, characterization, and influence of reaction parameters. *Carbohydrate Research.* **344.** 1764-1769

Yi˘gito˘glu, M. & Arslan, M. 2009. Selective removal of Cr(VI) ions from aqueous solutions including Cr(VI), Cu(II) and Cd(II) ions by 4-vinly pyridine/2-hydroxyethylmethacrylate monomer mixture grafted poly(ethylene terephthalate) fiber. *Journal of Hazardous Materials*. **166.** 435-444.

Yu, C., Yun-fei, L., Hui-min, T. & Jian-xin, J. 2009. Synthesis and characterization of a novel superabsorbent polymer of N,O-carboxymethyl chitosan graft copolymerized with vinyl monomers. *Carbohydrate Polymers* **75.** 287-292.

Yu, M.H. 2005. Environmental Toxicology. Niological and health Effects of Pollutants, second Edition. CRC Press, Boca Raton, Florida.

Zhai, M., Chen, J., Hasegawa, S., Li, D., Oku, H. & Maekawa, Y. 2009. Perfluorinated polymer film with functional group prepared by radiation-induced grafting *European Polymer Journal.* **45.** 1668-1673

Zhu, X., Hu, B., Jiang, Z. & Li, M. 2005. Cloud point extraction for speciation of chromium in water samples by electrothermal atomic absorption spectrometry. *Water Research.* **39.** 589-595.