UNIVERSITI PUTRA MALAYSIA

SYNTHESIS AND CHARACTERIZATION OF POLY(HYDROXAMIC ACID) AND POLY(AMIDOXIME) CHELATING RESINS FROM POLYMER GRAFTED SAGO STARCH

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By

MD. LUTFOR RAHMAN

Thesis Submitted in Fulfilment of the Requirements for the
Degree of Doctor of Philosophy in the Faculty of
Science and Environmental Studies
Universiti Putra Malaysia

December 1999

UPM

DEDICATED

To my parents and grand parents.

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirements for the degree of Doctor of Philosophy

SYNTHESIS AND CHARACTERIZATION OF POLY(HYDROXAMIC ACID) AND POLY(AMIDOXIME) CHELATING ION EXCHANGE RESINS FROM POLYMER GRAFTED SAGO STARCH

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December 1999

Chairman : Dr. Sidik Silong

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The graft copolymerization of methyl acrylate (MA) onto sago starch was performed by free radical initiating process in which ceric ammonium nitrate (CAN) was used as an initiator. It was found that the optimum yield of grafting, grafting efficiency and rate of graft polymerization were all dependent upon the concentration of CAN, MA, sago starch (AGU) and mineral acid (H_2SO_4) as well as reaction temperature and period. A new equation rate of polymerization was derived from the proposed reaction mechanism. A new kinetic model for graft fraction was proposed and the validity of the model was tested by the plot of $1/(1\text{-}GF)^{1/2}$ as a function of sago starch concentration and reciprocal monomer (MA) concentration. The required straight line and ordinate intercept unity was obtained and the predicted kinetic model was satisfactory supported by the experimental results until a certain limit of monomer (MA) concentration.

A chelating polymeric resin containing hydroxamic acid was synthesized from poly(methyl acrylate) (PMA) grafted sago starch. The binding capacity of the

poly(hydroxamic acid) resin with copper is high and other metal ions also show significant binding capacity. This chelating resin has the advantage of faster rate of equilibrium and negligible affinity for alkali metal ions. The sorption capacities of metal ions were pH dependent and its selectivity towards these metal ions is in the following order: $Cu^{2+} > Fe^{3+} > Cr^{3+} > Ni^{2+} > Co^{2+} > Zn^{2+} > Cd^{2+} > As^{3+} > Pb^{2+}$. The separation of Cu^{2+} from Co^{2+} and Cd^{2+}, and Fe^{3+} from Co^{2+} and Cd^{2+} were carried out by column technique.

Ion exchange equilibria of transition metal ions by the poly(hydroxamic acid) resin have been studied at 30, 45 and 60^0C. The thermodynamic equilibrium constant, K; standard Gibbs free energy, ΔG^o; standard enthalpy, ΔH^o; and entropy, ΔS^o were calculated from the exchange isotherms. The ΔG^o was negative for all exchange systems and standard enthalpy, ΔH^o and standard entropy ΔS^o changes in the exchange systems were positive for Cu^{2+} and Ni^{2+} and negative for Co^{2+} and Cd^{2+}. The thermodynamic affinity sequences were obtained for metal ions, which indicated the strong affinity for Cu^{2+} and Ni^{2+} of poly(hydroxamic acid) resin. The absorbency of poly(hydroxamic acid) in distilled water and various salt solutions increases with increasing of PMA concentration during the preparation stage.

Similarly, CAN was used to initiate the graft copolymerization of acrylonitrile (AN) onto sago starch and the grafting reaction was also optimized. The predicted model was also tested for AN monomer and sago starch concentrations. A chelating poly(amidoxime) resin was synthesized from PAN grafted sago starch. The binding capacities of resin with metal ions were investigated and separation of some metal ions was carried out by column technique.

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

SINTESIS DAN PENCIRIAN RESIN PERTUKARAN ION MENGKELAT POLI(ASID HIDROKSAMIK) DAN POLI (AMIDOKSIM) DARIPADA POLIMER TERCANGKUK KANJI SAGO

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pengkopolimeran cangkukan metil akrilat keatas kanji sago telah dilakukan melalui proses yang dimulakan oleh radikal bebas dimana serik amonium nitrat diguna sebagai permula. Hasil maksimum cangkukan, kecekapan cangkukan dan kadar pempolimeran cangkukan didapati bergantung kepada kepekatan serik amonium nitrat (CAN), metil akrilat (MA), kanji sago (AGU), asid mineral (H_2SO_4) dan suhu serta masa tindabalas. Satu persamaan kadar tindak balas pempolimeran diterbitkan daripada mekanisma tindakbalas yang dicadangkan. Satu model kinetik untuk pecahan cangkukan telah dicadangkan dan kebolehgunaan model tersebut diuji melalui pemplotan $1/(1\text{-}GF)^{1/2}$ sebagai rangkap kepekatan kanji sago terhadap salingan kepekatan monomer. Garis lurus yang didapati memotong pada uniti dan model kinetik didapati bersesuaian dengan keputusan ujikaji sehingga kepada had kepekatan monomer tertentu.

Resin polimer mgkelat yang ndungi asid hidroksamik telah disintesis daripada poli(metil akrilat) tercangkuk kanji sago. Kemampuan pengikatan resin poli(asid hidroksamik) dengan kuprum adalah tinggi dan agak tinggi juga terhadap ion-ion logam lain. Kelebihan resin pengkelat ini ialah disamping mempunyai kadar mencapai keseimbangan yang cepat, keafinan terhadap terhadap ion logam alkali boleh diabaikan. Kapasiti penyerapan ion-ion logam bergantung kepada pH dan kepilihannya terhadap ion-ion logam menurut turutan : $Cu^{2+} > Fe^{3+} > Cr^{3+} > Ni^{2+} > Co^{2+} > Zn^{2+} > Cd^{2+} > As^{3+} > Pb^{2+}$. Pemisahan Cu^{2+} daripada Co^{2+} dan Cd^{2+}, dan Fe^{3+} daripada Co^{2+} dan Cd^{2+} telah dilakukan melalui teknik kromatografi turus.

Keseimbangan penukar-ion ion logam peralihan resin poli(asid hidroksamik) dikaji pada 30, 45 and 60^0C. Pemalar keseimbangan termodinamik, K; tenaga bebas Gibbs piawai, ΔG^o; entalpi piawai, ΔH^o; dan entropi, ΔS^o telah dikira daripada pertukaran isoterma. ΔG^o adalah negatif untuk semua sistem pertukaran dan entalpi piawai, ΔH^o dan entropi piawai ΔS^o berubah dalam sistem pertukaran adalah positif untuk Cu^{2+}, Ni^{2+} dan negatif untuk Co^{2+} dan Cd^{2+} masing-masing. Turutan affiniti termodinamik yang diperolehi bagi beberapa ion logam menunjukkan keafinan yang kuat untuk Cu^{2+} and Ni^{2+} oleh resin poli(asid hidroksamik). Keserapan poli(asid hidroksamik) dalam air suling dan berbagai larutan garam bertambah dengan pertambahan kepekatan PMA.

CAN juga telah digunakan untuk memulakan pempolimeran cangkuk akrilonitril katas kanji sago dan tindakbalas pencangkukan ini telah di optimumlean. Model ramalan telah diuji untuk monomer AN dan kanji sago. Resin pengkelat poli(amidoksim) telah disintesis daripada poliakrilonitril (PAN) tercangkuk kanji sago. Kapasiti pengikatan resin dengan ion logam dikaji dan pemisahan bebarapa ion logam telah dijalankan melalui teknik kromatografi turus.

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I certify that an Examination Committee met on 23th December, 1999 to conduct the final examination of Md. Lutfor Rahman on his Doctor of Philosophy thesis entitled "Synthesis and characterization of poly(hydroxamic acid) and poly(amidoxime) chelating resins from polymer grafted sago starch" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the candidate be awarded the relevant degree. Members of the Examination Committee are as follows:

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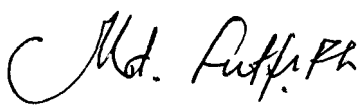
DECLARATION

I hereby declare that the thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that this thesis has not been previously or concurrently submitted for any other degree at UPM or any other institutions.

Signed



(MD. LUTFOR RAHMAN)

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