UNIVERSITI PUTRA MALAYSIA

PREPARATION AND APPLICATION OFPOLY(HYDROXAMIC ACID)-KENAF FIBER CHELATING ION EXCHANGER FOR THE REMOVAL OF CHROMIUM AND NICKEL FROM AQUEOUS SOLUTIONS

SOLEHA MOHAMAT YUSUFF

FS 2013 11

PREPARATION AND APPLICATION OF POLY(HYDROXAMIC ACID)-KENAF FIBER CHELATING ION EXCHANGER FOR THE REMOVAL OF CHROMIUM AND NICKEL FROM AQUEOUS SOLUTIONS

SOLEHA MOHAMAT YUSUFF

MASTER OF SCIENCE
UNIVERSITI PUTRA MALAYSIA

2013

PREPARATION AND APPLICATION OF POLY(HYDROXAMIC ACID)-KENAF FIBER CHELATING ION EXCHANGER FOR THE REMOVAL OF CHROMIUM AND NICKEL FROM AQUEOUS SOLUTIONS

By

SOLEHA MOHAMAT YUSUFF

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

May 2013

COPYRIGHT

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

PREPARATION AND APPLICATION OF POLY(HYDROXAMIC ACID)-KENAF FIBER CHELATING ION EXCHANGER FOR THE REMOVAL OF CHROMIUM AND NICKEL FROM AQUEOUS SOLUTIONS

By

SOLEHA MOHAMAT YUSUFF

May 2013

Chairman : Md. Jelas Haron, PhD

Faculty : Science

Research on the removal of heavy metal ions from water and wastewater is a necessary mission of protecting human health and the environment. Adsorption is the promising technique compared to the others due to its low-cost, easy operating and effectiveness characteristic. Besides produced the effective adsorbent, many researchers has great attention to use low-cost and non-petroleum based materials such as natural fibers. Fibrous plant of kenaf (*Hibiscus cannabinus L.*) is one of the commercial crops in Malaysia which is used in various sectors due to its properties. Therefore the application of kenaf fiber for removal of heavy metals from water and wastewater is worth explored. The fiber was grafted through polymerization with methyl acrylate and the ester group was reacted with hydroxylamine hydrochloride to form poly(hydroxamic acid) which is known able to form complex with metal ions.

The effects of important parameters during grafting process which can affect percentage of grafting such as amount of catalyst, co-catalyst and monomer, temperature and time of grafting were studied followed by the effects of pH and

amount of hydroxylamine hydrochloride during hydroxyaminolysis which can affect the percentage of metal removal. The characteristics of kenaf fiber, grafted kenaf fiber and functionalized kenaf fiber prepared were characterized by colored complex test with vanadium ion, TGA, CHN/O analysis, BET surface analysis, FTIR and SEM-EDX spectroscopy. This research also investigate the effects of pH, reaction time, initial metal concentrations, adsorbent dosage and temperature on the adsorption capacity for Ni (II), Cr (III) and Cr (VI) ions removal.

The optimum amount of catalyst, co-catalyst and monomer for grafting copolymerization of methyl acrylate onto 5.0 g of kenaf fiber were 15 mL, 0.50 g and 30 mL, respectively. The percentage of grafting value was higher with 2 hr of grafting reaction at 45 ^{o}C. In preparation of PHA-kenaf, 1.0 g of hydroxylamine hydrochloride in 15 mL of methanolic solution at pH 13 reacted with 1.0 g PMA-kenaf gave the high value of adsorption capacity. FTIR spectra, TGA, BET analysis, CHN/O elemental analysis, colored complex test with vanadium ion, SEM images and EDX spectra showed the characteristics of kenaf, PMA-kenaf and PHA-kenaf. The optimum pH for Ni (II), Cr (III) and Cr (VI) adsorptions were 6, 4 and 3, respectively. The adsorption capacities were dependent on Ni (II), Cr (III) and Cr (VI) ions concentrations, reaction time, and adsorbent dosage. The adsorption process of Ni (II), Cr (III) and Cr (VI) followed pseudo second-order model. The equilibrium data followed the Langmuir model with maximum adsorption capacity of Ni (II), Cr (III) and Cr (VI) were 43.29, 13.42 and 30.12 mg/g, respectively. The adsorption processes were endothermic and spontaneous.

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

PENYEDIAAN DAN APLIKASI PENUKAR ION PENGKELAT POLI (ASID HIDROSAMIK)-KENAF FIBER UNTUK PENYINGKIRAN KROMIUM DAN NIKEL DARIPADA LARUTAN AKUES

Oleh

SOLEHA MOHAMAT YUSUFF

Mei 2013

Pengerusi : Md. Jelas Haron, PhD

Fakulti : Sains

Penyelidikan tentang penyingkiran ion-ion logam berat daripada air dan air buangan merupakan satu misi penting untuk melindungi kesihatan manusia dan alam sekitar. Penjerapan adalah teknik yang lebih baik berbanding teknik-teknik lain kerana murah, mudah dijalankan dan berkesan. Selain menghasilkan penjerap yang berkesan, ramai penyelidik memberi tumpuan lebih kepada penggunaan bahan mentah yang murah dan bukan berasaskan petroleum seperti serat semulajadi. Tumbuhan berserabut kenaf (*Hibiscus cannabinus L.*) adalah salah satu tanaman komersial di Malaysia yang digunakan dalam pelbagai sektor kerana sifat-sifatnya. Oleh itu, penggunaannya untuk pengingkiran logam berat daripada air dan bahan buangan adalah bernilai untuk diterokai. Serat kenaf telah dicangkukkan melalui proses pempolimeran dengan metil akrilat dan diikuti oleh tindak balas dengan hidroksilamin hidroklorida untuk menukarkan keimplan esternya kepada poli(asid hidroksamik) yang diketahui mampu membentuk kompleks dengan ion logam.

Kesan-kesan pelbagai parameter penting ketika proses cangkukkan yang boleh mempengaruhi peratus cangkukkan seperti jumlah mangkin, mangkin bersama dan monomer, suhu dan masa pempolimeran telah dikaji diikuti kesan pH dan jumlah

hidroksilamina hidroklorida pada peratus penyingkiran ketika proses hidroksilaminolisis. Sifat serat kenaf, serat kenaf telah dicangkukkan dan serat kenaf telah difungsikan telah di uji dengan ujian kompleks berwarna dengan ion vanadium, TGA, analisis CHN/O, analisis permukaan BET, FTIR dan SEM-EDX spektroskopi. Penyelidikan ini juga mengkaji kesan-kesan pH, masa tindak balas, kepekatan logam asal, jumlah penjerap dan suhu pada kapasiti penjerapan untuk penyingkiran Ni (II), Cr (III) dan Cr (VI) ion.

Amaun mangkin, mangkin bersama dan monomer yang optimum untuk pempolimeran cangukkan metil akrilat ke atas 5.0 g serat kenaf ialah masing-masing 15 mL, 0.50 g dan 30 mL. Nilai peratus cantuman paling tinggi dengan 2 jam tindak balas pempolimeran pada suhu 45 ^{o}C. Ketika penyediaan PHA-kenaf, 1.0 g hidroksilamina hidroklorida dalam 15 mL larutan methanol pada pH 13 yang ditindak balas dengan 1.0 g PMA-kenaf memberikan nilai kapasiti penjerapan ion logam yang tinggi. Spektrum FTIR, TGA, analisis BET, analisis unsur CHN/O, ujian kompleks berwarna dengan ion vanadium, imej SEM dan spektra EDX telah menunjukkan PMA-kenaf dan PHA-kenaf telah berjaya dihasilkan. Optimum pH bagi penjerapan Ni (II), Cr (III) dan Cr (VI) masing-masing ialah 6, 4 dan 3. Kapasiti penjerapan juga bergantung pada kepekatan ion Ni (II), Cr (III) dan Cr (VI), masa tindak balas dan jumlah penjerap. Penjerapan Ni (II), Cr (III) dan Cr (VI) mematuhi pseudo oder kedua. Data keseimbangan menunjukkan penjerapan mematuhi model Langmuir dengan kapasiti maksimum penjerapan bagi Ni (II), Cr (III) dan Cr (VI) masing-masing ialah 43.29, 13.42 and 30.12 mg/g. Proses penjerapan adalah endotermik dan spontan.

ACKNOWLEDGEMENTS

In the Name of Allah, The Most Merciful and Most Beneficiet

First and foremost, I would like to take this opportunity to express my sincere appreciation to my project supervisor Prof. Dr. Hj. Md. Jelas Haron, and also co-supervisors Dr. Nor Azowa Ibrahim and Prof. Dr. Mansor Ahmad for their supervision, invaluable guidance, unfailing help, advice and suggestion throughout the duration of my study. I would like to thank to Universiti Putra Malaysia for financial support through Research University Grant Scheme funds and Graduate Research Fellowship. Special thanks to all the staff in Faculty of Science for their assistance and cooperation that in one way or another has contributed to the success of this study. Thanks too to my course mates, lab mates, and friends for their help, encouragement and comments in sustaining the morale and enthusiasm. Last but not least, I would like to express my deepest appreciation to my beloved family for their caring, patience, support and understanding during difficult times. With their unconditional and endless love, praise to Allah that make me possible to complete my study.

I certify that a Thesis Examination Committee has met on 31 May 2013 to conduct the final examination of Soleha Mohamat Yusuff on her thesis entitled "Preparation and Application of Poly (Hydroxamic Acid)-Kenaf Fiber Chelating Ion Exchanger for Removal of Chromuim and Nickel from Aqueous Solutions" 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.

Members of the Thesis Examination Committee were as follows:

Zulkarnain bin Zainal, PhD
Professor
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Abdul Halim bin Abdullah, PhD
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Internal Examiner)

Nor Azah binti Yusof, PhD
Professor
Faculty of Science
Universiti Putra Malaysia
(Internal Examiner)

Mohd. Asri Nawi, PhD
Associate Professor
Universiti Sains Malaysia
Malaysia
(External Examiner)

NORITAH OMAR, PhD
Associate Professor and Deputy Dean
School of Graduate Studies
Universiti Putra Malaysia

Date: 19 September 2013

This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Master of Science. The members of the Supervisory Committee were as follows:

Md. Jelas Haron, PhD
Professor
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Nor Azowa Ibrahim, PhD
Senior Lecturer
Faculty of Science
Universiti Putra Malaysia
(Member)

Mansor Ahmad, PhD
Professor
Faculty of Science
Universiti Putra Malaysia
(Member)

BUJANG BIN KIM HUAT, PhD
Professor and Dean
School of Graduate Studies
Universiti Putra Malaysia

Date:

DECLARATION

I declare that the thesis is my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously, and is not concurrently, submitted for any other degree at Universiti Putra Malaysia or at any other institution.

_____

SOLEHA MOHAMAT YUSUFF

Date: 31 MAY 2013

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

BET	Brunauer Emmett Teller
Ce	Final metal concentration
CHN/O	Carbon Hydrogen Nitrogen/ Oxygen
Co	Initial metal concentration
D	Distribution ratio
DTG	Derivative thermogravimetric
EDX	Energy dispersive X-ray
FTIR	Fourier transform infrared spectroscopy
Ge	Percentage of grafting efficiency
I	Increment
IUPAC	International Union of Pure and Applied Chemistry
OPEFB	Oil palm empty fruit bunch
Pg	Percentage of grafting
PHA	Poly(hydroxamic acid)
PMA	Poly(methyl acrylate)
Pr	Percentage of removal
q	Adsorption capacity
R	Universal gas constant
rpm	Revolution per minute
S	Selectivity
t	Time
T	Temperature
TGA	Thermogravimetric analysis

T_{max}	Maximum temperature
ν	frequency

TABLE OF CONTENTS