UNIVERSITI PUTRA MALAYSIA

PREPARATION AND CHARACTERIZATION OF AMINO-FUNCTIONALIZED Fe3O4/POLY(MALEIC ANHYDRIDE-CO-ACRYLIC ACID) MAGNETIC NANOCOMPOSITE FOR REMOVAL OF Cu(II) AND Ni(II) IONS

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By

MAHNAZ MAHDAVI SHAHRI

Thesis Submitted to the School of Graduates Studies, Universiti Putra Malaysia, in Fulfilment of Requirements for the Degree of Doctor of Philosophy

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DEDICATION

To God, who gave me the life, strength, and the perseverance

To my husband who stayed with me in difficult times

and

To my parents for their prayers and moral support

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in Fulfilment of the requirement for the degree Doctor of Philosophy

PREPARATION AND CHARACTERIZATION OF AMINO-FUNCTIONALIZED Fe_3O_4/POLY(MALEIC ANHYDRIDE-CO-ACRYLIC ACID) MAGNETIC NANOCOMPOSITE FOR REMOVAL OF Cu(II) AND Ni(II) IONS

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Chairman : Assoc. Prof. Mansor B. Ahmad, PhD

Faculty : Science

Toxic metal contamination in water systems is a serious problem threatening human health and environment. Hence, many researches have been carried to develop effective technique for the removal of metal ions from water. Adsorption is one of the methods use in this field due to its effectiveness and easy operation. Magnetite nanocomposites are exceptional nano-adsorbent materials that can be effective in heavy metal removal.

In this work, a novel amino-functionalized Fe_3O_4/poly(maleic anhydride-co-acrylic acid) (MAH-co-AA) magnetic nanosized adsorbent with a core/shell structure was successfully synthesized by a dispersion polymerization route. Iron oxide nanoparticles were used as a core, and poly(MAH-co-AA) as a shell and followed by amino-functionalization using diethylenetriamine (DETA) via carbodiimide activation. The suitability of the magnetic

nanocomposites for adsorption of Cu(II) and Ni(II) cations and its efficiency were investigated.

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) showed that the magnetic Fe_3O_4/poly(MAH-co-AA) nanocomposites were highly uniform in size and cubic shape with the average size about 17.06 nm. The infrared spectroscopy suggested the existence of core/shell type. X-ray diffraction confirmed magnetite cores and also indicated that the binding process did not change the phase of Fe_3O_4. Magnetic measurement by vibrational sample magnetometer (VSM) revealed the nanoparticles were superparamagnetic and the saturation magnetization was 83.6 and 46.6 emu g^{-1} for pure Fe_3O_4 and composite nanoparticles, respectively. Measurements by VSM also showed that the degree of saturation magnetization increased with increasing iron oxide concentration from 1% to 7 wt % of Fe_3O_4.

The binding of DETA on the magnetic Fe_3O_4/poly(MAH-co-AA) nanocomposites was demonstrated by the analyses of fourier transform infrared (FTIR) spectroscopy and energy dispersive X-ray spectrometry (EDX) attached to the SEM. The DETA concentration for the amino-functionalization was fixed at 1.85 mol for 2 g Fe_3O_4/poly(MAH-co-AA). The amino-functionalized magnetic nano-adsorbent Fe_3O_4/poly(MAH-co-AA)–NHR shows a good capability for the rapid and efficient adsorption of metal cations from aqueous solutions via the chelation mechanism. The ability of Cu(II) and Ni(II) adsorption of these nanoparticles for removal from aqueous solutions was measured by inductively coupled plasma optical emission

(ICP-OES). Various factors affecting the metal uptake behavior such as contact time, temperature, pH, amount of nano-adsorbent and initial concentration of metal ions were investigated. The adsorption capacity for metal ions was greatly influenced by pH. The optimum pH for maximum adsorption on the magnetic nano-adsorbent was observed to be 6.5 and 6.0 for Cu(II) and Ni(II) respectively. The kinetic data showed that the adsorption process followed the pseudo-second order kinetic model. The best interpretation for the equilibrium data was given by Langmuir isotherm and the maximum adsorption capacities was 55.2 and 43.6 mg g^{-1} for Cu(II) and Ni(II), respectively.

Thermodynamic parameters such as the changes in free energy, enthalpy, and entropy of adsorption of copper and nickel were also evaluated. The negative values of the change in free energy indicate the feasibility and spontaneous nature of the process, and the positive values of the change in enthalpy indicate the endothermic nature of the adsorption process of Cu(II) and Ni(II).

The metal-loaded Fe_3O_4/poly(MAH-co-AA)–NHR magnetic nano-adsorbent could be recovered readily from aqueous solution by magnetic separation and regenerated easily by acid treatment. Findings of the present work highlight the potential for using magnetic nanoparticles prepared as an effective nano-adsorbent with magnetic separability for the removal of heavy metal ions in water and wastewater treatment.

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

PENYEDIAAN DAN PENCIRIAN NANOKOMPOSIT AMINO-FUNGSIAN Fe_3O_4 BERMAGNET/POLI(MALEIK ANHIDRIDA-CO-ASID AKRILIK) UNTUK PENYINGKIRAN Cu(II) DAN Ni(II) ION

Oleh

MAHNAZ MAHDAVI SHAHRI

Mei 2013

Pengerusi : Profesor Madya Mansor B. Ahmad, PhD

Fakulti : Sains

Pencemaran logam toksik dalam sistem perairan adalah masalah serius yang boleh mengancam kesihatan manusia dan alam sekitar. Oleh itu, banyak kajian telah dijalankan untuk membangunkan teknik yang berkesan untuk penyingkiran ion logam dari air. Penjerapan adalah salah satu kaedah yang banyak digunakan dalam bidang ini kerana keberkesanan dan operasi yang mudah. Nanokomposit magnetit merupakan bahan nano-penjerap istimewa yang berkesan dalam penyingkiran logam berat.

Dalam kajian ini, sejenis penjerap bermagnet berukuran nano yang baru amino-fungsian Fe_3O_4/poli(maleik anhidrida-co-asid akrilik) (MAH-co-AA) dengan struktur teras/cengkerang telah berjaya disintesis melalui kaedah pempolimeran penyerakan. Partikel nano ferum oksida sebagai teras digabungkan dengan poli(MAH-co-AA) sebagai cengkerang dan diikuti dengan pengfungsian amino menggunakan dietilenatriamina (DETA) melalui

pengaktifan karbodiimida. Kesesuaian nanokomposit bermagnet untuk menjerap kation Cu(II) dan Ni(II) dan tahap kecekapannya telah diselidik.

Mikroskopi pengimbas elektron (SEM) dan mikroskop transmisi elektron (TEM) menunjukkan bahawa nanokomposit Fe_3O_4/poli(MAH-co-AA) bermagnet mempunyai keseragaman sais yang tinggi dan berbentuk kubik dengan sais purata 17.06 nm. Spektroskopi inframerah mencadangkan kewujudan bahan jenis teras/cengkerang. Pembelauan sinar-X mengesahkan kehadiran teras magnetit dan juga menunjukkan bahawa proses pengikatan tidak mengubah fasa Fe_3O_4. Pengukuran kemagnetan oleh magnometer getaran sampel (VSM) menunjukkan partikel nano adalah superparamagnetik dan pemagnetan tepu pula adalah masing-masing bernilai 83.6 dan 46.6 emu g^{-1} bagi Fe_3O_4 tulen dan komposit nanopartikel. Pengukuran melalui VSM juga menunjukkan bahawa darjah ketepuan pemagnetan meningkat dengan peningkatan kepekatan Fe_3O_4 daripada 1% kepada 7 wt %.

Pengikatan DETA pada nanokomposit bermagnet Fe_3O_4/poli(MAH-co-AA) telah ditunjukkan oleh spektroskopi inframerah transformasi Fourier (FTIR) dan spektroskop serakan tenaga sinar-X (EDX) yang digandingkan bersama SEM. Kepekatan DETA terhadap fungsian amino telah ditetapkan pada 1.85 mol untuk 2 g Fe_3O_4/poli(MAH-co-AA). Penjerap amino-fungsional bermagnet menunjukkan kebolehan yang baik untuk mendapatkan kadar penjerapan kation logam yang cepat dan cekap daripada larutan akueus melalui mekanisma pengkelatan. Keupayaan penjerapan Cu(II) dan Ni(II)

terhadap partikel nano daripada larutan akueus ini telah diukur menggunakan spektrometri pemancaran optic plasma berganding aruh (ICP-OES). Banyak faktor yang mempengaruhi sifat pengambilan logam seperti masa sentuhan, suhu, pH, jumlah penjerap nano dan kepekatan awal ion logam telah dikaji. Kapasiti penjerapan ion logam sangat dipengaruhi oleh pH. Nilai pH optimum bagi penjerapan maksimum pada penjerap nano bermagnet ialah masing-masing pH 6.5 dan 6.0 bagi Cu(II) dan Ni(II). Data kinetik menunjukkan proses jerapan mematuhi model kinetik pseudo tertib kedua manakala data keseimbangan mematuhi model isoterma Langmuir dengan kapasiti penjerapan maksimum masing-masing ialah 55.2 dan 43.6 mgg^{-1} bagi Cu(II) dan Ni(II).

Parameter termodinamik seperti perubahan tenaga bebas, entalpi, dan entropi bagi penjerapan kuprum dan nikel juga dikaji. Nilai negatif pada perubahan tenaga bebas menunjukkan keupayaan kebolehlaksanaan peroses jerapan Cu(II) dan Ni(II) berlaku secara spontan dan nilai positif bagi entalpi menunjukkan sifat endotermik bagi proses trrsebut.

Bahan penjerap bermagnet Fe_3O_4/poli(MAH-co-AA)–NHR yang telah menjerap ion logam boleh diperolehi semula daripada larutan akueus melalui pemisahan secara magnet dan dijanakan semula dengan rawatan asid. Penemuan kajian ini menekankan potensi penggunaan nanopartikel bermagnet yang disediakan sebagai penjerap yang efektif dan boleh diasingkan secara magnet untuk menyingkirkan ion logam berat di dalam air dan dalam rawatan air sisa.

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I am grateful to the dean of faculty, the administrators, staff, lecturers, secretaries and librarians in the Chemistry Department of Faculty of Science, Universiti Putra Malaysia, for their help and assistance in many different ways. I must express my gratitude to my beloved husband, Behzad Nadi, for his continued support and encouragement. I would also like to specially thank my parents and my family in law. Lastly, I offer my regards and blessings to all of those who supported me in any respect during the completion of the project.

I certify that a Thesis Examination Committee has met on **13 May 2013** to conduct the final examination of Mahnaz Mahdavi Shahri on her thesis entitled "**Preparation and Characterization of Amino-Functionalized Fe_3O_4/Poly(Maleic Anhydride-co-Acrylic Acid) Magnetic Nanocomposite for Removal of Cu(II) and Ni(II) Ions**" 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 Doctor of Philosophy.

Members of Examination Committee were as follows:

Mohd Aspollah b Hj Md Sukari, PhD
Professor
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Tan Wee Tee, PhD
Associate Professor
Faculty of Science
Universiti Putra Malaysia

Asmah bt Hj. Yahaya, PhD
Associate Professor
Faculty of Science
Universiti Putra Malaysia

Z. V. P. Murthy, PhD
Professor
Department of Chemical Engineering
S. V. National Institute of Technology, SURAT-395007 INDIA

_____

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

Date:

This thesis submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfillment of the requirement for the degree of Doctor of Philosophy. The members of the Supervisory committee were as follow:

Mansor B. Ahmad, PhD
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Chairman)

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

Mohamad Zaki Ab. Rahman, PhD
Associate 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 hereby declare that the thesis is based on my original work except for the quotation and citation which have been dully acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at Universiti Putra Malaysia or other institute.

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MAHNAZ MAHDAVI SHAHRI

Date:

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