UNIVERSITI PUTRA MALAYSIA

PREPARATION, ANTIBACTERIAL PROPERTIES AND HEAVY METALS SORPTION OF NANOCOMPOSITES BASED ON RICE STRAW, Fe3O4 AND POLYCAPROLACTONE

ROSHANAK KHANDANLOU

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By

ROSHANAK KHANDANLOU

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfillment of the Requirement for the degree of Doctor of Philosophy

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Chairman: Prof. Mansor B. Ahmad, PhD

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Since the availability of natural biofibers from renewable resources, the use of biocomposites is expanding in recent years. Rice straw as a natural fiber, is being used as a filler to improve the properties of polymer matrix and in biosorption of heavy metals. However, the yield of heavy metal removal by a natural fiber is low and separation of adsorbent from solution is difficult. The aim of this project was preparation of rice straw/Fe_3O_4 nanocomposite, studied its application in removal of heavy metals and used as a filler to improve the polymer properties.

In this study, spherical Fe_3O_4 nanoparticles (Fe_3O_4-NPs) were synthesized on the surface of rice straw (RS). The optimum condition for the synthesis of Fe_3O_4-NPs on the rice straw surface is described in terms of the initial concentrations of $FeCl_3.6H_2O$ and $FeCl_2.4H_2O$ and volume of NaOH. The samples were studied using X-ray powder diffraction (PXRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), Fourier transform infrared spectroscopy (FT-IR), and vibrating sample magnetometer (VSM). The TEM images showed the mean diameters of Fe_3O_4- NPs in solid support decreased gradually from 18.47 to 9.93 nm with the increase of NaOH volumes. The VSM showed that the RS/Fe_3O_4-NCs has magnetic properties. The antibacterial activity of NCs indicated strong antibacterial activity against Gram-negative and Gram-positive bacteria, which was increased with the decreasing particle size.

In addition, the suitability of the rice straw/Fe_3O_4 nanocomposites (RS/Fe_3O_4-NCs) for adsorption of Cu(II) and Pb(II) from aqueous solution was investigated. The ability of RS/Fe_3O_4-NCs for Cu(II) and Pb(II) adsorption was measured by atomic absorption spectroscopy (AAS). Various factors affecting the metal uptake behavior such as contact time, amount of adsorbent and initial concentration of metal ions were investigated using response surface methodology (RSM). The characteristic parameters for each isotherm including Langmuir and Freundlich isotherm were determined. The experimental data were analyzed using the first-order kinetic and the second-order kinetic models. Desorption and reusability of the RS/Fe_3O_4-NCs

were studied using a dilute solution of mineral acid. The optimum conditions for the sorption of Cu(II) and Pb(II) were obtained 100 and 60 mg/L of initial ion concentration, 41.96 and 59.35 s of removal time and 0.13 g of adsorbent for both ions, respectively. The adsorption data and kinetics fitted well with Langmuir isotherm and second-order kinetic model. The regeneration results confirmed that the prepared nanocomposites can offer excellent reusability from the adsorption medium. Therefore, RS/Fe_3O_4-NCs had highly removal efficiency for elimination of Cu(II) and Pb(II).

Furthermore, unmodified rice straw (RS), modified rice straw (ORS) and ORS/Fe_3O_4-NCs were incorporated with polycaprolactone (PCL) in different percentages loading of the filler by solution casting method. The samples were characterized with PXRD, TEM, FESEM, EDX, FT-IR, and VSM. Mechanical and thermal properties were studied by using Instron Universal Testing Machine and thermal gravimetric analysis, respectively. ORS/PCL composites and ORS/Fe_3O_4/PCL-NCs showed superior mechanical properties due to greater compatibility of ORS and ORS/Fe_3O_4-NCs with PCL, but RS/PCL composites displayed poor adhesion between RS and PCL matrix. The tensile strength was improved with the addition of 5.0 wt.% of ORS and ORS/Fe_3O_4-NCs. The TGA showed the thermal stability of ORS/Fe_3O_4/PCL-NCs was higher than RS/PCL-Cs and ORS/PCL-Cs. The antibacterial activities of ORS/Fe_3O_4-NCs in PCL matrix was investigated against Gram-negative and Gram-positive bacteria by the disc diffusion method. The results showed the strong antibacterial activity against Gram-negative and Gram-positive bacteria, and it was increased with the increasing amount of Fe_3O_4-NPs. In conclusion, the nanocomposites of natural fibers show good potential in the field of nanotechnology for development of reliable and ecofriendly processes.

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

PENYEDIAAN, CIRI-CIRI ANTIBAKTERIA DAN PENYERAPAN LOGAM BERAT NANOKOMPOSIT MENGGUNAKAN JERAMI PADI, Fe_3O_4 DAN POLIKAPROLAKTON

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Sejak adanya biofiber semula jadi daripada sumber yang boleh diperbaharui, penggunaan biokomposit sedang berkembang sejak tahun-tahun kebelakangan ini. Jerami padi sebagai serat semula jadi, telah digunakan sebagai pengisi untuk memperbaiki sifat-sifat matriks polimer dan dalam penyerapan logam berat. Walau bagaimanapun, hasil daripada penyingkiran logam berat oleh serat semula jadi adalah rendah dan pengasingan bahan penjerap daripada larutan adalah sukar. Tujuan projek ini adalah untuk menyediakan nanokomposit jerami padi/Fe_3O_4, mengkaji aplikasinya dalam penyingkiran logam berat dan digunakan sebagai pengisi untuk memperbaiki sifat-sifat polimer.

Dalam kajian ini, nanopartikel sfera Fe_3O_4 (Fe_3O_4-NPs) telah disintesis di atas permukaan jerami padi (RS). Keadaan optimum untuk mengsintesis Fe_3O_4-NPs di permukaan jerami padi ialah dari segi kepekatan awal $FeCl_3.6H_2O$ dan $FeCl_2.4H_2O$ dan jumlah NaOH. Sampel-sampel dikaji dengan menggunakan pembelauan sinar-X serbuk (PXRD), mikroskopi elektron transmisi (TEM), mikroskop imbasan elektron (SEM), spektroskopi tenaga-serakan X-ray (EDX), spektroskopi pengubah Fourier inframerah (FT-IR), dan magnetometer getaran sampel (VSM). Imej TEM menunjukkan diameter min Fe_3O_4-NPs dalam sokongan pepejal menurun secara beransur-ansur dari 18.47 kepada 9.93 nm dengan peningkatan jumlah NaOH. VSM menunjukkan bahawa RS/Fe_3O_4-NCs mempunyai sifat magnet. Aktiviti antibakteria NCS menunjukkan aktiviti anti-bakteria yang kuat terhadap bakteria Gram-negatif dan Gram-positif, yang telah meningkat dengan saiz zarah berkurangan.

Di samping itu, kesesuaian jerami padi/Fe_3O_4 nanokomposit (RS/Fe_3O_4-NCs) untuk penjerapan Cu(II) dan Pb(II) daripada larutan akueus telah disiasat. Keupayaan RS/Fe_3O_4-NCs untuk penjerapan Cu(II) dan Pb(II) telah diukur oleh spektroskopi penyerapan atom (AAS). Pelbagai faktor mempengaruhi tingkah laku dalam pengambilan logam seperti masa sentuhan, jumlah bahan penjerap dan kepekatan awal ion logam telah dikaji dengan menggunakan kaedah respon permukaan (RSM). Parameter ciri bagi setiap isoterma Langmuir termasuk dan Freundlich isoterma telah

ditentukan. Data ujikaji dianalisis menggunakan model kinetik tertib pertama dan kinetik tertib kedua. Penyahjerapan dan kebolehgunaan RS/Fe_3O_4-NCs dikaji menggunakan larutan asid mineral. Keadaan optimum untuk penjerapan Cu(II) dan Pb(II) telah diperolehi iaitu kepekatan awal ion 100 dan 60 mg/L, masa pembuangan 41.96 dan 59.35 s dan adsorben untuk kedua-dua ion ialah 0.13 g. Data penjerapan dan kinetik bersesuaian dengan Langmuir isoterma dan model kinetik tertib kedua. Hasil pertumbuhan semula mengesahkan bahawa nanokomposit yang telah dihasilkan menawarkan kebolehan untuk diguna semula yang sangat baik dari media penjerapan. Oleh itu, RS/Fe_3O_4-NCs mempunyai kecekapan penyingkiran yang tinggi untuk menghapuskan Cu(II) dan Pb(II).

Tambahan pula, jerami padi tidak diubahsuai (RS), diubah suai jerami padi (ORS) dan ORS/Fe_3O_4-NCs digabungkan dengan polikaprolakton (PCL) dalam peratusan yang berbeza pemuatan pengisi dengan kaedah pengacuan larutan. Sampel telah dicirikan dengan PXRD, TEM, FESEM, EDX, FT-IR, dan VSM. Sifat mekanikal dan haba telah dikaji dengan menggunakan mesin pengujiaan universal instron dan analisis gravimetrik termal. komposit ORS/PCL dan ORS/Fe_3O_4/PCL-NCs menunjukkan sifat-sifat mekanik unggul kerana keserasian ORS dan ORS/Fe_3O_4-NCs dengan PCL, tetapi RS/komposit PCL menunjukkan lekatan yang lemah antara RS dan matriks PCL. Kekuatan tegangan telah dipertingkatkan dengan penambahan berat sebanyak 5.0% ORS dan ORS/Fe_3O_4-NCs. TGA menunjukkan kestabilan haba ORS/Fe_3O_4/PCL-NCs adalah lebih tinggi daripada RS/PCL-Cs dan ORS/PCL-Cs. Aktiviti antibakteria ORS/Fe_3O_4-NCs pada matriks PCL telah disiasat terhadap bakteria Gram-negatif dan Gram-positif dengan kaedah resapan cakera. Hasil kajian menunjukkan aktiviti anti-bakteria yang kuat terhadap bakteria Gram-negatif dan Gram-positif, dan ia telah meningkat dengan peningkatan jumlah Fe_3O_4-NPs. Kesimpulannya, nanokomposit gentian asli menunjukkan potensi yang baik dalam bidang nanoteknologi untuk pembangunan proses yang baik dan mesra alam.

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APPROVAL

I certify that a Thesis Examination Committee has met on (4. February. 2014) to conduct the final examination of Roshanak Khandanlou on her thesis entitled **"Preparation, Antibacterial Properties and Heavy Metals sorption of Nanocomposites based on Rice Straw, Fe_3O_4 and Polycaprolactone"**. 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.
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This thesis submitted to the Senate of Universiti Putra Malaysia has been accepted as fulfillment for the degree of Doctor of Philosophy. The members of the Supervisory committee were as follows:

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

AAS	Atomic absorption spectroscopy
ABC	Activated bagasse carbon
AC	Alternating current
ANOVA	Analysis of variance
BC	Bacterial cellulose
BNCs	Bionanocomposites
BPO	Benzoyl peroxide
CCRD	Central composite rotatable design
CV	Coefficient of variation
DCP	Dicumyl peroxide
DLTA	Dl-Thioctic acid
DTG	Differential thermal gravimetric
E.coli	Escherichia coli
EDX	energy-dispersive X-ray fluorescence
EFB	Empty fruit bunch
EDX	energy-dispersive X-ray fluorescence
fcc	face-centered cubic
FT-IR	Fourier transform infrared
LDPE	low density polyethylene
Me_3NO	Trimethylamine N-oxide
MEUF	Micellar-enhanced ultrafiltration
PEG	Polyethylene glycol
CTS	Chitosan
PVA	Poly(vinyl alcohol)
PLA	Poly(lactide acid)
PAA	Poly(acrylic acid)
PMMA	Polymethylmethacrylate
Me_3NO	Trimethylamine N-oxide
MNPs	Magnetic Nanoparticles
M_S	Saturated magnetization
NA	Nutrient agar
NaAc	Sodium acetate
NCs	nanocomposites
NPs	nanoparticles
ODA	Ocatdecylamine
ORS/Fe_3O_4/PCL-NCs	Rice straw/Fe_3O_4/polycaprolactone nanocomposites
ORS/PCL-Cs	Modified rice straw/polycaprolactone composites
PAA	Poly(acrylic acid)
PAF	Pandanus amaryllifolius fiber

PBAT	Poly(butylene adipate-co-terephtalate)
PBS	Phosphate buffer saline
PCL	Polycaprolactone
PCL-g-MA	Maleic anhydrate grafted polycaprolactone
PEG	Polyethylene glycol
PLA	Poly(lactide acid)
PMMA	Polymethylmethacrylate
PPNa	Polypropiolate sodium
PPO	Polyphenylene oxide
PVA	Poly(vinyl alcohol)
PXRD	Powder X-ray diffraction
R^2	Regression coefficient
RS	rice straw
RSM	Response surface methodology
RS/PCL-Cs	Rice straw/polycaprolactone composites
SAH	Succinic anhydride
S.aureus	*Staphylococcus aureus*
SDR	Sawdust raw
SDS	Dodecyle sulfate
SEM	Scanning electron microscopy
SPIONs	Superparamagnetic iron oxide nanoparticles
TEM	Transmission electron microscopy
TGA	Thermogravimetric analysis
VSM	vibrating sample magnetometer

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Nanoscience has been widely identified as the most essential and leading edge development in modern science. Professor Norio Taniguchi from Tokyo Science University created the term nanotechnology in 1974 to explain the production of materials at level of nanometer (Rai *et al.*, 2009). Nanoscience and nanotechnology are associated to synthesize, characterize, explore, develop, and utilize nanostructured materials, by having one of its component in the nanometer (1 nm = 10^{-9} m) range. The use of nanoparticles (NPs) materials has many advantages such as distinctive size and physical characteristics. Preparation of various types of magnetic nanoparticles (MNPs) such as Fe_3O_4-NPs has been growing due to extensive use of MNPs, in various fields, namely material science, biotechnology, engineering, and environment (Akbarzadeh *et al.*, 2012), Up to the present time, many researchers developed various preparation methods of MNPs, like chemical co-precipitation, thermal decomposition, microemulsion, solvothermal and sonochemical. Even though, by application of these methods, manufacturing monodispersed MNPs is challenging since accurate control of MNPs size, form, and surface is required.

The nanocomposite (NCs) consists of several phases of solid material that one of the phases has less than 100 nanometers (nm), or compositions contain nano-scale repeat distances among various phases of structuring the material (Chang *et al.*, 2003). Nanocomposite characteristics such as optical, thermal, catalytic, mechanical, and electrical features are considerably different from that of the component materials. A modern invention of NCs materials named as Bionanocomposites (BNCs), represent a favorable field in the leading edge of nanotechnology and material sciences (Darder *et al.*, 2007). The components of BNCs include a polymer matrix and organic or inorganic filler by using no less than one dimension on the nanometer scale. Furthermore, BNCs exhibit the noticeable merits and applications in terms of biocompatibility in different medical properties and agriculture (Mangiacapra *et al.*, 2006).

Natural fibers are materials obtained from natural substances. Natural fibers have been utilized in textile industries before synthesizing the first polymer and improving polymer characteristics in recent three decades. Natural fibers are divided into three major classifications: vegetables (plant fibers), minerals fibers, and animals. As illustrated in Figure 1.1 non-wood plant fibers can be categorized into five sub categories: (a) straw fiber (e.g., rice straw); (b) leaf fibers (e.g., oil palm, pineapple, and abaca leaf); (c) bast fibers (e.g., kenaf, jute, and flax); (d) seed fibers (e.g., rice husk, kapok, and coir) and (e) grass fiber. With respect to global environmental problems and insufficient sources of fibers and due to their low cost and density, environmentally friendly, and appropriate mechanical characteristics, many scientists have widely started to take advantage of using many potential of plant fibers (Wollerdorfer *et al.*, 1998) . The plant fiber can be used to produce many natural

fiber reinforced composites such as with polylactic acid, poly hydroxy alkaloide and polycaprolactone.

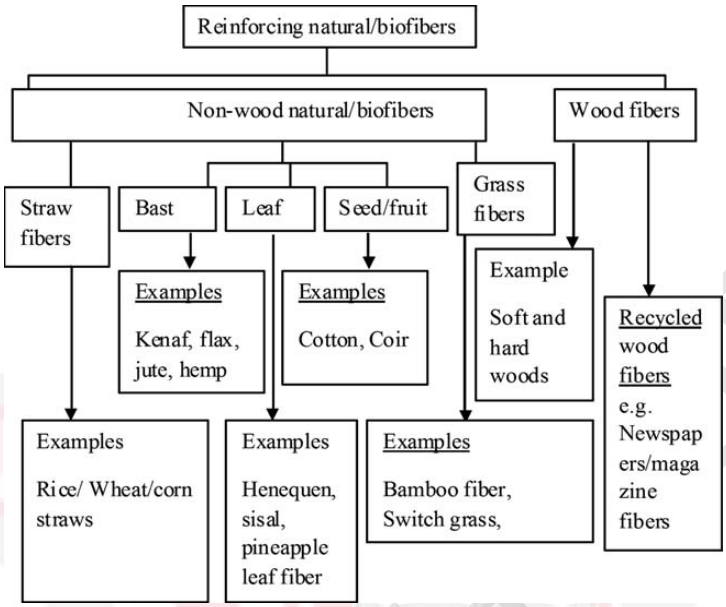

Figure 1.1 Schematic classifications of reinforcing natural fibers or biofibers (Wahit et al., 2012)

1.2 Problem Statement

Rice straw (RS) used in some applications such as in waste water treatment as a serious environmental problem, but the yield of heavy metals removal is low and separation of adsorbent from solution is difficult. Also rice straw applied in polymer as filler in packaging industry to improve the polymer properties but it does not show any antibacterial properties which are useful in packaging. On the other hand, polycaprolactone (PCL) has been used and applied in different biomedical, biomaterial functionsand also in packaging industry. Unfortunately, the commercialization of PCL has been widely restricted due to that PCL is a biodegradable polymer and has low modulus, its production is complex, It has comparatively expensive price and no antibacterial properties for packaging industry.

Some solutions have been developed to overcome these problems. Among the solutions the use of nanoparticles has obtained more attention in recent years due to the non- toxicity of these materials. Coating the Fe_3O_4 nanoparticles (Fe_3O_4-NPs) on the surface of RS causes it shows antibacterial activity and the yield of heavy metals removal from aqueous solution is higher than neat RS because of the high surface area to volume ratio. In addition, incorporation of rice straw and rice straw/Fe_3O_4 nanocomposites (RS/Fe_3O_4-NCs) with PCL leads to improve the PCL properties and it possesses strong antibacterial activity. Adding the RS and RS/Fe_3O_4-NPs by the simple method is an efficient and operable approach to improve the PCL properties.

1.3 Research Approach

In this research, the Fe_3O_4-NPs were prepared by exploiting chemical co-precipitation approach on the surface of rice straw by chemical reducing agent, also

the usage of RS/Fe_3O_4-NCs to remove heavy metals from aqueous solution and its antibacterial properties were investigated. Furthermore, unmodified rice straw (RS), octadecyamine (ODA) modified rice straw (ORS) and ORS/Fe_3O_4-NCs were incorporated with polycaprolactone (PCL) as a biodegradable polymeric support. The antibacterial activity of ORS/Fe_3O_4/PCL nanocomposite was studied. There has been no investigation on the use of Fe_3O_4-NPs on the RS surface and ORS/Fe_3O_4-NCs incorporated with PCL. The primary interest is to determine the effect of concentration of $FeCl_3.6H_2O$ and $FeCl_2.4H_2O$ on the particle size of Fe_3O_4-NPs.

In the first part of the research, Fe_3O_4-NPs were prepared by exploiting sodium hydroxide as a reducing agent and $FeCl_3.6H_2O$ and $FeCl_2.4H_2O$ as a precursor on the RS surface. In the second part, RS/Fe_3O_4-NCs are used to remove of copper(II) and lead(II) from aqeous solution, also utilize RSM for the modeling and optimization of metal ions removal. Finally, RS, ORS and ORS/Fe_3O_4-NCs were incorporated with PCL by solution casting method with different percentages loading.

The crystalline structure of NPs in RS, average size, size distributions, surface morphology, and functional groups were characterized by operating powder X-ray diffraction (PXRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), and Fourier transform infrared (FT-IR) techniqes, Mechanical and thermal properties of RS/PCL-Cs, ORS/PCL-Cs and ORS/Fe_3O_4/PCL-NCs were studied by using Instron Universal Testing Machine and thermogravimetric analysis (TGA), respectively. The antibacterial activities for Fe_3O_4-NPs in natural and organic polymer were investigated against Gram- positive and Gram- negative bacterium at different size and the amount of Fe_3O_4-NPs and ORS/Fe_3O_4-NCs.

1.4 Objectives

The main objectives of this research are:

1. To prepare and characterize rice straw/Fe_3O_4 nanocomposites by co-precipitation method and to evaluate antibacterial properties and its application to remove copper(II) and lead(II) from aqueous solution.
2. To prepare rice straw/polycaprolactone composites by solution casting method using unmodified and octadecylamine-modified rice straw fiber and to characterize the thermal, morphological and mechanical properties.
3. To prepare rice straw/Fe_3O_4/polycaprolactone nanocomposites by solution casting method to characterize the thermal, morphological and mechanical properties , and to evaluate antibacterial properties.

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