



UNIVERSITI PUTRA MALAYSIA

***BLENDS OF POLYACRYLONITRILE AND LIGNIN OF SAGO WASTE
FOR PRODUCTION OF CARBON NANOFIBERS FOR REMOVAL OF
LEAD(II) FROM AQUEOUS SOLUTION***

NURUL AIDA BINTI NORDIN

FS 2020 51



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PRODUCTION OF CARBON NANOFIBERS FOR REMOVAL OF LEAD(II)
FROM AQUEOUS SOLUTION**

By

NURUL AIDA BINTI NORDIN

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

November 2019

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

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NURUL AIDA BINTI NORDIN

November 2019

Chairman : Norizah Abdul Rahman, PhD
Faculty : Science

Heavy metal pollution such as lead(II) tends to cause serious environmental problems and brought toxicity effect to human and indicates that an effort must be taken in order to reduce its concentration in waste water effluents. Adsorption was proven to be economical and efficient to remove heavy metals in aqueous solution compared to other methods. There is an increasing amount of research focusing on the use of waste materials as adsorbents, aligned with the environmental protection awareness. In this study, activated carbon nanofibers (ACNFs) were produced from blends of polyacrylonitrile (PAN) and lignin of sago waste via electrospinning technique for the removal of Pb(II) ions from aqueous solution. PAN/SL ACNFs was characterized by different spectroscopic techniques and the application of PAN/SL ACNFs as the adsorbent for removal of Pb(II) ions from aqueous solution was increased three times after activation. The activation of PAN/SL ACNFs with nitric acid resulted in the attachments of oxygenated functional groups that responsible for the decreased in hydrophobicity thus promoting the metal adsorption in aqueous solution. The equilibrium time of adsorption of PAN/SL ACNFs towards Pb(II) ions was achieved in 240 mins by using 40 mg of adsorbent. The effect of initial concentration of Pb(II) was studied and the removal of Pb(II) ions from 125 mg/L solution was almost reached the monolayer coverage with the value of 555.56 mg/g. The adsorption was also dependent on the pH of the solution and the percentage removal was higher at pH 5 — 6 with 66.9 and 67.6% of Pb(II) removal. It was observed that pseudo-second order kinetic model was well-fitted with the experimental data which indicated that the adsorption process was controlled by chemisorption. The adsorption behaviour were best described by Langmuir isotherm model in which the q_{max} was 588.24 mg/g. From the intra-particle diffusion multilinear plot, it was suggested that two steps of adsorption were involved in the adsorption of Pb(II) ions. Therefore, in this study the adsorbent was successfully prepared from the blended of PAN and lignin of sago

waste and PAN/SL ACNFs have a potential to be used as the adsorbent for the removal of Pb(II) from aqueous solution.



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

**CAMPURAN POLYAKRYLONITRIL DAN LIGNIN DARIPADA SISA SAGU
UNTUK PENGHASILAN KARBON NANOFIBER BAGI MENYINGKIRKAN
PLUMBUM(II) DARIPADA LARUTAN AKUES**

Oleh

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Pencemaran logam berat seperti plumbum(II) cenderung untuk menyebabkan masalah alam sekitar yang serius dan membawa kesan toksik kepada manusia dan ini menunjukkan bahawa usaha perlu diambil untuk mengurangkan kepekatan plumbum(II) dalam cecair sisa air. Penjerapan telah terbukti sebagai jimat dan efisien untuk menyingkirkan logam berat di dalam larutan akues berbanding kaedah-kaedah lain. Terdapat peningkatan dalam penyelidikan yang memberi fokus kepada penggunaan bahan buangan sebagai penjerap, sejajar dengan kesedaran untuk melindungi alam sekitar. Dalam kajian ini, karbon nanofiber yang aktif (ACNFs) telah dihasilkan daripada campuran polyakrylonitril (PAN) dan lignin daripada sisa sagu melalui teknik elektrospining untuk menyingkirkan Pb(II) daripada larutan akues. PAN/SL ACNFs telah dicirikan melalui teknik spektroskopi yang berbeza dan aplikasi PAN/SL ACNFs sebagai penjerap untuk penyingkiran ion-ion Pb(II) daripada larutan akues telah meningkat tiga kali selepas pengaktifan. Pengaktifan PAN/SL ACNFs menggunakan asid nitrik telah menyebabkan pelekatan kumpulan berfungsi beroksigen yang bertanggungjawab kepada penurunan sifat hidrofobik dan seterusnya menggalakkan penjerapan logam dalam larutan akues. Masa keseimbangan untuk penjerapan PAN/SL ACNFs terhadap ion-ion Pb(II) telah dicapai dalam masa 240 minit dengan menggunakan 40 mg penjerap. Kesan kepekatan permulaan Pb(II) telah dikaji dan penyingkiran ion-ion Pb(II) daripada larutan 125 mg/L adalah hampir meliputi lapisan tunggal dengan nilai 555.56 mg/g. Penjerapan ini juga bergantung kepada pH larutan dan peratusan penyingkiran adalah lebih tinggi pada pH 5 — 6 dengan 66.9 dan 67.6% Pb(II) yang disingkir. Model kinetik pseudo kedua telah diperhatikan sangat bersesuaian dengan data eksperimen yang menunjukkan bahawa proses penjerapan telah dikawal oleh penjerapan kimia. Kelakuan penjerapan telah digambarkan secara baik oleh model isoterma Langmuir dimana q_{max} adalah 588.24 mg/g. Daripada plot pelbagai linear penyebaran intra partikel,

mencadangkan bahawa dua langkah penjerapan telah terlibat dalam penjerapan ion-ion Pb(II). Oleh itu, dalam kajian ini penjerap telah berjaya dihasilkan daripada campuran PAN dan lignin daripada sisa sagu dan PAN/SL ACNFs mempunyai potensi untuk digunakan sebagai penjerap bagi menyingkirkan Pb(II) daripada larutan akues.



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I certify that a Thesis Examination Committee has met on 4 November 2019 to conduct the final examination of Nurul Aida Nordin on her thesis entitled "Blends of Polyacrylonitrile and Lignin of Sago Waste For Production of Carbon Nanofibers for Removal of Lead(II) From Aqueous Solution" 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.

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LIST OF ABBREVIATIONS

AC	Activated carbon
ACNFs	Activated carbon nanofibers
BE	Binding energy
BET	Brunauer-Emmett-Teller
b_L	Langmuir constant
CNFs	Carbon nanofibers
CNTs	Carbon nanotubes
CVD	Chemical vapour deposition
DMF	N-N, dimethylformamide
DSC	Differential Scanning Calorimetry
DTG	Differential Thermal Gravimetric
FTIR	Fourier Transform Infrared
ICP	Inductively Coupled Plasma
IPD	Intra-particle diffusion
k_1	Pseudo-first rate constant
k_2	Pseudo-second rate constant
K_F	Freundlich constant
PAN	Polyacrylonitrile
Pb	Lead (plumbum)
q	Adsorption capacity
R^2	Correlation coefficient
SEM	Scanning Electron Microscopy
TGA	Thermal Gravimetric Analysis
XPS	X-Ray Photoelectron Scanning
XRD	X-Ray Diffraction

CHAPTER 1

INTRODUCTION

1.1 Heavy metals

Heavy metals are considered to be toxic to human and other biological system due to its non-biodegradable and persistent nature, which has become a public health concern (Jiang *et al.*, 2010). The main sources of heavy metal contamination are mostly contributed from metal bearing industries such as industries of batteries, tanneries, electrical, electroplating, fertilizers, pesticides, mining, and refining ores (Baneerje *et al.*, 2012, Nguyen *et al.*, 2013, Yunus *et al.*, 2006).

Heavy metals can contribute to the environmental problems which could have an impact to human due to its toxicity. The heavy metal pollution could bring an implication to the aquatic life bodies, natural water bodies and possibly get trapped in the soil through bioaccumulation (Desta, 2013). Its high solubility in aquatic environment allows it to be absorbed by living organisms and large concentrations of heavy metals might accumulate in human body once they entered our food chain and caused serious health disorder (Barakat, 2011).

Lead has been utilized as industrial raw materials for battery manufacturing, printing, pigments, fuels, photographic materials, and dyeing (Zulkali *et al.*, 2006). Lead is metal which might be at the highest of the environmental concerns (Jalali *et al.*, 2002, Volesky, 1994). A few techniques have been generally developed for removal of lead from wastewater such as electrochemical treatment, ion exchange, coagulation, reverse osmosis, membrane filtration, adsorption, etc. (Quintelas *et al.*, 2009).

Previous study had proved that water treatment by adsorption to be the most convenient, simple, economical, and effective to be used in practical applications (Chen *et al.*, 2013, Wang *et al.*, 2015a). Many adsorbents such as fly ash, kaolinite clay, zeolites, industrial by-products, agricultural waste, polymeric materials and carbon materials had been used in the treatment of wastewater (Barakat, 2011). Carbon-based materials were found to be effective adsorbents for removal of heavy metal due to their well-developed internal pore structures, large specific surface area, and presence of surface functional groups (Pyrzyńska and Bystrzejewski, 2010).

The surface of carbon materials can be transformed into more hydrophilic by introducing oxygen-containing groups which could improve their wettability for polar solvents that can be utilized for the attachments of Pb(II) ions (Dongil *et al.*, 2011). Among various oxidation treatments, nitric acid was considered to be the most conventional and widely used in wet oxidation treatment (Soudani *et al.*, 2013). The presence of oxygen functional groups on the surface of carbon adsorbents was investigated for the removal of Pb(II) ions from aqueous solution and Pb(II) ions have a tendency to form metal complexes with the negatively-charged oxygen functional groups and the adsorption was found to be highly favorable (Bhatnagar *et al.*, 2013).

1.2 Sago lignin

Sago palm was scientifically known as *Metroxylan sago* and it was originated from the species of palm in the *Metroxylan* genus (Nordin *et al.*, 2018). The stems will develop into a huge frond that flourishes with fruits as it terminates its life cycle (Orwa *et al.*, 2009). Sago palm will convert its nutrients into starch just before flowering because it exhibits hapaxanthic characteristics in which it dies shortly once it flowers (Awg-Adeni *et al.*, 2010). One of the physical characteristics of sago palm is its fruits which are not encapsulated or in other words can be said as naked-seed or scientifically termed as gymnosperms. Most gymnosperms are known to be softwood. Sago palm grows well in swampy areas in Sarawak, Malaysia. Ishazaki (2009) reported that approximately 5 to 11 tons of wastes are produced every day from a single sago starch processing mill that contain starchy lignocellulosic by-products. Common products derived from sago palm besides sago starch are the ground pith as animal feed, the cortex of the trunk used for firing in paper mills and the leaves that can be turned into mats (Orwa *et al.*, 2009).

Previous study stated that natural polymers received massive attention from researchers in order to reduce the consumption of petroleum-based polymer (Abdel-Halim and Al-Deyab, 2011). Cellulose, starch and lignin are among the natural polymers which possessed interesting characteristics such as biodegradable, non-toxic, and low cost. Lignin is the second most abundant natural polymer after cellulose (Watkins *et al.*, 2015). Sago lignin is renewable and it is readily available from the sago wastes which comprised of lignocellulosic by-products of sago starch extraction process. Lignin plays an important role as to provide the stiffening and rigidity to the plants by holding the fibers together. According to Awg-Adeni *et al.* (2010), lignin is usually linked with the hemicelluloses in the cell walls of sago pith and it is the main component of sago bark.

Lignin is the largest available resource of natural aromatic polymers that composed of three-dimensional and highly crosslinked macromolecule which made up of three types of substituted phenols: coniferyl, sinapyl and p-coumaryl alcohols (Eudes *et al.*, 2014, Okutan *et al.*, 2014, Watkins *et al.*, 2015). The most

common lignin sources come from hardwood lignin, softwood lignin and grass lignin. Figure 1.1 shows the schematic representation of the lignin structure. As lignin is strongly associated with hemicelluloses, the extraction process usually started by dissolving the lignin from the wood and followed by isolation process (Chang *et al.*, 2016). Sago lignin has the potential in the production of carbon-based adsorbents owing to its structure which consist of many aromatic components.

In order to reduce the environmental problem due to the used of polyacrylonitrile (PAN), PAN was blended with sago lignin and electrospun, followed by thermal treatment to formed carbon nanofibers (CNFs). In this method, there is no consumption of elemental transition metal catalyst and no significant amount of catalyst residue was left. Therefore, electrospinning method is suitable in producing a free catalyst and high product yield. Besides that, blending is an effective method to improve the ability of sago lignin to be electrospun into nanofibers.

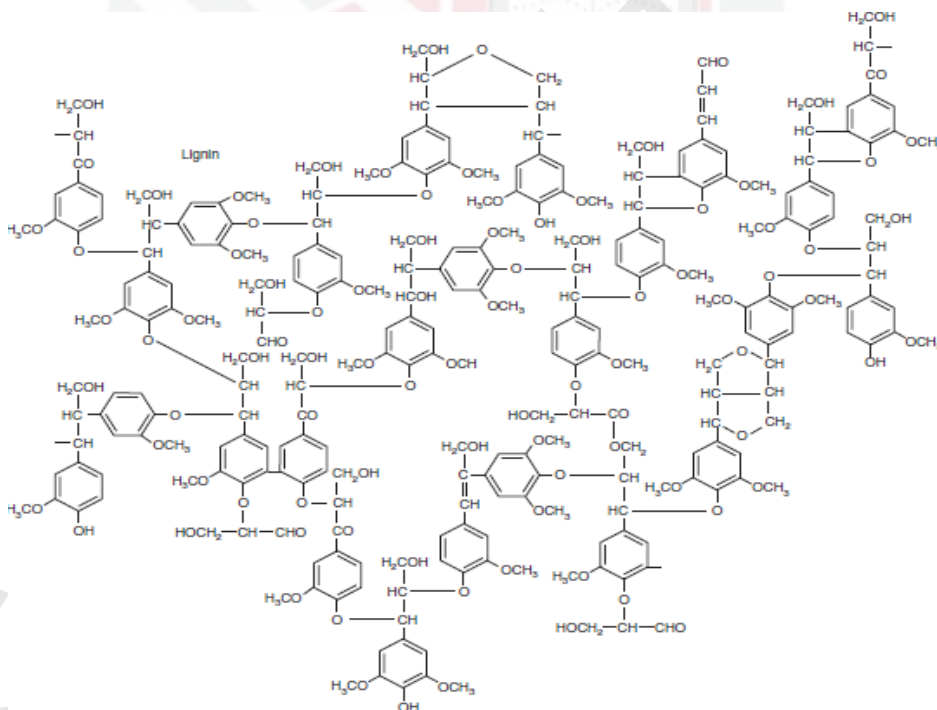


Figure 1.1 : Schematic representation of lignin structure
(Watkins *et al.*, 2015)

1.3 Problem statement

Development of adsorbents to remove heavy metal ions is crucial to our present society as heavy metals cannot be destroyed or degraded. In order to reduce human intake of heavy metals both chemical and physical treatment has been investigated and water treatment by adsorption was found to be the most economical and practical treatment alternative (Ihsanullah *et al.*, 2015).

Chemical and thermal stability accompanied with large surface area could make CNFs as a good material to be employed as an adsorbent (Li *et al.*, 2015b). However, common precursors to produce carbon fibers are PAN, cellulose, and pitch (Frank *et al.*, 2012). The most commonly used precursor, PAN was extensively used due to its high carbon yield compared to cellulose and pitch. PAN is petroleum-based material and it is accounted as the precursor for about 95% of carbon fibers manufactured today (Lin *et al.*, 2013). In today's world, sustainable and renewable resources are overcoming the so-called petroleum-based resources because they are abundant, cheaper and causing less harmful to the environment.

There is an increasing amount of research focusing on the use of waste materials as adsorbents, aligned with the environmental protection awareness. In this study, sago lignin was isolated from sago waste and was blended with PAN. The nanofibers undergo thermal treatment followed by activation by nitric acid to produce activated CNFs. ACNFs was used as the adsorbent because it has high specific surface area and presence of oxygen-functional groups which could enhance the metal uptake by the adsorbent. In this research, the adsorption of Pb(II) ions by CNFs and activated CNFs from aqueous solution was observed. The adsorption of Pb(II) was more effective when CNFs were activated with nitric acid and its kinetic and adsorption isotherm were studied.

1.4 Significance of the study

It was reported that a single sago starch processing mill will create about 7 tons of sago waste every day (Pushpamalar *et al.*, 2006). These waste are usually managed by discharging them into the river which can contribute to the environmental pollution. It is only wise if these waste can be recycled into something beneficial since they contain large amount of lignocellulosic by-products which are cellulose, hemicellulose and lignin. Due to its biodegradability and non-toxicity, it is easier to degrade and safer compared to synthetic polymers.

In addition, lignin was less explored as the precursors to produce CNFs. Lignin has the potential in the production of carbon-based materials due to its structure which consists of many aromatic components. Unlike catalytic synthesis,

electrospinning polymer such as PAN followed by thermal treatment has become a simple and straightforward method to make continuous carbon nanofibers (CNFs).

Electrospinning method has many advantages such as simple setup, cheap, easy to control fiber diameter and less time consuming for nanofibers preparation compared to other methods. Electrospinning is a straightforward method that does not require any catalyst which could produce catalyst residue and continuous fibers were easy to formed.

1.5 Objectives of the study

1.5.1 General objective

The objective of this research is to produce ACNFs from blends of PAN and lignin of sago waste as the adsorbent for the removal of Pb(II) ions from aqueous solution.

1.5.2 Specific objectives

1. To prepare and characterize the ACNFs from electrospun PAN/SL prepared by electrospinning.
2. To evaluate the potential of PAN/SL-based ACNFs as adsorbent for Pb(II) ions removal.

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