UNIVERSITI PUTRA MALAYSIA

SYNTHESIS OF POLY(ACRYLONITRILE-co-ACRYLAMIDE) AND ITS CHEMICAL MODIFICATION WITH HYDRAZINE FOR REMOVAL OF Cu(II), Zn(II), Pb(II) AND Cr(VI) IONS FROM AQUEOUS SOLUTION

MASTURA BINTI KHAIRUDDIN

FS 2016 30

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By

MASTURA BINTI KHAIRUDDIN

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

May 2016

DEDICATION

To my beloved parents and family

Thank you for everything

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

SYNTHESIS OF POLY(ACRYLONITRILE-*co*-ACRYLAMIDE) AND ITS CHEMICAL MODIFICATION WITH HYDRAZINE FOR REMOVAL OF Cu(II), Zn(II), Pb(II) AND Cr(VI) IONS FROM AQUEOUS SOLUTION

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Chairman: Siti Nurul Ain Binti Md.Jamil, PhD
Faculty: Science

The water pollution caused by heavy metal ions gives serious effect in different form of life especially to human health. The adsorption process is an alternative way for heavy metal ions removal. The polymer-based adsorbent was chosen as material to remove heavy metal ions due to its economic cost, can be prepared with convenient method and excellent capability to make high adsorption towards metal ions.

In this study, redox polymerisation of acrylonitrile to form polyacrylonitrile (PAN) and copolymerisation of acrylonitrile with acrylamide to form poly(acrylonitrile(AN)-*co*-acrylamide(AM)) were carried out at 40 °C in deionised water under N_2 gas by varying the ratio of acrylonitrile (AN) and acrylamide (AM) in the feed. The highest yield of poly(AN-*co*-AM) was 75%. Poly(AN-*co*-AM) was further chemically modified using hydrazine hydrate to form hydrazine-modified poly(AN-*co*-AM). The poly(AN-*co*-AM) and hydrazine-modified poly(AN-*co*-AM) were characterised by Fourier Transform Infrared (FT-IR) spectroscopy, microanalysis, Scanning Electron Microscope (SEM), thermogravimetric analysis (TGA) and amine capacity analysis. The IR spectra showed that the cyano functional group in poly(AN-*co*-AM) was disappeared which confirmed the chemical modification with hydrazine hydrate. Elemental microanalysis showed that the percentage of nitrogen was increased as the feed ratios of AM were increased. Amine capacities were increased as the mole fraction of AM in poly(AN-*co*-AM) increased in the feed. Hydrazine-modified poly(AN-*co*-AM) 97/3 had the highest amine capacity value at 0.8 $mmol.g^{-1}$. The SEM micrographs revealed that the PAN and poly(AN-*co*-AM) retained their spherical shape even after chemical modification with hydrazine hydrate. The specific surface area of poly(AN-*co*-AM) 97/3 was 21 $m^2.g^{-1}$ and increased up to 41 $m^2.g^{-1}$ after chemical modification with hydrazine hydrate. The TG thermogram revealed that the hydrazine-modified poly(AN-*co*-AM) was thermally more stable than poly(AN-*co*-AM).

The ability of the hydrazine-modified poly(AN-*co*-AM) to adsorb metal ions; Cu(II), Zn(II), Pb(II) and Cr(VI) ions were carried out by batch experiments and analysed by Inductively Coupled Plasma (ICP). The batch experiments were carried out to study the effects of solution pH, metal ions concentration, contact time, sorbent dosage and sorption temperature on metal ions sorption. The maximum sorptions capacities were achieved at pH 5 with 17.64 $mg.g^{-1}$, 18.94 $mg.g^{-1}$, and 20.13 $mg.g^{-1}$ of sorption for Cu(II), Zn(II) and Pb(II) ions, respectively at 25 °C. However, the optimum sorption capacity of Cr(VI) was occurred at pH 2 with 29.11 $mg.g^{-1}$ of sorption at 25 ˚C. The sorption capacity of Pb(II) achieved equilibrium (18.8 $mg.g^{-1}$) at 4-6 hours, followed by Cu(II) (17.3 $mg.g^{-1}$) at 4-6 hours, Zn(II) (16.6 $mg.g^{-1}$) at 1-2 hours and Cr(VI) (11.9 $mg.g^{-1}$) at 2-4 hours. Kinetic studies of Cu(II), Zn(II), Pb(II) and Cr(VI) ions followed the pseudo-second order model, suggesting the chemical sorption as the rate-limiting step of the sorption process. As the heavy metal ions concentration were increased, the sorption capacities were increased from 12.3 $mg.g^{-1}$ to 63.8 $mg.g^{-1}$ for Cu(II), 10.2 to 21.8 $mg.g^{-1}$ for Zn(II), 9.6 $mg.g^{-1}$ to 35.0 $mg.g^{-1}$ for Pb(II) and 10.6 $mg.g^{-1}$ to 13.3 $mg.g^{-1}$ for Cr(VI). The equilibrium data of Cu(II), Zn(II), Pb(II) and Cr(VI) ions onto hydrazine-modified poly(AN-*co*-AM) were well described by the Langmuir isotherm. This indicates that the monolayer sorption of the adsorbates possibly occurred on the adsorbent. As the sorbent dosage were increased from 0.05 g to 0.40 g, the sorption capacities were decreased. The sorption process were increased by raising the temperature of Cu(II), Zn(II), and Pb(II) solution system (from 25 ℃ up to 75 ℃. Therefore, the sorption processes were endothermic in nature. However, the sorption capacity was decreased as the temperature of Cr(VI) ion solution system was increased. This indicates that the sorption process was exothermic in nature for Cr(VI) ion sorption.

The present work demonstrated that the hydrazine-modified poly(AN-*co*-AM) is a potential adsorbent for applications in heavy metal ions; Cu(II), Zn(II), Pb(II) and Cr(VI) removal from aqueous solution. The adsorption capacities of hydrazine-modified poly(AN-*co*-AM) under various conditions were comparable with adsorption capacities by other polymeric-based sorbent.

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

SINTESIS POLI(AKRILONITRIL-*ko*-AKRILAMIDA) DAN PENGUBAHSUAIAN KIMIA DENGAN HIDRAZIN UNTUK PENYINGKIRAN ION Cu(II), Zn(II), Pb(II) DAN Cr(VI) DARI LARUTAN AKUEUS

Oleh

MASTURA BINTI KHAIRUDDIN

Mei 2016

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Fakulti: Sains

Pencemaran air yang disebabkan oleh ion logam berat memberikan kesan yang serius dalam pelbagai bentuk kehidupan terutamanya kepada kesihatan manusia. Proses penjerapan adalah cara alternatif untuk pengingkiran ion logam berat. Penjerap polimer telah dipilih sebagai bahan untuk mengingkirkan ion logam berat kerana kos yang rendah, boleh disediakan dengan kaedah yang mudah dan keupayaan terbaik untuk membuat penjerapan yang tinggi terhadap ion logam.

Dalam kajian ini pempolimeran redoks akrilonitril untuk membentuk poliakrilonitril (PAN) dan pengkopolimeran akrilonitril dengan akrilamida untuk membentuk poli(akrilonitril(AN)-*ko*-akrilamida(AM)) telah dijalankan pada 40 °C dalam air ternyah ion menggunakan gas N_2 dengan mengubah nisbah akrilonitril (AN) dan akrilamida (AM) dalam suapan. Hasil tertinggi poli(AN-*co*-AM) 97/3 diperolehi ialah 75%. Poli(AN-*co*-AM) telah diubahsuai menggunakan hidrazin hidrat untuk membentuk hidrazin-diubahsuai poli(AN-*co*-AM). Poli(AN-*co*-AM) dan hidrazin-diubahsuai poli(AN-*co*-AM) telah dianalysis menggunakan Fourier Transform Infrared (FT-IR) spektroskopi, mikroanalisis, Mikroskop Imbasan Elektron (SEM), analisis Termogravimetri (TGA) dan analisis kapasiti amina. Spektrum IR menunjukkan bahawa kumpulan berfungsi siano dalam poli(AN-*co*-AM) telah hilang yang mengesahkan kejayaan pengubahsuaian kimia dengan hidrazin hidrat. Mikroanalisis bahan menunjukkan bahawa peratusan nitrogen telah meningkat apabila nisbah suapan AM telah meningkat. Kapasiti amina telah meningkat apabila pecahan mol AM dalam poli(AN-*co*-AM) meningkat dalam suapan. Hidrazin-diubahsuai poli(AN-*co*-AM) 97/3 mempunyai nilai kapasiti amina tertinggi pada 0.8 $mmol.g^{-1}$. Mikrograf SEM mendedahkan bahawa partikel PAN dan poli(AN-*co*-AM) mengekalkan bentuk sfera walaupun selepas pengubahsuaian kimia dengan hidrazin hidrat. Kawasan permukaan spesifik poli(AN-*co*-AM) 97/3 adalah 21 $m^2.g^{-1}$ dan

meningkat sehingga 41 $m^2.g^{-1}$ selepas pengubahsuaian kimia dengan hidrazin hidrat. Termogram TG mendedahkan bahawa hidrazin-diubahsuai poli(AN-*co*-AM) adalah lebih stabil secara terma berbanding poli(AN-*co*-AM).

Keupayaan hidrazin-diubahsuai poli(AN-*co*-AM) untuk menjerap ion logam; Cu(II), Zn(II), Pb(II) dan ion Cr(VI) telah dijalankan menggunakan eksperimen kelompok dan dianalisis oleh Plasma Induktif Bersama (ICP). Eksperimen berkelompok telah dijalankan untuk mengkaji kesan pH, kepekatan ion logam, masa sentuhan, kuantiti penjerap dan suhu penjerapan pada ion logam. Kapasiti maksimum penjerapan dicapai pada pH 5 dengan 17.64 $mg.g^{-1}$, 18.94 $mg.g^{-1}$, dan 20.13 $mg.g^{-1}$ kapasiti penjerapa untuk Cu(II), Zn(II) dan Pb(II) ion, masing-masing pada 25 °C. Walau bagaimanapun, kapasiti penjerapan optimum Cr(VI) telah berlaku pada pH 2 dengan 29.11 $mg.g^{-1}$ kapasiti penjerapan pada 25 °C. Kapasiti penjerapan Pb(II) mencapai keseimbangan (18.8 $mg.g^{-1}$) pada 4-6 jam, diikuti oleh Cu(II) (17.3 $mg.g^{-1}$) pada 4-6 jam, Zn(II) (16.6 $mg.g^{-1}$) pada 1-2 jam dan Cr(VI) (11.9 $mg.g^{-1}$) pada 2-4 jam. Kajian kinetik Cu(II), Zn(II), Pb(II) dan Cr(VI) ion mengikuti model perintah kedua, menunjukkan penjerapan kimia sebagai langkah kadar-mengehadkan dalam proses penjerapan ini. Apabila kepekatan ion logam berat ditingkatkan, kapasiti penjerapan telah meningkat daripada 12.3 $mg.g^{-1}$ kepada 63.8 $mg.g^{-1}$ untuk Cu(II), 10.2 $mg.g^{-1}$ kepada 21.8 $mg.g^{-1}$ untuk Zn(II), 9.6 $mg.g^{-1}$ kepada 35.0 $mg.g^{-1}$ untuk Pb(II) dan 10.6 $mg.g^{-1}$ kepada 13.3 $mg.g^{-1}$ untuk Cr(VI). Data keseimbangan Cu(II), Zn(II), Pb(II) dan Cr(VI) ion terhadap hidrazin-diubahsuai poli(AN-*co*-AM) telah diterangkan oleh isoterma Langmuir. Ini menunjukkan bahawa penjerapan satu lapisan mungkin berlaku pada penjerap. Apabila kuantiti penjerap telah meningkat daripada 0.05 g kepada 0.40 g, kapasiti penjerapan telah berkurangan. Proses penjerapan meningkat dengan menaikkan suhu larutan Cu(II), Zn(II), dan Pb(II) (dari 25 ℃ hingga 75 ℃) Oleh itu, proses penjerapan adalah endotermik dalam alam semula jadi. Walau bagaimanapun, penjerapan menurun dengan menaikkan suhu sistem ion Cr(VI). Ini menunjukkan bahawa proses penjerapan adalah eksotermik dalam alam semula jadi untuk penjerapan Cr(VI) ion.

Kajian menunjukkan bahawa hidrazin-diubahsuai poli(AN-*co*-AM) adalah penjerap yang berpotensi untuk diaplikasikan dalam penyingkiran ion logam berat; Cu(II), Zn(II), Pb(II) dan Cr(VI) dari larutan akueus. Kapasiti penjerapan hidrazin-diubahsuai poli(AN-*ko*-AM) di bawah pelbagai keadaan setanding dengan kapasiti penjerapan oleh penjerap berasaskan polimer yang lain.

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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:

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

AN	Acrylonitrile
PAN	Polyacrylonitrile
AM	Acrylamide
Poly(AN-*co*-AM)	Poly(acrylonitrile-co-acrylamide)
PAM	Polyacrylamide
EPA	Environmental Protection Agency
WHO	World Health Organisation
IST	Individual Septic Tank
CST	Communal Septic Tank
DOE	Department of Environment
WQI	Water Quality Index
NWQS	National Water Quality Standards for Malaysia
DO	Dissolved Oxygen
BOD	Biochemical Oxygen Demand
COD	Chemical Oxygen Demand
NH_3-N	Ammoniacal Nitrogen
SS	Suspended Solids
VOCs	Volatile organic compounds
TDS	Total dissolved solids
SEM	Scanning electron microscopy
TGA	Thermogravitmetric analysis
FT-IR	Fourier Transformed Infrared Spectroscopy
ODR	Optical density ratio
BET	Brunauer–Emmett–Teller
ICP	Inducetively Coupled Plasma
SBS	Sodium bisulfite
KPS	Potassium persulphate
Cu(II)	Copper (II) ions
Zn(II)	Zinc (II) ions
Pb(II)	Lead (II) ions
Cr(VI)	Chromium (VI) ions
HCl	Hydrochloric acid
NaOH	Sodium hydroxide
q_e (mg.g^{-1})	Amount of ions adsorbed on the surface of sorbent at equilibrium
q_t (mg.g^{-1})	Amount of metal ions adsorbed on the surface of sorbent at time
C_o	Concentration of metal ion before sorption
C_e	Equilibrium concentration of metal ion after sorption
K	Rate constant
k_1t (1.min^{-1})	Rate constant of the pseudo-first order sorption
k_2 (g.mg^{-1}min^{-1})	Rate constant of the pseudo-second order sorption
h (mg.g^{-1}min^{-1})	Initial sorption rate, $k_2(q_e^2)$
R^2	Correlation coefficients
Q_{max} (mg.g^{-1})	Maximum sorption capacity

b (L.mg^{-1})	Langmuir constant related to energy of sorption
K_f (L.mg^{-1})	Freundlich relating to sorption capacity
n	Freundlich isotherm exponent constant
ΔG°	Free energy of the sorption
ΔH°	Enthalpy of the sorption
ΔS°	Entropy of the sorption
C_{ad} (mg.L^{-1})	Concentration of solute adsorbed at equilibrium
R	Gas constant
(1/T)	reciprocal of temperature

LIST OF APPENDICES

CHAPTER 1

INTRODUCTION

1.1 Background of study

Water pollution has caused international concern especially for various pollutants that are entering aquatic systems as a result of the rapid growth of the world population, industrialization, unplanned urbanization, agricultural activities as well as the excessive use of chemicals (Zhang *et al.*, 2016). Organic dyes, pesticides, pharmaceuticals, heavy metal ions, and natural organic matter can contaminate water through industrial activity (Setyono *et al.*, 2016). Recent years, the pollution caused by heavy metal ions especially from industrial effluents gives serious effect in different form of life. The accelerating process of industrialisation promotes the rapid development of social economy, but at the same times causes serious pollution of the environment, especially water pollution caused by heavy metal (Li *et al.,* 2016). The presence of heavy metal ions in environment become a serious issue because of their toxicity towards living species (Ramya *et al.*, 2011) and cause accumulative poisoning, cancer and brain damage (Neagu *et al.*, 2003). Unlike organic waste, heavy metals are nonbiodegradable and cannot be metabolised or decayed which increase the toxicity effects in living organism by entering the food chain through numerous of pathway (Zhao *et al.*, 2014; Abdel-Halim *et al.*, 2011; Mishra *et al.*, 2011; Arsalani *et al.,* 2009). 'Heavy metal' is a common term used to the group of metalloids and metal which have density of atomic more than 6 $g.cm^{-3}$ (O'Connell *et al.*, 2008). There are eleven heavy metal elements of highest concern in environment protection; arsenic, nickel, cadmium, copper, cobalt, mercury, manganese, chromium, lead, tin and thallium (Zukal *et al.*, 2015). It is well acknowledged that these heavy metals are harmful and extremely toxic to ecological environments and human being (Abdel-Halim *et al.*, 2011; Yavuz *et al.*, 2008). There are general signs in human that are associated with the toxicity of heavy metal ion such as tremor, ataxia, paralysis, gastrointestinal (GI) disorders, heamoglobinuria causing a rust-red colour to stool, diarrhea, depression, stomatitis, vomiting and convulsion, and pneumonia when volatile vapours and fumes are inhaled (Shanmugapriya *et al.*, 2013).

Wastewater consists of the mixture of toxic and nontoxic ions and which valuable and invaluable ions. Thus, it is very significant to separate the specific ions from the water mixture either by removal or recycle process for beneficial outcomes (Kim *et al.*, 2013). The usual methods that are regularly used for elimination of metal ions from aqueous solution including surface complexation, filtration, solvent extraction, ion-exchange, lime coagulation, chemical precipitation, electro dialysis, reverse osmosis, nanofiltration, and sorption (Mishra *et al.*, 2011; Liu *et al.*, 2011; Arsalani *et al.*, 2009; Song *et al.*, 2008; Yavuz *et al.*, 2008; Saliba *et al.*, 2000; Zhao *et al.*, 2010a). The major disadvantage of conventional treatment technologies is the production of toxic chemical sludge, whose disposal/treatment becomes a costly affair and is not eco-friendly (Al-Qahtani, 2015). Although all the heavy metal wastewater treatment techniques can be employed for heavy metals removal, they have their inherent advantages and limitations as listed in Table 1.1.

Table 1.1: Treatment technologies for the heavy metal ions removal from wastewater and their associated advantages and disadvantages (Fu *et al.*, 2011; O'Connell *et al.*, 2008)

Technique	Advantages	Disadvantages
Chemical precipitation	• Simple process • Inexpensive capital cost	• Adapted to treat high concentration of wastewater containing heavy metal ions • Not economical • Produce large amount of sludge to be treated with great difficulties
Ion exchange	• High removal efficiency	• Must be regenerated by chemical reagents when they are exhausted and the regeneration can cause serious secondary pollution. • Expensive, especially when treating a large amount of wastewater • Cannot be used at large scale due to high cost
Membrane filtration	• High removal efficiency • Low chemical consumption	• High cost • Process complexity • Membrane fouling • Low permeate flux
Coagulation-flocculation	• The sludge has good sludge settling and dewatering characteristics	• Involves chemical consumption • Increase sludge volume generation
Flotation	• High metal selectivity • High removal efficiency • High overflow rates • Low detention period • Low operating cost and production of more concentrated sludge	• High initial capital cost • High maintenance and operation costs
Electrochemical	• Rapid and well-	• High initial capital

treatment	controlled. • Require less chemicals • Provide good reduction yields • Produce less sludge	investment • Expensive electricity supply
Reverse osmosis	• High removal efficiency	• High power consumption in operation
Sorption	• High capacity • Economical method • Fast kinetics	• Sorption efficiency depends on the type of adsorbents

Amongst these techniques, most investigations have focused on metal ions removal by sorption due to its low cost, reusable, easily separation, high sorption capacity, high selectivity and high physical and chemical stabilities (Li *et al.*, 2015; Mishra *et al.*, 2011; Wan *et al.*, 2010; Liu *et al.*, 2011; Arsalani *et al.*, 2009; El-Ghaffar *et al.*, 2009; Neagu *et al.*, 2003). Sorption can be used together with filtration to yield better efficiency in application especially for drinking water purification. The sorption process is reversible and can be regenerated by suitable desorption process (Yang *et al.*, 2014). Thus, various chelating groups of numerous adsorbents are significantly used in treatment heavy metal ions have been reported. The adsorbents are originated from organics, biological origin or mineral sources (Kirupha *et al.*, 2012b; Abdel-Halim *et al.*, 2011; Morgado *et al.*, 2011).

An ideal adsorbent for heavy metal ion removal has the following properties: large surface area and high sorption capacity, suitable pore size and volume, mechanical stability, compatibility, easy accessibility, ease of regeneration, cost effectiveness, environmental friendliness, simple processing procedures and high selectively (Zhang *et al.*, 2016). The sorption property of the adsorbents depends to the functional groups on the surface of the adsorbents. Surface functional groups of adsorbents does not only affect the sorption behavior, but also control the sorption mechanism. Adsorbent with sulfonic, carboxyl and phosphonic groups (Figure 1.1) on the adsorbent surface remove adsorbates through ionic exchange while those containing nitrogen-based ligands such as amine, hydrazine, thioamide and imidazoline group (Figure 1.2) not only chelate cationic metal ions, but also adsorb anionic adsorbates through electrostatic interaction (Niu *et al.*, 2010; Deng *et al.*, 2003b) and effective in forming complexation with metal ions (Kampalanonwat *et al.*, 2010). It was reported that amine groups are the most effective functional groups for heavy metal ions removal from aqueous solutions (Deng *et al.*, 2003b).

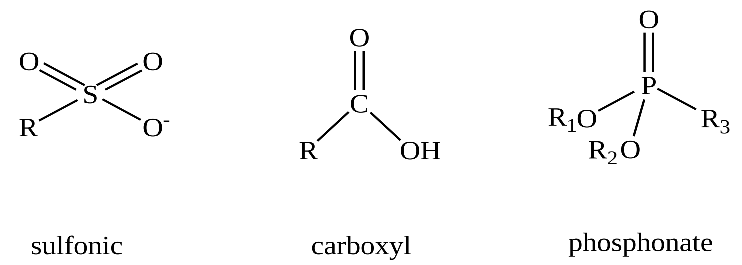


Figure 1.1: Active functional groups on the adsorbent surface

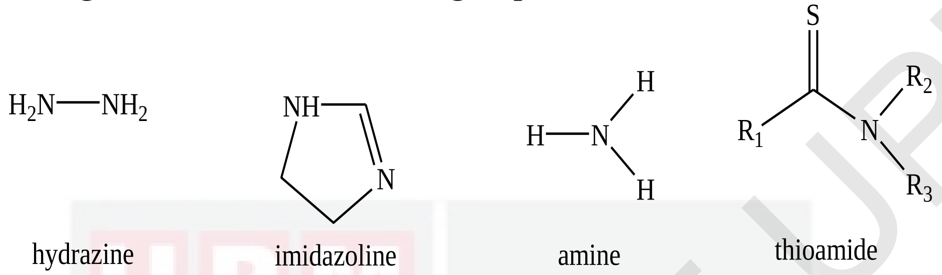


Figure 1.2: Nitrogen-based ligands groups

The uses of chemically modified copolymer network beads for the wastewater treatment have a great concern. These materials are modified according to their application such as carbon fiber precursor, composite and hydrogel adsorbent. The modification was carried out to manipulate the morphology of the sorbent, fitting the physical and chemical properties to adjust the chemical composition of the sorbent and to achieve certain porosity which depends on their application in industries (Riqueza *et al.*, 2005).

The aim of this work is to synthesise copolymer beads based on acrylonitrile (AN) and chemically modify the copolymers with hydrazine hydrate and thiourea. We utilised the chemically modified AN beads as adsorbents in a series of batch sorption experiments for the removal of Cu(II), Pb(II), Zn(II) and Cr(IV) from aqueous solutions. The sorption capacity was examined by using Inducetively Coupled Plasma (ICP).

1.2 Polyacrylonitrile (PAN)

Polyacrylonitrile is a commercially important polymer due to its unique properties, including hardness and rigidity, chemical resistance, compatibility with certain polar substances, low gas permeability and its application may be broader with its further improved properties (Liu *et al.*, 2011; Houa *et al.*, 2011). Polyacrylonitrile is easily prepared and consist of reactive pendant groups (cyano groups) which can be modified by different types of reagents such as hydroxylamine, hydrazine, ethylenediamine and thiosemicarbazide through nucleophilic addition and cycloaddition reactions (Liu *et al.*, 2011; Kiani *et al.*, 2011; Liu *et al.*, 2010). Strong polar nitrile groups are existence at an intermolecular distance of only a few tenths of nanometer along PAN chains (Jamil *et al.*, 2007). PAN forms a ladder structure *via* nitrile polymerisation then easily to obtain stabilized products (Nataraj *et al.*, 2012; Jamil *et al.*, 2007). PAN is the most commonly used polymer mainly due to its high carbon yield (up to 56%) (Nataraj *et al.*, 2012). Polyacrylonitrile (PAN) has several well-known desirable properties such as resistance to organic solvents, good mechanical strength and good thermal stability (~200 °C). Considerably, active nitrile groups present in PAN provide resistancy towards most organic solvents except to DMF and DMSO. Moreover, PAN do not melt without decomposing (do not dissolve in water) and PAN has high attention due to its commercial availability and environmentally benign nature which is none of the hazardous properties monomer (Nataraj *et al.*, 2012).

Polyacrylonitrile (PAN) can be modified by incorporation with suitable comonomer during polymerisation to improve its properties. PAN has few demerits such as moderate hydrophilicity, low moisture absorption and the lack of active functionality which limit its usages in certain areas. Incorporation of PAN with acidic comonomers increases the PAN hydrophilicity and support the cyclization of nitrile groups during heat treatment (Bajaj *et al.*, 1993). Since AN is partly soluble in water, a two phase liquid system can exist which (i) monomer-rich phase and (ii) monomer-poor phase. The distribution of comonomers between these two phases would affect the progress of polymerisation (Bajaj *et al.*, 1993). The hydrophilicity of PAN was improved for beneficial applications such as coating, sorption, surface plasma treatment, surface hydrolysis, surface graft polymerisation and chemical modification (Mishra *et al.*, 2011). Chemically modified polyacryonitrile has excellent adsorbability with many metal ions, which has been considered to be valuable in the application of sorption materials and prompted us to investigate the sorption property of metallic ions (Liu *et al.*, 2011; Houa *et al.*, 2011). Modification of polymers is a highly interesting domain to introduce desirable properties so that the resulting materials may be used for specific applications (Mishra *et al.*, 2011). Acrylonitrile can be polymerised with numberous of comonomer by using various methods such as emulsion, solution, solvent-water suspension polymerisation and aqueous suspension. The properties of PAN influenced by the method of polymerisation and type of initiators used during polymerisation (Bajaj *et al.*, 1993). The formation of poly(acrylonitrile) is shown in Figure 1.3.

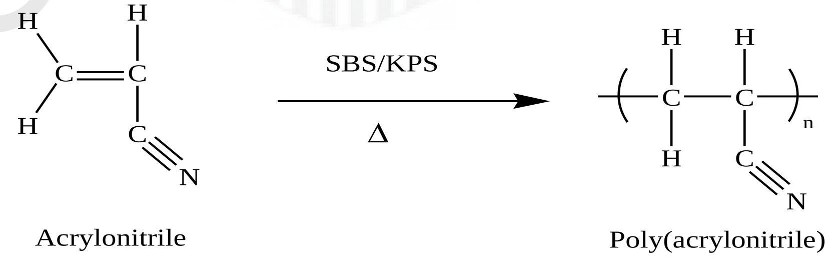


Figure 1.3: Formation of poly(acrylonitrile)

1.3 Acrylamide (AM)

Acrylamide (AM) was incorporated with AN in this study. The formation of poly(acrylonitrile(AN)-*co*-acrylamide(AM)) is shown in Figure 1.4. In the present study, the preparation of poly(AN-*co*-AM) was carried out via free radical polymerisation. The purpose to use amide group is to overcome the strong dipolar interactions along the PAN chains and improve the hydrophilicity of PAN for greater affinity with water. The copolymer networks with controlled morphology and porous structure are widely used as specific sorbents, as catalyst support, as starting materials for ion exchangers, and as packing material for gel permeation chromatography (Riqueza *et al.*, 2005). The copolymer with controlled morphology and their porous structures may increase the removal process of metal ions or other pollutants in wastewater. These characteristic of AM functional groups have strong influence on removal kinetics and flow properties of copolymer (Riqueza *et al.*, 2005).

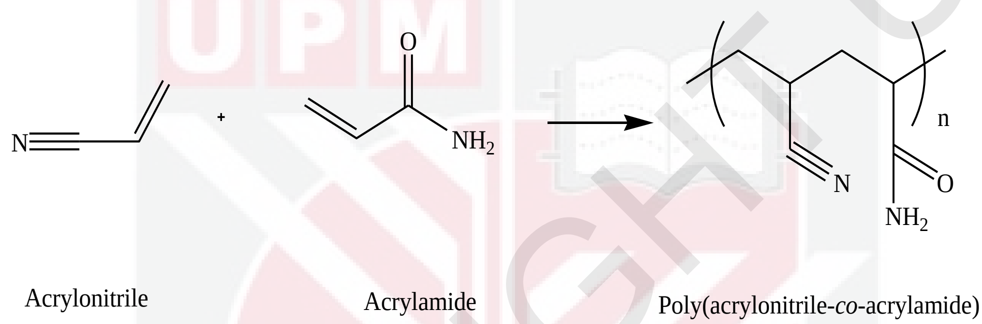


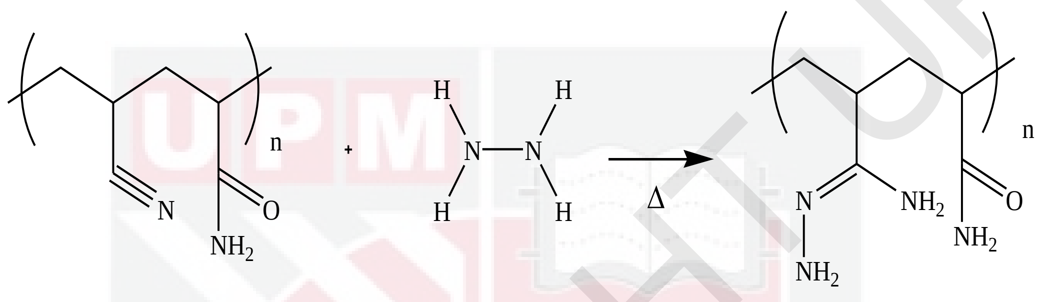
Figure 1.4: Formation of poly(AN-*co*-AM)

Polyacrylamide (PAM) gel containing large number of amide side group has been successfully used as selective sorbent for removal of heavy metal ions from aqueous solution and act as water soluble polymer. The presence of amide groups provide the opening for rapid interaction with aqueous Cu(II) to form copper-amide linkage (Mishra *et al.*, 2011). PAM is widely used in industrial wastewater as a flocculating agent (Zhao *et al.*, 2010a). The presence of functional groups like -CO_2H, -$CONH_2$, and -SO_3H not only improve the water uptake capacity of the hydrogels, but these also act as efficient anchors for active molecular species and metal ions.

1.4 Chemical modification of poly(AN-*co*-AM)

Although PAN polymers have cyano groups that are able to form complexes with metal ions, the strong interaction of cyano groups along PAN chains reduce the polymer swelling in aqueous media and with lack hydrophilicity of polymer. Cyano-containing polymers have not been extensively used in metal sorption from aqueous solutions without unless have been chemically modified with suitable reagents (Liu *et al.*, 2011; Liu *et al.*, 2010).

The functional groups (amidrazone, carboxyl and hydrazidine groups) were introduced in PAN system by chemically modified the PAN with hydrazine (Riqueza *et al.*, 2005). Hydrazine is a volatile, toxic substance and is readily absorbed by oral, dermal or inhalation routes of exposure. Adverse health effects caused by hydrazine on people living near hazardous waste sites have been described (Zare *et al.*, 2006). Contact with hydrazine irritates the skin, eyes and respiratory track. Hydrazine is used as an oxygen scavenger for corrosion control in boilers with wide application in antioxidant, photographic developer, polymers, pesticides, plant-growth regulators, pharmaceuticals and insecticides. Moreover, hydrazine is applied in fuel in the fuel cells and rocket fuel due to its high capacity and no contamination (Zare *et al.*, 2006). In this study, poly(AN-*co*-AM) was chemically modified by using hydrazine hydrate. Chemical modification of poly(AN-*co*-AM) with hydrazine as heavy metal ions adsorbent has not been reported elsewhere. Figure 1.5 shows the formation of hydrazine-modified poly(AN-*co*-AM).



Poly(acrylonitrile-*co*-acrylamide) | Hydrazine | Hydrazine-modified poly(acrylonitrile-*co*-acrylamide)

Figure 1.5: Formation of hydrazine-modified poly(AN-*co*-AM)

1.5 Removal of heavy metal ions from wastewater

Water is polluted in many ways such as effluent from leather and chemical industries, electroplating and dye industries. Heavy metals are classified into the following three categories ; toxic metals (Hg, Cr, Pb, Zn, Cu, Ni, Cd, As,Co, Sn, etc.), precious metals (Pd, Pt, Ag, Au, Ru, etc.) and radionuclides (Ra, Am, etc.) (Ramya *et al.*, 2011). The presence of heavy metals in environment is of major concern because of their transformation from relatively low toxic into more toxic species. Heavy metals appear in the environment through various anthropogenic activities. These metals mainly include cadmium, nickel, copper, lead, zinc, mercury, arsenic, chromium, etc. Metal bearing effluents are produced by a broad spectrum of sources like copper and cadmium from electroplating industry, chromium from tanning, wood preservative and textile industry, mercury from caustic soda and chlorine industries and arsenic from fertilizers (Kumar *et al.*, 2007). Therefore, it is important to control the concentration of heavy metals in wastewater before disposal into the environment. Considering deleterious effects of heavy metals on environment, various agencies throughout the world have fixed certain limits in potable water supplies and effluent discharges such are EPA (Environmental Protection Agency) and WHO(World Health Organisation) (Kumar *et al.*, 2007).

The presence of copper in industrial wastewater is now a global problem due to the manufacturing facilities of the microelectronic industries have moved their operations to many developing countries during the past two decades (Chatterjee *et al.*, 2011). Due to the mobility and toxicity in natural water ecosystems the presence of Cu(II) ions in surface water and groundwater pose major inorganic contamination problems (Zhao *et al.*, 2010a). Among the ionic species of copper, Cu(II) ions have a great concern because they are easily attached to organic and inorganic compounds based on the pH of the solution (Hasan *et al.*, 2008). Copper has unique regulatory standards because of its toxicity to aquatic life and human. Previous studies demonstrated that among all transition metal cations, copper is unique due to its extraordinarily high sorption affinity toward chelating polymer containing only nitrogen donor atoms under very acidic conditions. This due to the Cu(II) ions that are moderately soft Lewis acid while secondary and tertiary amines are soft Lewis bases (Chatterjee *et al.*, 2011). High exposure level of Cu(II) ions lead to anorexia, body weakness, damage to the gastrointestinal tract and lethargy, liver problem and kidney failure (Futalan *et al.*, 2011; Theophanides *et al.*, 2002).

Moreover, Pb(II) ions is widely used in industrial applications such as in printing, photographic materials, batteries, pigments, explosive manufacturing and fuels (Wan *et al.*, 2010; Paulino *et al.*, 2007). High exposure of lead causes harmful to both ecological environment and human health (Li *et al.*, 2013). At high concentration levels and long term exposure to 0.015 ppm of Pb(II) ions causes headache, irritancy, kidney damage, encephalopathy, anaemia, cognitive impairment, toxicity to the reproductive system and nerves system, and behavioural disturbances (Yang *et al.*, 2014; Li *et al.*, 2013). Developing fetus and infant are more sensitive to these adverse effect compared to adult (Rivas *et al.*, 2011). Pb(II) ions pollute the environment from anthropogenic sources as well as by natural geochemical processes (Wan *et al.*, 2010).

Chromium is widely recognized to exert the toxic effect in its hexavalent form (Li *et al.*, 2015; Anna L. Rowbotham, 2000) because of its mutagenicity, carcinogenicity and teratogenicity to human body (Li *et al.*, 2015). Industrial sources of chromium include electroplating, plating, leather tanning, rinse water, cooling tower blowdown, anodising baths, etc (Owlad *et al.*, 2009). Chromium is present in the environment in various forms. The most common forms are chromium(0), chromium(III) and chromium(VI) (Owlad *et al.*, 2009). Human exposure to Cr(VI) compound have high risk to respiratory cancers, leads to pulmonary congestion, liver damage and causes skin irritation resulting in ulcer formation (Kumar *et al.*, 2013; Owlad *et al.*, 2009). Long term exposure at maximum level over 0.1 ppm (Yang *et al.*, 2014) causes respiratory problem, dermatitis, nerve tissue damage, damage to kidney circulation, cited renal dysfunctions, bone defect, increase blood pressure and effects on the myocardium (Rivas *et al.*, 2011; Kotaś *et al.*, 2000). Cr(III) is less toxic than Cr(VI) and is nearly insoluble at neutral pH. Cr(III) however can listed as micronutrient, to maintain a good health and help in maintaining the normal metabolism of cholesterol, fat and glucose in human body. It is poisoning at high exposure level (Owlad *et al.*, 2009).

Zinc is naturally released into the environment even though mostly the zinc pollution comes from industrial activities. Mining and foundry activities, zinc, lead and cadmium refining, solid waste incineration and carbon combustion mostly lead to zinc pollution (Ramos *et al.*, 2002).

1.6 Problem statement

Recently, the environment problem has becomes a critical issue. It is well known that heavy metal ions are found in wastewaters greatly threaten the health of human population and natural ecosystem. The Water Quality Index (WQI) is used to indicate the level of pollution and the corresponding water classes and uses compared to National Water Quality Standards for Malaysia (NWQS). Heavy metals were analysed for Mercury (Hg), Arsenic (As), Cadmium (Cd), Chromium (Cr), Plumbum (Pb), and Zinc (Zn) from river water quality. About 99.98% of Pb data and 97.97% of As data recorded were within the Class IIB limits of the NWQS followed by 99.95% of Zn data, 99.93% of Cr data, 99.91% of Cd data and 99.20% of Hg data. One of the potential solutions is the adsorbent. Sorption is an efficient method to remove metal ions utilisation from water and industrial wastewater. Many research works have focused on metal ions removal by sorption due to its low cost, reusable, easily separable, high sorption capacities, effectiveness and high selectivity and has physical and chemical stabilities (Li *et al.*, 2015; Mishra *et al.*, 2011; Wan *et al.*, 2010; Liu *et al.*, 2011; Arsalani *et al.*, 2009; El-Ghaffar *et al.*, 2009; Neagu *et al.*, 2003).

PAN has few demerits such as moderate hydrophilicity, low moisture absorption and the lack of active functionality which limit its usages in certain areas. The chemical modification of PAN based polymer is an interesting attempt to produce microbeads adsorbent of metal ions. In this study, AM comonomer was incorporated into PAN system to overcome the strong dipolar interactions along the PAN chains and increase the hydrophilicity of the PAN for greater affinity with water. AM consists of amide functional groups that is expected to increase the performance of PAN as heavy metal ions adsorbent. Amide groups are very effective for metal ions sorption attributed by behavior of higher dielectric constant and dipole moment of amide group (Deng *et al.*, 2003b). Redox polymerisation method is an effective method due to its low cost, easy to handling and green environment. The poly(AN-*co*-AM) then chemically modified by using hydrazine and thiourea, respectively to introduced desired functional group (-NH_2 group for hydrazine and –NH_2-C=S for thiourea) into polymeric sorbent for formation of complex coordination with heavy metal ions. The sorption process is the alternative way to carried out in heavy metal ion removal due to its low cost, reusable, easily separation, high sorption capacity, high selectivity and high physical and chemical stabilities (Li *et al.*, 2015).

1.7 Objectives

This project involving the following objectives:

- To synthesise microbeads of poly(acrylonitrile(AN)-*co*-acrylamide(AM)) by using redox method.
- To chemically modify microbeads of poly(acrylonitrile(AN)-*co*-acrylamide(AM)) by using hydrazine.
- To study the effect of sorption kinetic and sorption isotherms of Cu(II), Zn(II), Pb(II) and Cr(VI) ions towards chemically modified poly(acrylonitrile(AN)-*co*-acrylamide(AM).

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