PREPARATION OF RADIATION GRAFTED KENAF ADSORBENT FOR ALUMINIUM REMOVAL VIA CHEMICAL VAPOUR DEPOSITION

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Specially dedicated to my beloved family.

Thank you for all the love, encouragement and support.

Ayah, if only you were here. Al-fatihah.

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ABSTRACT

Vapour phase grafting of kenaf fibre with glycidyl methacrylate (GMA) using radiation-induced grafting was studied to develop an adsorbent for removal of aluminium from water. The pre-irradiation of kenaf fibre was carried out at different doses from electron beam accelerator at various absorbed radiation doses (10 to 100 kGy). The grafting process was carried out in a chemical vapour deposition reactor operated at temperature of 40 °C and gauge pressure of 0 MPa to -0.1 MPa with time range of 15 to 90 minutes. The percentage of grafting, Pg (%) was calculated based on quantitative Fourier transform infra-red spectroscopy (FTIR) analysis. The grafted fibre was confirmed using FTIR and scanning electron microscopy. The optimal condition for enhancing Pg was obtained at irradiation dose of 50kGy, -0.025 MPa gauge pressure, and temperature and reaction time of 40 °C and 30 minutes, respectively. Optimization of these parameters will be a guide for subsequent development of grafted copolymer for further functionalization for preparation of adsorbent. The effect in thermal stability of polymeric material after the incorporation of GMA was also investigated. It was found that incorporation of GMA increased the thermal stability of kenaf fibre. The adsorption capacity was assessed to evaluate the efficiency of the adsorbent towards aluminium removal. It was found that the adsorbent could remove more than 99% aluminium with the highest adsorption capacity of 4.98 mg/g.

ABSTRAK

Cangkukan fasa gas gentian kenaf dengan monomer, glisidil metakrilat (GMA) melalui pencangkukan aruhan sinaran dikaji bagi menghasilkan bahan penjerap untuk menyingkirkan aluminium dalam air. Pra-sinaran ke atas gentian kenaf telah dijalankan pada dos sinaran alur elektron yang berbeza (10 hingga 100 kGy). Proses cangkukan dijalankan di dalam reaktor pengendapan wap kimia pada julat suhu 40 °C, tekanan tolok 0 MPa hingga -0.1 MPa dan juga pada julat masa antara 15 hingga 90 minit. Peratus cangkukan, Pg (%) dikira menggunakan analisis kuantitif spektroskopi inframerah transformasi Fourier (FTIR). Gentian kenaf cangkuk GMA yang berjaya terbentuk ini dianalisis dengan menggunakan FTIR dan mikroskop imbasan elektron untuk mengesahkan pengkopolimeran cangkuk. Keadaan optimum untuk meningkatkan peratus cangkukan didapati pada dos sinaran 50 kGy, tekanan tolok -0.025 MPa, dan suhu dan masa tindakbalas pada 40 °C dan 30 minit. Pengoptimuman parameter ini akan menjadi garis panduan bagi menghasilkan kopolimer cangkuk dengan penambahan GMA yang seterusnya akan ditambah kumpulan berfungsi bagi penyediaan penjerap. Kesan terhadap sifat terma polimer selepas penambahan GMA ke dalam polimer juga telah dikaji. Keputusan menunjukkan bahawa penambahan GMA telah meningkatkan kestabilan terma bahan. Kapasiti penjerapan dikaji bagi menilai kebolehupayaan penjerap untuk menyingkirkan aluminium. Didapati bahawa penjerap berkenaan mampu menyingkirkan lebih dari 99% aluminium dengan kapasiti penjerapan sebanyak 4.98 mg/g.

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LIST OF ABBREVIATION

GMA	-	Glycidyl methacrylate
PGMA	-	Poly(glycidyl methacrylate)
Im	-	Imidazole
$NaClO_2$	-	Sodium chlorite
C	-	Carbon
H	-	Hydrogen
N	-	Nitrogen
Al	-	Aluminum
Cu	-	Copper
Co	-	Cobalt
Pb	-	Plumbum
Ni	-	Nickel
Ag	-	Silver
Hg	-	Mercury
WHO	-	The World Health Organization
CVD	-	Chemical vapour deposition
RSM	-	Response surface method
NSDWQ	-	National Standard Drinking Water Quality
PE	-	Polyethylene
PP	-	Polypropylene
PP	-	Polypropylene
PS	-	Polystyrene
PTFE	-	Polytetrafluoroethylene
E-beam	-	Electron beam
RiGP	-	Radiation-induced graft polymerization
kGy	-	kiloGray

MeV	-	Megaelectronvolt
mA	-	miliamps
kW	-	kilowatts
kV	-	kilovolt
cm	-	centimetre -
ml/min	-	mililiter per minute
nm	-	nanometer
μm	-	micrometer
mm	-	milimeter
FTIR	-	Fourier Transformed Infra-Red Spectroscopy
SEM	-	Scanning Electron Microscopy
FESEM	-	Field Emission Scanning Electron Microscopy
UV-Vis	-	Ultra Violet Viscosmeter
Pg	-	Percentage of grafting
PVC	-	Polyvynil chloride
EVA	-	Ethylene vinyl acetate
AIBN	-	Azoisobutyronitrile
H_2O_2	-	Hydrogen peroxide
BPO	-	Benzoyl peroxide
ppm	-	parts per million
W_i	-	Initial weight
W_f	-	Final weight
C_i	-	Initial concentration
C_f	-	Final concentration

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CHAPTER 1

INTRODUCTION

1.1 Background of the Study

The demand for clean and potable water has increased over the years in line with the rapid development and growing population. Government faces the challenge of ensuring adequate sustainable supply of drinking water at the right price and quality, where quality water means it is safe for consumption right from the tap. In Malaysia, the water quality must comply with World Health Organization (WHO) International Standards and local standards regulated by Ministry of Health, Malaysia (MOH).

Quality of drinking water is measured in terms of several characteristics such as (a) microbiological, by ensuring the water is safe to drink by detecting any microbiological contaminants such ascholera, cryptosporidium, Giardia or Hepatitis A that pose a threat to human health, (b) chemicals, by monitoring levels of disinfection byproducts, solvents, fluoride and pesticides, (c) radiation, by ensuring the presence of radionuclides contaminants either from natural sources such as radium, radon or human-made nuclear materialsis at acceptable limits and (d) heavy metals, by ensuring the amount of lead, arsenic or aluminum is in compliance with standard regulations [1]. Heavy metals are very toxic elements and unlike many organic pollutants, heavy metals are not easily degraded in nature.

Conventional coagulation, flocculation and sedimentation practices are commonly used in local pre-treatment for river water purification in Malaysia. Chemical coagulant such as aluminum salts and polymers is added to river water to facilitate bonding among particulates. The coagulant-river water mixture is then slowly bubbled in a process known as flocculation. This water bubbling induces particles to collide and clump together into larger sizes which are more easily settled down. This process is often followed by gravity separation (sedimentation) and filtration. The sediment is filtered out and discharged to downstream as sludge.

A cross-sectional study done by M.S. Qaiyum *et al.* [2] demonstrated that treated water samples collected from two residential areas in Mukim Parit Lubok and Parit Raja, Batu Pahat, Malaysia contain high amounts of aluminum (Al) exceeding the standard limit set by the MOH for drinking water guideline. According to National Standard Drinking Water Quality (NSDWQ), the acceptable limit in standards set to regulate drinking water quality of treated water is 0.2 mg/L [3]. The study reported that treated water samples taken from 100 respondent houses in Mukim Parit Lubok have recorded 0.18 ± 0.022 mg/L aluminum concentration in drinking water, while treated water samples taken from 100 respondent houses in Parit Raja have been recorded at 0.22 ± 0.044 mg/L [2]. It is believed that high amount of Al comes from the coagulant which is used during the river water pre-treatment process. Although Al is a naturally occurring metal presence abundant in the environment, excessive addition of Al salts remain as residuals in the treated water which may result in highly concentrated Al in the system.

High amount of Al have a significant impact on the environment. Aluminium is recognized as a toxic agent to aquatic freshwater organisms whereby it causes acidic precipitation. Acidification of catchments leads to increased Al ion concentrations in soil solution and freshwaters. Large parts of both the aquatic and terrestrial ecosystems will be affected as well. Oral exposure of human to high levels of Al can cause a large number of health problems. It is believed that these exposures originated from drinking water. This was confirmed by a study of the relation between aluminum concentrations in drinking water and Alzheimer's disease conducted by Rondeau *et al.* [4] where 3,777 subjects aged 65 years and over were followed up for 8 years with an active search for incident cases of Alzheimer's disease. A total of 182 Alzheimer patients including 13 who were exposed to high aluminum levels were identified. These findings support the hypothesis that a high concentration of aluminum in drinking water may be a risk factor for Alzheimer's disease. Later on, Rondeau *et al.* [5] published a report linking aluminum in drinking water and Alzheimer's disease to a major transport protein in the human body system for both iron and Al called transferrin.

Coagulation is also important in several wastewater treatment operations. The addition of coagulant chemicals to primary physical separation process is to reduce the load to downstream biological processes, or in some cases for direct discharge to the river [6]. Aluminum is among elements existing in aluminum-based coagulants and having added to the water, a part of coagulant will be dissolved and remained in high concentration in the water. Controlling unwanted elements such as aluminium or heavy metals at this stage of wastewater treatment is an effective step for controlling contaminations from resources in drinking water. Although there are various methods for removal of metals from water, either currently in use or are at various stages of development around the world, chemical precipitation continues to dominate the industry due to low operating costs and simple operation. Liquid extraction, ion exchange, reverse osmosis, electrodialysis techniques are proven to be very efficient but very expensive to implement in large scale. However, the major drawback of precipitation is the generation of bulky precipitated materials and colloidal particles which have motivated researchers around the world to search for a more effective and economical method for removing metal elements from water. Adsorption is an efficient yet simple method for metal ions removal.

Adsorption using grafted materials that could filter out immediately and easily the contaminants in tandem with other processes could be a solution. Most commercially available filter membranes are synthesized by chemical processing that requires some chemicals to attach suitable functional groups onto the polymer backbone. Polymeric substances with the ability to complex metal ions from solution are very common. There are several modification techniques for polymer such as polymerization reactions, grafting, followed by functionalization, copolymer formation, chain extension, cross-linking, branching, and controlled degradation [7]. Considerable amount of research has been conducted on the synthesis of polymeric adsorbent over the years, both by the conventional chemical grafting technique [8, 9] and by the radiation-induced grafting technique [10].

Radiation-induced grafting technique has generated much interest and shown to be advantageous means of grafting over conventional chemical grafting [11]. Actives sites can be created via radiation whereby a large number of free radicals is produced on the polymeric backbones without the use of chemical initiators. These radicals undergo reaction with a monomer of choice to produce macromolecular chains that are covalently bound to the irradiated specimen. The polymeric backbones can be in different geometries such as films, powders and ~~fiber~~fibres that can possibly be grafted by this technique. By the utilization of different monomers or combinations of monomers to vary the penetration of monomer into the bulk, choosing the right absorbed radiation dose to suit the polymer and varying other parameters that may give effect to grafting can produce bulk materials with "tailor made" properties. The major advantage of radiation grafting is that it allows more flexibility in attaching functional groups to different geometries and different kinds of trunk polymers needed for the removal process. Other techniques such as thermal-chemical systems have been commercially practiced, however, concerns over the sensitivity of reaction catalysts to temperature and trunk polymers can be eliminate using electron beam irradiation [12]. Thus, considering the advantages of radiation grafting, different types of contaminants from water can easily be removed with this "tailor made" grafted matrices that facilitates easy clean-up of water.

Grafting of monomer with functional groups is an interesting way for obtaining new materials of special physical-chemical properties. The use of carboxylic acid such as acrylic acid (Aac) or methacrylic acid (MAA), produced functional group −COOH and COO− on the polymer trunk. Carboxyl group have two lone pairs of electrons on the oxygen atoms therefore two carboxyl groups are needed to form a chelate that binds with divalent cations such as Cu^{2+}, Pb^{2+} and Ni^{2+} [13]. Moreover, the attachment of covalent bond provides long lifetime of chemical stability by means of introduced chains, compared to physically coated polymer chain [14]. Seko *et al.* [15] demonstrated that polyethylene graft polystyrene sulphonic acid adsorbent can be prepared by mutual radiation-induced grafting of styrene/divinyl benzene mixture onto PE film followed by sulfonating the grafted PE with chlorosulfonic acid in 1,2-dichloromethane. The adsorbent was used for metal ions sorption study and results show that the preference order of Ni(II)>Co(II)>Cu(II)>Pb(II)>Ag(II).

Natural polymers are abundant, normally low in cost, biodegradeable and cause flocculation. However, natural polymers have short shelf life due to the severe drawback of biodegradation. Synthetic polymers on the other hand, are easy to tailor, have good mechanical properties but are very poor in degradability property. Chemically modified natural polymers with improved properties play an important role in polymer research, not only because they are low in cost but due to their degradability property. Extensive studies have been done using radiation-induced grafting technique to modify chemical and physical properties of polymers. Grafting using high energy radiation, by gamma or electron beam irradiation through the formation of radicals is more environmental friendly than the conventional redox grafting method. This technique has been widely used to graft various monomers onto different type of polymers.

In this work, kenaf fiberfibres is used as natural adsorbent to remove aluminum ion from water. Kenaf or its scientific name, *Hibiscus cannabinus* is a herbaceous plant in the malvaceae family. Kenaf fiberfibre is normally comprises of bast (bark) and core (wood). The bast is about 40% of the plant and the fiberfibres are long and slender, meanwhile the core is about 60% of the plant and the fiberfibre is short.

Kenaf fiberfibres have many environmental advantages like renewable, biodegradable, good mechanical properties, abundant and relatively low cost. Kenaf is cultivated for its fiberfibre in mostly in Asia regions, some parts of Africa, and also can be found in southeast Europe. Kenaf fiberfibre is commonly used to make rope, cloth and the most common use is for paper production. A part from that, kenaf fiberfibre is extensively used in engineered wood, insulation and packing material [16, 17]. It is also useful as filler for plastic composites and can be used as an additive for drilling muds in oil wells [18, 19]. Kenaf also can be made into various types of environmental absorbent agent to absorbs oil, cleaning up liquid leakages in industrial area and as filtering product [20].

A number of agricultural fiberfibres that can serve the purpose as natural adsorbent have been investigated by other researchers, including oil palm fiberfibre [21], coconut fiberfibre [22] and jute fiberfibre [23]. However, little is known on the potential of kenaf fiberfibre as adsorbent. Kenaf fiberfibre has several advantages in term of ecological and economical such as abundancy, exhibiting low density, non-abrasiveness during processing, excellent mechanical properties, biodegradability and inexpensive pricing.

The main aim of this work is to prepare an adsorbent by graft copolymerization using pre-irradiation method, where the material is first irradiated with electron beam processing system, EPS 3000 before the grafting is carried out in the vapour phase inside a chemical vapour deposition (CVD) reactor followed by chemical functionalization. Glycidyl methacrylate (GMA) was used as monomer and amine group was introduced to the polymer matrix using imidazole. GMA was chosen because of its advantages due to reactive epoxide group present in the structure that can be tailored according to target application by introducing functional group on the trunk polymer [24]. Imidazole was selected for functionalization because of its high selectivity towards aluminum ions during adsorption [25]. Preparation of the kenaf adsorbent and its ability to remove aluminum are discussed in this study.

1.2 Problem Statement

Existing adsorbent such as membranes are very expensive, thus making it unrealistic to apply in large scale water treatment application. Therefore, there is a need for a cost effective alternate material for heavy metals adsorbent, such as aluminum. Synthetic polymers such as PP, PE, PS and PVC have been well-established in the market. However, as they are non-biodegradable in nature, the risk of clogging land fills and increase environmental pollution and emissions during incineration will pose danger to mankind [17]. Therefore, many researchers have aggreed that biodegradable natural polymers is the answer to this problem [26]. Natural ~~fiber~~fibre adsorbent is preferable because of its ability to biodegrade, recyclable and presence abundance in environment, as alternative to expensive synthetic adsorbent.

Kenaf bast ~~fiber~~fibre has received growing attention among researchers as a renewable resources with several advantages in term of ecological and economical such as abundancy, exhibiting low density, non-abrasiveness during processing, excellent mechanical properties, biodegradability and inexpensive pricing. These crops have been planted as a substitute to tobacco plantation since 2002 around East Coast Peninsular Malaysia. While seen as a natural polymer with many potential applications, kenaf ~~fiber~~fibre suffers weak interfacial bonding between the polar ~~fiber~~fibre surface, resulting in poor mechanical properties due to this weak interfacial bonding. This problem needs to be solved in order to improve mechanical properties and cost-efficiency of bulk production. One of the most effective ways to solve this problem is by ~~fiber~~fibre surface modification. Kim *et al.* [27] have recently grafted acrylamide onto kenaf ~~fiber~~fibre using gamma-ray radiation to improve compatability between the ~~fiber~~fibres and cements. The results exhibit that mechanical properties of gamma-ray grafted kenaf ~~fiber~~fibre-cement composite is superior to those of the ungrafted kenaf-~~fiber~~fibre composite. Meanwhile, the study on effect of glycidyl methacrylate grafted on mechanical properties of polyvinyl chloride (PVC)/ethylene vinyl acetate (EVA) composite were done by Bakar N. *et al.* (2014). The results revealed that the presence of PGMA on the surface of kenaf

~~fiber~~fibre has improved the interfacial adhesion between the ~~fiber~~fibre and PVC/EVA matrix [28].

Although many researches on producing grafted polymer using natural material such as chitosan, cellulose and other materials has been reported, most was done in liquid phase, either in solution or emulsion. None has so far been conducted in producing grafted natural polymer in vapour phase using a CVD reactor. Furthermore, no systematic research has been reported on radiation-induced graft polymerization (RiGP) via chemical vapour deposition. This new process by a combination of radiation and chemical vapour deposition on preparation of adsorbent purposed in this study can simplify the current process of conventional RiGP. The grafting rates is likely to be higher in conventional liquid-phase grafting than in vapour-phase grafting because grafting in vapour-phase is limited to the surface of the trunk polymer, meanwhile liquid-phase grafting allows the monomer to penetrate inside the trunk polymer. However, depends on the application of the end products, some polymers only required modification on the surfaces. Vapour-phase grafting also posses several advantages over liquid-phase grafting such as no solvent is required and the efficiency of monomer usage as there is no parasitic loss of monomer by homopolymerization. Since initiator or catalysts are not required for RiGP, a number of chemicals can be eliminated which complies with the requirements of consumers to reduce chemicals. Some chemicals might be harmful to health, thus reduction of chemicals will contributes to the society. Significant reduction in chemical consumption in the process leads to reduce of cost and due to the simple operation, the possibility to apply this process in large scale for mass production make it attractive for industrial application.

The following are questions pertaining to radiation grafting of glycidyl methacrylate unto kenaf bast fiberfibre:-

i. Can glycidyl methacrylate be grafted onto kenaf bast fiberfibre using RiGP method?

ii. Can the grafting process be done in vapour phase using chemical vapour deposition?

iii. What are the effect of the grafting process parameters on the percentage on grafting?

iv. Can the radiation modified grafted material be used as an adsorbent to remove aluminum ion from water?

1.4 Research Objectives

The objective of this research is to study a new process by a combination of electron beam irradiation and chemical vapour deposition on the preparation of GMA-grafted kenaf adsorbent for removal of aluminum from water. In detail, this objective can be divided into three as follows;

1. to investigate the effect of pretreatment with $NaClO_2$ to remove phenolic compound and reduce lignin content of kenaf fiberfibre.

~~4.~~3. to determine the adsorption capability of prepared adsorbent to adsorb aluminum ion in water.

1.5 Scope of the study

The kenaf ~~fiber~~fibre was treated using $NaClO_2$. Pre-irradiation grafting method was used to graft GMA onto kenaf ~~fiber~~fibre. The grafting process was done in vapour phase inside a chemical vapour deposition reactor. The effects of grafting process parameters were studied on absorbed radiation dose given to the substrate, deposition time and reactor pressure. The developed GMA-grafted kenaf then was functionalized using imidazole to introduce amine group to the polymer matrix. The modified adsorbent was tested in a batch adsorption test. Subsequently, determination of the adsorption capacity was carried out to evaluate the effectiveness of kenaf adsorbent for aluminum removal. Characterization of the ungrafted and grafted kenaf were carried out using Fourier Transformed Infra-Red Spectroscopy (FTIR), Field Emission Scanning Electron Microscopy (FESEM), ThermalGravimetric Analyzer (TGA) and organic elemental analyser (CHN) to evaluate the presence of GMA grafted layer and functionalized amine on the ~~fiber~~fibre. The evaluation of adsorption efficiency was carried out using Ultra Violet Visible Spectroscopy (UV-Vis) by performing adsorption test in batch unit using aluminum standard stock solution.

1.6 Significant of study

The following two new areas which have not been discussed by previous researchers will be presented in this study:-

i. A new process of grafting in vapour phase using chemical vapour deposition.

ii. The combination of high energy radiation and chemical vapour deposition in the grafting process.

1.7 Structure of Thesis

This thesis is comprised of 5 chapters and each chapter gives informations related to the research work.

- Chapter 1 contains introduction of the project. It provides an introduction of the research background, the problem statements, the research objectives and scope of the study.
- Chapter 2 contains the literature review. It provides a brief explanation of natural polymers, polymer modification using radiation method, chemical vapour deposition technique and related previous studies.
- Chapter 3 contains information about the material specifications, equipments and experimental procedures used in this study.
- Chapter 4 contains results and discussion of this study. It present the results obtained from the study that covers grafting process parameters, material characterizations and adsorption studies.
- Chapter 5 concludes the findings an some recommendations for futureworks.

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