

**UREA ADSORPTION BY ACTIVATED CARBON
DERIVED FROM OIL PALM KERNEL SHELL AND
EMPTY FRUIT BUNCH FIBER**

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OIL PALM KERNEL SHELL AND EMPTY FRUIT BUNCH FIBER**

by

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LIST OF ABBREVIATIONS

AC	Activated Carbon
ACF	Activated Carbon Fiber
ARF	Acute Renal Failure
BET	Brunauer–Emmett–Teller
BUN	Blood Urea Nitrogen
CaO	Calcium Oxide
CaS	Calcium Sulfide
CKD	Chronic Kidney Disease
CO ₂	Carbon Dioxide
CPO	Crude Palm Oil
DFT	Density Functional Theory
DR	Dubinín–Radushkevich
EFB	Empty Fruit Bunch
ESRD	End-Stage Renal Disease
FFB	Fresh Fruit Bunch
FTIR	Fourier Transform Infrared
GAC	Granular Activated Carbon
HCl	Hydrochloric Acid
H ₂ SO ₄	Sulfuric Acid
H ₃ PO ₄	Phosphoric Acid
IUPAC	International Union of Pure and Applied Chemistry
KBr	Potassium Bromide
KOH	Potassium Hydroxide
K ₂ CO ₃	Potassium Carbonate
MF	Mesocarp Fiber
N ₂	Nitrogen
NaOH	Sodium Hydroxide
Na ₂ CO ₃	Sodium Carbonate
OPF	Oil Palm Fronds

OPT	Oil Palm Trunks
PAN	Polyacrylonitrile
PAC	Powdered Activated Carbon
PKS	Palm Kernel Shell
POME	Palm Oil Mill Effluent
PSD	Pore Size Distribution
PTH	Parathyroid Hormone
SC	Sludge Cake
SEM	Scanning Electron Microscopy
TGA	Thermogravimetric Analysis
TG-DSC	Thermogravimetry and Differential Scanning Calorimetry
XRD	X-ray Diffractometry
ZnCl ₂	Zinc Chloride

LIST OF SYMBOLS

2θ	Angle of Diffraction
%	Percentage
wt %	Weight Percent
$^{\circ}\text{C}$	Unit of Temperature on Celcius Scale
K	Unit of Temperature on Kelvin Scale
g	Gram
kg	Kilogram
L	Liter
ml	Mililiter
mg	Miligram

**PENJERAPAN UREA OLEH KARBON TERAKTIF YANG DIHASILKAN
DARIPADA TEMPURUNG KELAPA SAWIT DAN TANDAN SAWIT
KOSONG**

ABSTRAK

Sistem hemodialisis tidak dapat menyingkirkan toksin uremik daripada darah pesakit secara berkesan. Tempurung kelapa sawit dan serat tandan kosong boleh digunakan untuk sintesis karbon teraktif dan digunakan dalam sistem ginjal tiruan untuk penjerapan urea. Granul karbon teraktif telah disintesis daripada tempurung kelapa sawit melalui suhu dan masa karbonisasi yang berbeza serta rawatan asid sulfurik. Serat karbon teraktif dihasilkan daripada tandan kosong kelapa sawit dengan nisbah asid-kepada-serat yang berbeza. Sifat-sifat fizikal dan kimia sampel-sampel tersebut telah dikaji. Peningkatan suhu karbonisasi dari 400 ke 600°C mengakibatkan peningkatan penjerapan urea. Ia disebabkan oleh peningkatan luas permukaan. Peningkatan tempoh karbonisasi dari 3 ke 6 jam tidak meningkatkan penjerapan urea apabila luas permukaan bertambah. Sebaliknya, kumpulan berfungsi C-H merupakan faktor utama yang mempengaruhi penjerapan urea. Rawatan asid sulfurik meningkatkan luas permukaan granul karbon teraktif dan meningkatkan penjerapan urea. Keadaan optimum untuk mensintesis serat karbon teraktif yang mempunyai ciri yang baik ialah melalui rawatan asid pada nisbah asid-kepada-serat 1.5. Peningkatan lagi nisbah asid-kepada-serat menyebabkan penurunan luas permukaan. Ia disebabkan oleh pengewapan air yang berlebihan melalui dehidrasi asid sulfurik. Peningkatan nisbah rawatan asid sulfurik mengakibatkan kemerosotan penjerapan urea oleh sampel serat karbon teraktif. Ia disebabkan oleh kehilangan

kumpulan berfungsi C-H. Secara keseluruhan, kehadiran kumpulan berfungsi C-H pada permukaan karbon teraktif terbukti sebagai faktor penting untuk kapasitas penjerapan urea yang tinggi.

UREA ADSORPTION BY ACTIVATED CARBON DERIVED FROM OIL PALM KERNEL SHELL AND EMPTY FRUIT BUNCH FIBER

ABSTRACT

The present hemodialysis treatment is expensive and seriously affects the life of a patient due to its low effectiveness and efficiency in uremic toxin removal. Thus, nanoporous materials are needed to improve the treatment. Palm kernel shell (PKS) and empty fruit bunch (EFB) fiber biomass from palm oil mills can be utilized to synthesize low cost nanoporous activated carbon (AC) which can be applied in artificial kidney system for urea adsorption. In this study, granular activated carbon (GAC) was synthesized from PKS via different carbonization temperatures and durations as well as the sulfuric acid (H_2SO_4) treatment. Activated carbon fiber (ACF) was derived from EFB via the treatment with different acid impregnation ratios followed by the carbonization and CO_2 gas activation at $900^\circ C$. The physical and chemical properties of the samples were studied. Increase of carbonization temperatures from 400 to $600^\circ C$ resulted in the increase in urea adsorption predominantly due to increase in surface area. The increase of carbonization duration from 3 to 6 hours improved surface area but does not improve urea adsorption. Instead, C-H functional group is the main factor that influences urea adsorption. The H_2SO_4 treatment enhances surface area of GAC sample and eventually improves the urea adsorption. The optimum condition for the synthesis of ACF sample with excellent pore characteristic is the acid treatment at 1.5 acid-to-EFB fiber ratio. Further increase of the ratio reduces the surface area due to excess water vaporization via H_2SO_4 dehydration. Regardless of the obtained surface area, increase of acid

impregnation ratio deteriorates the urea adsorption by ACF samples due to the decrease in C-H surface functional groups. Overall, the presence of C-H surface functional group in AC was proven the vital factor for higher urea adsorption capacity.

CHAPTER 1

INTRODUCTION

1.1 General Introduction

Urea adsorption is an important process in the dialysis system for patient suffered from renal failure. The dialysis treatment is a crucial process to remove and reduce the uremic toxins to a safe level in a patient's body. In conventional dialysis system, uremic toxins from a patient's blood were removed through semipermeable membranes into dialysate. Patients suffered from permanent renal failure or end-stage renal disease (ESRD) need to undergo renal replacement therapies to excrete the wastes from body to sustain life.

Hemodialysis is a type of renal replacement therapy that removes wastes from blood by diffusion through a semipermeable membrane into the dialysate fluids (Debowska et al., 2011). During the hemodialysis process, a patient needs to be connected to dialysis machine for 3 to 4 hours per session and the procedure is repeated 3 to 4 times per week (Davankov et al., 1997). It seriously affects the life and freedom of patients and their employments.

The present hemodialysis process cannot fully carry out the functions of healthy human kidneys. The polymeric membrane used in the current hemodialysis process has several drawbacks. It has poor blood compatibility (Barzin et al., 2004) and not efficient in the removal of uremic toxins such as *p*-cresol, urea and creatinine (Wernert et al., 2005). Thus, research and study should be focused on the

development of new and better hemodialysis device for efficient removal of uremic toxins that improve quality of life of a patient. Research and development have been carried out on the improvement of artificial kidneys. Barzin and his co-workers conducted research on new materials for the hemodialysis membrane (Barzin et al., 2004), while design and development of wearable artificial kidney were carried out by Gura and his co-workers (Gura et al., 2009).

Porous materials with good properties can be utilized in the artificial kidney to improve the efficiency of uremic toxins removal from blood. A desirable porous material should be biocompatible, non toxic, chemically inert and has high adsorption capacity. Wernert and co-workers utilized zeolites for the removal of uremic toxins in artificial kidney system (Wernert et al., 2005). The results have proven the possibility in applying nanoporous materials as adsorbents for the removal of uremic toxins in artificial kidney system.

1.2 Research Background

Activated carbon (AC) is an ideal nanoporous material to be used in various adsorption applications due to its outstanding pore characteristics. AC has large surface area, high porosity, good biocompatibility and chemically inert surface (Stavropoulos et al., 2008, Ye et al., 2007). AC can be found in the powder, granular and fiber forms. The shapes and properties of AC are greatly influenced by the types of raw materials used and the activation condition.

Palm kernel shell (PKS) and empty fruit bunch (EFB) fibers are major biomass generated by palm oil mills during palm oil extraction process. All these biomass are normally used as low energy fuel for boilers in the oil palm mills or disposed as landfills. The burning of such biomass in boiler causes air pollution to the environment and could seriously affect the air quality. Since all these biomass have very little commercial values in conventional disposals, conversion and utilization of this biomass to become functional materials is essential to contribute to wealth generation for the nation.

AC is normally produced by carbonization prior to activation process. Carbonization process is an important process to create rudimentary porous structures and enrich the carbon content in carbonaceous materials. The activation process further develops the pores and eventually produced AC with high porosity. Carbonization temperatures and duration are important parameters in the AC production. These parameters would affect the pore characteristics and adsorption capacity of AC. H_2SO_4 treatment is an important pretreatment which could enhance the porosity development in AC via the intercalation and exfoliation of H_2SO_4 compound into the carbonaceous materials

In this study, PKS and EFB fiber were converted into AC and utilized for urea adsorption. The aim of this research is to explore the possibility of applying these materials as adsorbents for efficient removal of urea and hence improve the design of present hemodialysis system.

1.3 Problem Statement

The current hemodialysis technology is far from a perfect solution for the patients suffered from renal failure. This is because hemodialysis could not to remove all uremic toxins effectively. The cost of hemodialysis treatment is expensive (Mallick and Gokal, 1999). The polymeric membrane used in the current hemodialysis process has poor blood compatibility (Barzin et al., 2004). It seriously affected the mobility, freedom and employability of patients. Therefore, research and study should be carried out on the development of new artificial kidney device that are portable, wearable, light weight and able to provide efficient dialysis function. The selection and development of good porous materials in the dialysis system is essential for the efficient removal of uremic toxins.

Activated carbon is an ideal nanoporous material for the adsorption of uremic toxins due to its exceptional properties. In previous study, EFB fiber was successfully converted to activated carbon fiber (ACF) with desired pore characteristics through the carbonization and activation processes (Tan, 2011).

In the present study, further investigation was extended to the urea adsorption by ACF derived from EFB fiber and granular activated carbon (GAC) derived from PKS. The EFB fiber derived ACF and PKS derived GAC were investigated for their physical as well as chemical properties and then utilized for urea adsorption. The performances of urea adsorption by ACF and GAC samples were studied and compared. These studies explore their potential to improve the urea adsorption in present hemodialysis system. By further enhancing the design of an ideal artificial kidney system through application of nanoporous materials, it does not only prolong

the life and improve quality of life of the renal failure patients, but also generating the wealth for the nation.

1.4 Objectives

The purpose of this research is to study the urea adsorption performance by nanoporous carbon derived from oil palm biomass. To achieve the goal, the project carried the following objectives:

1. To synthesize granular activated carbon (GAC) and activated carbon fiber (ACF) from palm kernel shell (PKS) and empty fruit bunch (EFB) fiber respectively.
2. To characterize the morphology, composition and porous structure of the PKS derived GAC and EFB fiber derived ACF.
3. To evaluate the urea adsorption performance by GAC and ACF samples.

1.5 Scope of Research

In this study, GAC and ACF samples were respectively synthesized from PKS and EFB fiber. The PKS and EFB fiber are biomass collected from local palm oil mills. AC was produced from biomass via carbonization and followed by physico-chemical activation. The effects of carbonization temperatures and durations as well as the H₂SO₄ treatment on the GAC samples derived from PKS were studied. On the other hand, EFB fiber was used as a precursor for the synthesis of AC in fiber form (ACF) sample. The effect of acid impregnation ratio on properties of ACF was studied.

PKS and EFB fiber were first characterized via thermogravimetric analysis (TGA). Both GAC and ACF samples derived from PKS and EFB fiber were characterized by scanning electron microscopy (SEM), Fourier transform infrared (FTIR), X-ray diffractometry (XRD), Raman spectroscopy and nitrogen adsorption analysis. The urea adsorption tests were carried out on the so produced GAC and ACF using a UV-Vis spectrophotometer simulating the urea level in renal failure patient's body. The urea adsorption performance by GAC and ACF samples were then compared with commercial AC.

CHAPTER 2

LITERATURE REVIEW

2.1 Urea Adsorption

Urea adsorption is a crucial process involved in a variety of applications such as household waste water purification, fertilizing plants, synthesis of dimethyl carbonate (DMC) and removal of uremic toxins in dialysis system. Urea is a main nitrogen containing compound found in the household waste water. Urea adsorption process is applied in the purification of these waste water to ensure the safe and quality of life (Wickramasinghe and Premachandra, 2012). Urea fertilizers have been applied in the planting via the urea adsorption by leaves of numerous plant species using foliar spray technique or applying liquid fertilizers directly to the leaves (Bowman and Paul, 1992). DMC can be produced via the urea adsorption and decomposition on the surface ZnO catalyst (Gao et al., 2012).

Amongst various applications, urea adsorption is particularly essential in the dialysis treatment for patient suffered from renal failure. The dialysis treatment is a crucial process to remove and reduce the uremic toxins to a safe level in the patient's body. In a conventional dialysis system, uremic toxins from patient's blood were removed through semipermeable membranes into dialysate fluid. However, not all uremic toxins were efficiently removed from the patient's blood via the semipermeable membranes. Hence, many studies have been made to remove the uremic toxins via adsorption by adsorbents. Zeolites (Wernert et al., 2005) and AC

(Lehmann et al., 1981) have been utilized as efficient adsorbents for the urea removal in the current artificial kidney system.

2.1.1 Uremic Toxins

Uremic toxins are wastes generated from metabolism process and normally eliminated by healthy kidneys via the urine (Miyamoto et al., 2012). Uremic toxins are divided into three groups according to their molecular weight. The three groups of uremic toxins are low, middle and high molecular weight solutes.

Low molecular weight solutes have weight below 500 Daltons and water-soluble. Urea, uric acid and creatinine are examples of this group. Middle molecular weight solutes have molecular weight range from 500 to 60000 Daltons. Examples of this group molecule are peptides, β_2 -microglobulin (β_2 -M), parathyroid hormone (PTH) and leptin (Jørrres et al., 2010). The molecules of the middle molecular weight group are not efficiently removed by the conventional hemodialysis machine (Brunet et al., 2003). High molecular weight molecules are protein bound solutes, examples of this group are p-cresol and indoxyl sulfare (Wernert et al., 2005).

An estimation of 180 liter (L) of blood passed through kidneys per day and generated about 1.5 L of urine (Davankov et al., 1997). Urine consists of metabolism products such as urea, uric acid, creatinine and organic compounds. Urea is a major nitrogenous waste product of protein metabolism in human body (San Pietro and Rittenberg, 1953). About 7 to 25 mg of urea nitrogen can be found in 100 ml of healthy adult human blood (Johnson et al., 1972).

High level of urea is detected in the blood of patient suffered from renal failure. The amount of nitrogen in the blood that comes from urea can be measured by Blood Urea Nitrogen (BUN) test. BUN value above 60 mg/dL indicates a moderate to severe degree of renal failure (Johnson et al., 1972). According to retrospective analysis of 13473 patients undergone hemodialysis treatment, a urea reduction ratio of 65 to 69 % was associated to the lower risk of death (Owen Jr et al., 1993).

Urea is a small molecule with molecular weight of 60 g/mol and its chemical formula is $\text{CO}(\text{NH}_2)_2$. It is a polar molecule with melting point 133 °C (Pickering, 1987). The molecular size of urea is 0.63 nm (Wernert et al., 2005). Urea is highly soluble in water rather than in alcohol. This is because of hydrogen bonding is possible at both N-H sites in the urea molecule. There is also polarity at the C=O bond and additional interactions could occur there (Pickering, 1987). The structure of urea molecule is shown in Figure 2.1.

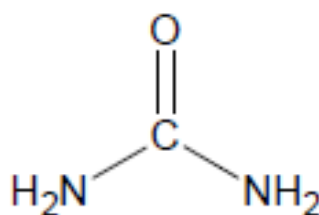


Figure 2.1: Structure of urea molecule (Gao et al., 2012)

2.1.2 Renal Failure

The condition of partial or complete loss of kidney functions is termed as a renal failure. The signs of renal failure are the accumulation of uremic toxins in body, retention of fluids and shift of electrolyte balance in body (Jørrres et al., 2010). Renal failure causes serious health problems and affects the quality of life. Renal failure is divided into acute renal failure (ARF) and chronic kidney disease (CKD).

Acute renal failure is condition where the kidneys loss its functions over a period of hours to days. The symptoms for the ARF are the elevated blood urea nitrogen (BUN), creatinine and electrolyte, unable to produce sufficient amount of urine (Byham-Gray and Wiesen, 2004). Chronic kidney disease occurs due to the progressive loss of kidney functions over a period of months to years. The accumulation of uremic toxins and toxic wastes in blood due to malfunction of kidneys caused death within 10 to 12 days (Davankov et al., 1997). Patients suffered from renal failure have to undergo renal replacement therapy to sustain life.

2.2 Artificial Kidney

Patients suffered from renal failure or end-stage renal disease (ESRD) need to undergo renal replacement therapies in order for them to live a healthy life. Renal replacement therapies are treatments used to support and prolong the lives of patients with renal failure problems. Renal replacement therapies consist of renal transplantation, peritoneal dialysis and hemodialysis.

Kidney transplant is the process of permanently replacing a failed human kidney with functioning kidney from another human donor. The donor-recipient compatibility and other medical complications are the factors that determine the suitability of patient to survive with the transplant kidney (Hariharan et al., 2002). In addition, the amount of kidneys ready for transplants is very limited. Peritoneal dialysis uses the peritoneum in abdomen as membrane to remove the waste from blood. It is home based dialysis treatment for patient with renal failure problem. However, this treatment is associated with the risk of effluent protein losses during the dialysis (Lai, 2009) and higher risk of infection (Li et al., 2010a). The quality of peritoneal membranes deteriorates with the peritoneal dialysis duration (Baroni et al., 2012).

Hemodialysis treatment removes the toxic wastes from patient's blood through the semipermeable membranes into the dialysate fluids. Hemodialysis is normally carried out at clinics, dialysis centres and hospitals. During the treatment, the patient with renal failure problem is connected to a dialysis machine for 3 to 4 hours per session and repeated 3 to 4 times per week (Finkelstein et al., 2012). The treatment is usually managed by specialized staff, technicians and nurses. It seriously limits the mobility and employability of patients.

2.2.1 Hemodialysis Technology

In a hemodialysis system, a blood pump channels the blood into a dialyzer for filtration of uremic toxins from blood. In the dialyzer, blood flows over semipermeable membranes in one direction only while the dialysis fluid (dialysate) flows in an opposite direction which is also known as counter current flow. Due to

the concentration gradient, the nitrogenous wastes and electrolytes in blood pass through the semipermeable membranes and flow into the dialysate (Cameron, 1996).

Figure 2.2 shows a schematic diagram which represents the conventional hemodialysis system.

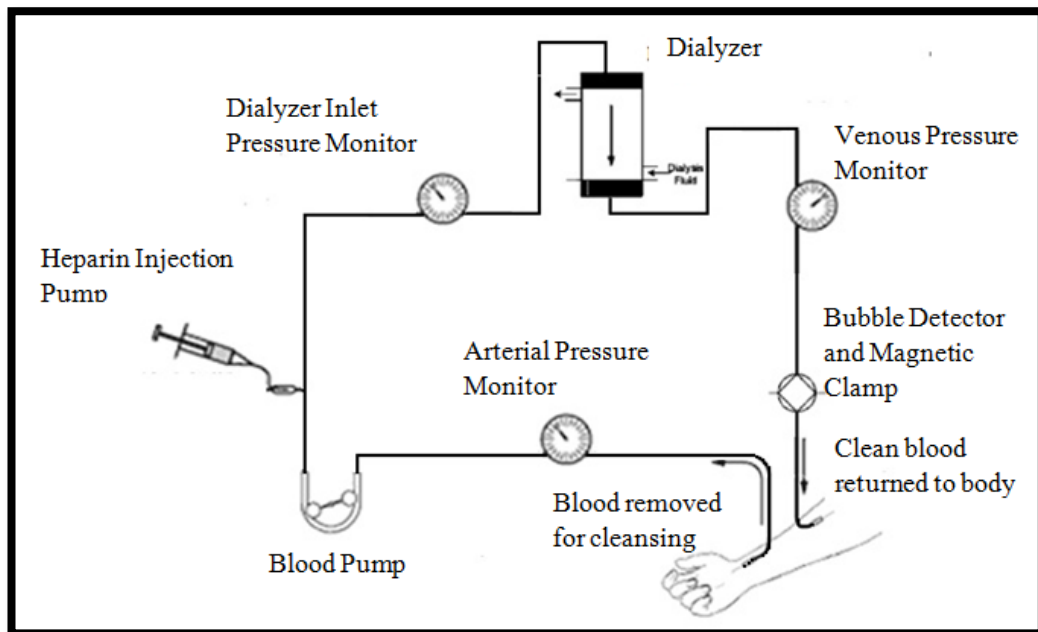


Figure 2.2: Conventional hemodialysis system (Jørrres et al., 2010)

2.2.1 (a) Hemodialysis Membrane

Hemodialysis membranes are placed in the dialyzer to remove toxic wastes from blood. Conventional hemodialysis system used cellulose membranes for filtration but the membranes were only excellent in removal of small molecular weight uremic toxins (Jørrres et al., 2010). These membranes have to meet certain requirements in order to achieve maximum efficiency of dialysis. These requirements include excellent biocompatibility, low cost, fiber spinning ability and appropriate morphology (Barzin et al., 2004). In the recent technology, such membranes are

normally made from synthetic polymers such as polysulfone, polyethersulfone, polycarbonate, polyamide and polyacrylonitrile.

Hemodialysis membranes are designed with different pore size. Membranes with small pore size are termed as low flux while those with big pore size are termed as high flux. The β 2-microglobulin and other middle molecules cannot be removed clearly by low flux membranes. The use of high flux membranes is able to remove middle molecules efficiently, but it also filtered out the desirable proteins such as albumin (66,000 Da) into the dialysate (Barzin et al., 2004). This high flux dialyzer requires new dialysis machine and high quality dialysis solution to monitor the rate of fluid removal and prevent the back flow of dialysis fluid impurities into patient's blood through the membranes.

2.2.1 (b) Dialysate

During a dialysis treatment, patients are exposed to large quantities of water in the form of dialysate. Patients could potentially be poisoned by chemical and microbiological impurities of the dialysate used if it is not clean enough. The water used for dialysate should contain very low level of aluminium, fluoride and trace metals.

The dialysate has to undergo a series of treatments before used for the dialysis. The water is treated through the pretreatment filtration, softeners, carbon beds, reverse osmosis systems, ultraviolet irradiators, endotoxin filters and detects for the presence of chlorine or chloramines (Ronco and Cruz, 2008). All these series of treatments complicate the dialysis system and increase the treatment costs.

2.2.2 Drawbacks of Hemodialysis

Current hemodialysis system could not remove all uremic toxins efficiently (Vanholder et al., 2003). It only prolongs a patient's life instead of providing a solution for renal failure problems. Patients have to go to a nearby hemodialysis center to perform hemodialysis for two to three times per week for a duration of three to four hours (Roberts and Lee, 2009). This seriously affects their mobility, quality of life and thus employability. Moreover, the cost of hemodialysis treatment is expensive (Mallick and Gokal, 1999).

The dialysis membranes used in current hemodialysis systems are not efficient enough to remove medium molecular weight solutes such as *p*-cresol (Wernert et al., 2006). The remaining of these middle molecular weight molecules might cause progressive intoxicification to patients which may lead to death. The interaction of blood with dialyzer components and dialysate may cause the activation of complement components (Craddock et al., 1977). The complement system in human body is made up of numerous distinct plasma proteins that react with each other to opsonise pathogens and eliminate infection (Janeway et al., 2001). Recurrent chest pain, dyspnea and hypotension are the symptoms of complement activation that could be experienced by certain patients during hemodialysis treatment (Hakim et al., 1984).

Biocompatible issues are of great concern during the hemodialysis treatment. These could be related to the hydrophobic surface of the polymer sorbents. Such problem might be overcome by coating layers of hemocompatible materials. However, the coating deteriorates the efficiency of the removal of middle molecules.

The dialysate used in a dialysis system has to undergo a series of treatments to free from waterborne impurities, chemical toxins such as aluminium and chloramines (Jørrres et al., 2010). All these treatments increase the cost and size of a dialysis system. A better design of a portable artificial kidney system based on an efficient reuse and recycle of dialysate is seriously needed by the patients suffer with the renal failure problems. The reuse and recycle of dialysate via adsorbents in an artificial kidney system could reduce the cost of dialysate generation (Ronco and Fecondini, 2007) and thus granting more freedom to the patients.

2.2.3 Research and Development in Artificial Kidney

An ideal artificial kidney can be developed if it can continuously operate and remove all types of renal toxins efficiently. It must be portable or wearable, light weight, low cost and safe to use (Kirwan and Andrew Frankel, 2009). Therefore, research and development activities on efficient artificial kidney systems should meet all the criteria as mentioned above.

Many studies have been carried out to develop a better and efficient artificial kidney system to liberate patients from miserable renal failure. Improvements have been made on the current hemodialysis system and some researchers utilized new types of materials in the hemodialysis membranes to optimize the dialysis process.

A wearable artificial kidney system has been developed by Davenport and co-workers (Davenport et al., 2007). The results indicated the potential of the wearable artificial kidney to remove middle molecules efficiently. However, clotting occurred due to inadequate amount of heparin and blood circuit disconnect.

Nanoporous parylene film coated polyethersulfone (PES) membranes were used in a dialyzer of hemodialysis system (Setia Prihandana et al., 2014). These parylene coated PES membranes shows excellent biocompatibility than the bare PES membranes. The results of platelets adhesion and aggregation test show that about 90% of a bare PES membrane was covered with platelets, while the parylene film coated PES membrane had better biocompatibility with platelet coverage of only 20-30%. The permeability of the parylene film coated PES membranes exhibited more consistent performance than the bare PES membranes.

Zeolites were used as adsorbents for the adsorption of uremic toxins (Wernert et al., 2005, BergÉ-Lefranc et al., 2008). The types of zeolites used in the study are Linde Type A, stilbite, silicalite, mordenite and faujasite. They showed the efficient adsorption of *p*-cresol, creatinine and urea by zeolites. This is because zeolites have channel systems wide enough to allow the access of low molecular weight uremic toxins. Moreover, the zeolites show selective adsorption, high adsorption capacities and non-toxic.

2.2.4 Porous Material used for Hemodialysis Application

Current hemodialysis system should be improved by introducing effective adsorbents to complement the existing design (Gura et al., 2009). Nanoporous materials with special properties should be applied in the artificial kidney system to enhance the efficiency in removing uremic toxins from human body.

Nanoporous materials with excellent properties such as excellent biocompatibility, low or zero toxicity and good adsorption kinetics should be

developed and utilized in the artificial kidney system. In general, nanoporous materials have been proven to be adsorbents with great potential for artificial kidney system (Hagstam et al., 1966). Activated carbon is a nanoporous material potentially be used as adsorbent in the artificial kidney system due to its special properties such as large surface area and high porosity (Ronco and Fecondini, 2007, Gura et al., 2009).

2.3 Activated Carbon

The useful and extraordinary properties of activated carbon have been recognized since long times ago. In 1500 BC, Egyptians utilized AC in the form of carbonized wood as an adsorbent for medical purpose and purifying agent in their daily life. Meanwhile in India, ancient Hindus used charcoal as filter to purify the water for drinking and daily use (Bansal et al., 1988).

Activated carbon (AC) is a porous carbonaceous solid material that has high porosity and large surface area (Angin et al., 2013). The unique porous structure of AC allows it to adsorb substances from liquid and gas phase (Jankowska et al., 1991). AC can be derived from many different sources of raw materials and synthesized in various production methods. The properties and adsorption kinetic of AC are greatly influenced by the types of precursors used and activation processes.

Carbon is a major constituent element in the AC and normally present in the amount of 85 to 95%. Other elements that might present in AC are hydrogen, nitrogen, sulfur and oxygen (Bansal and Goyal, 2010). The commonly used ACs have specific surface area in the range of 800 to 1500 m²/g and pore volume ranged

from 0.20 to 0.60 cm³/g (Bansal and Goyal, 2010). Fixed carbon is a carbon content of AC which is not easily decomposed during carbonization and activation processes (Malik et al., 2007).

2.3.1 Applications of Activated Carbon

ACs were used in many adsorption applications due to their high surface area, microporous structure and high degree of surface reactivity (Bansal and Goyal, 2010). AC can be used in gas phase and liquid phase adsorption applications. AC has been used as adsorbent, catalyst, electronic material and energy storage material (Shen et al., 2008b). AC is widely used in purification of water to remove the color, odor, taste and natural organic compounds (Achaw and Afrane, 2008). In addition, AC is used in sugar refining, preparation of alcohol beverage and pollution control such as the removal of volatile organics from industrial processed gases (Hsieh and Teng, 2000a). AC has excellent properties such as good biocompatibility, non toxic, no immune reaction with body, high adsorption capacity and low coefficient of friction. It is normally used for removal of toxins and bacterial infections in certain ailments (Bansal and Goyal, 2010).

2.3.2 Classification of Activated Carbon

Activated carbon could be classified based on their physical characteristics and forms. The physical forms of AC influenced the adsorption rate and kinetic of adsorbates. Granular activated carbon (GAC) and powdered activated carbon (PAC) are traditional ACs and commonly been used in various adsorption applications. Activated carbon fiber (ACF) is a relatively new type of AC developed for adsorption and purifying applications (Ko et al., 2002).

2.3.2 (a) Powdered Activated Carbon

Powdered activated carbon (PAC) is a pulverized carbon with particle size less than 0.18 mm. This results in the large external surface area with a small diffusion distance (Nik et al., 2006). During the synthesis process, the raw materials is crushed into a coarser size than final desired PAC size before undergo activation process. This is due to difficulty in controlling the size of powdered material at high temperature. The size of PAC is reduced to powder form only after the activation process (Bandosz, 2006).

PAC is normally made from wood, lignite and coal. Its apparent density is ranged from 0.36 to 0.74 g/cm³ (Najm et al., 1992). PAC is commonly produced via a two-stage carbonization followed by activation. The carbonization process enriches the carbon content and creates an initial porosity, while the activation process helps to enhance the pore structure. PAC is commonly used in the waste water treatment, removal of colour in pharmaceuticals and purification of household water.

2.3.2 (b) Granular Activated Carbon

Granular activated carbon (GAC) has irregular shapes of particle and sizes range from 0.2 to 5.0 mm (Nik et al., 2006). GAC is usually used in fixed bed adsorbers in continuous processes for the adsorption of gases and vapours. The use of GAC in gas phase adsorption included gas purification, air filtering, deodorants in waste water treatment plants and solvent recovery (Marsh and Reinoso, 2006).

GAC is also more preferable than PAC in liquid phase adsorption applications such as gold extraction and drinking water filtration. This because the

large particle size of GAC prevent the excessive pressure drop along the bed and hinder the carbon particles being carried away (Bandosz, 2006). Moreover, GAC in fixed bed adsorber can be reactivated and reused for more than one time (Bandosz, 2006).

2.3.2 (c) Activated Carbon Fiber

Activated carbon fiber (ACF) is a light porous carbon in fiber shape with diameter ranged from 10 to 40 μm . ACF is a relatively new type of porous carbon materials and has several advantages compared to conventional PAC and GAC. These advantages included large surface area, high adsorption capacity of liquid and gas phase of adsorbates (Ko et al., 2002).

ACF contain large amount of open or accessible micropores and mesopores which is connected directly to external surface. This enables adsorbate molecules to diffuse easily into the adsorption site without having resistance from mesopores and macropores network or shorter diffusion length (Bandosz, 2006). In GAC on the other hand, adsorbate molecules have to diffuse through macropores and mesopores before entering the micropores for adsorption to occur. This slow process results in lower adsorption rate of GAC compared to ACF. Figures 2.3 (a) and (b) show the locations of micropores in GAC and ACF respectively.

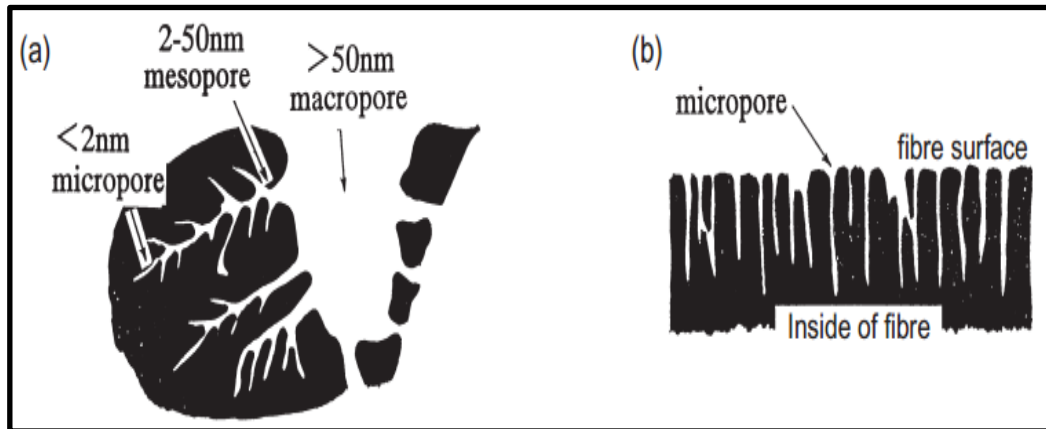


Figure 2.3: Location of micropores in (a) GAC and (b) ACF (Manocha, 2003)

2.3.3 Precursors

Bituminous coal, charcoal, phenolic resin, acrylic fiber and polyacrylonitrile (PAN) are common conventional starting materials used in the production of activated carbon for a very long time. The selection of precursors influenced the physical properties and adsorption kinetic of AC. Hence, the selection of precursors should meet several crucial criteria to produce AC with excellent properties and cost effective. Such criteria are availability, cost, low inorganic matter, low degradation upon storage and ease of activation (Marsh and Reinoso, 2006).

2.3.3 (a) Conventional Starting Materials

Coal is a common precursor used for the production of AC due to its availability (Carrasco-Marín et al., 1996). It is normally treated with carbonization and activation processes to develop highly porous structure. Among all type of coal-based materials, bituminous coal is a preferred material for AC production due to its greater density, hardness, abrasion resistance and durability (Teng et al., 1997). Coal is normally obtained through the coal mining processes. However, the mining

processes result in environmental issues such as land degradation, changes in topography, soil and water pollution (Yenilmez et al., 2011, Bell et al., 2001).

Polyacrylonitrile (PAN) is another common precursor used in the production of ACF (Esrafilzadeh et al., 2009). PAN wastes could be used for the production of AC with a relatively high content of nitrogen and it is useful for the adsorption of sulfur species (Marsh and Rodriguez-Reinoso, 2006). Numerous studies showed that PAN used as precursors to synthesize ACF with specific surface area varying from 500 to 900 m²/g (Yusof et al., 2012, Martín-Gullón et al., 2001). Phenol formaldehyde resin carbon has similar structural features to coal, but contains less mineral impurities (Li et al., 2010b). It can be a precursor to prepare AC with high quality. The low ash content of synthesized phenolic resin enable the impurities of AC can be controlled to a very low level during the synthesis process.

2.3.3 (b) Biomass

Activated carbon is a useful adsorbent used in many adsorption and filtration processes. However, the widely use of this AC is restricted due to the expensive conventional starting materials. The synthesis of AC is not straight forward and greater cost is needed to produce AC with excellent properties and adsorption performance (Babel and Kurniawan, 2003). Biomass from industry and agricultures could be used as starting materials for low cost adsorbents since they are available in large quantities, inexpensive and require little processing (Crini, 2006, Streat et al., 1995).

Many studies have been made to search for alternative low cost biomass from industry and agricultures as starting materials to produce low cost AC with excellent properties. Empty fruit bunch fiber (Foo and Hameed, 2011), palm kernel shell (Jumasiah et al., 2005), sugar cane bagasse (Valix et al., 2008), coconut shell (Yang et al., 2010a), rice straw (Yun et al., 2001), jute fiber (Senthilkumaar et al., 2006), corncob (Tseng et al., 2006), bamboo (Hameed et al., 2007) and sawdust (Malik, 2003) are several biomass used to prepare low cost and useful AC. All these biomass are cheaper and easily available, with consistent quality and desirable purity (Abdullah et al., 2011) compared to the conventional starting materials such as coal, which caused environmental issues.

2.3.4 Oil Palm Biomass

Malaysia is the world leading palm oil producer and exporter. Malaysia produces about 47 % of the total world's supply of palm oil (Sumathi et al., 2008, Umar et al., 2014). Such huge amount of palm oil production resulted in large amount of solid and liquid biomass generated from palm oil industry annually.

Figure 2.4 shows the process flow chart for the extraction of crude palm oil and generation of oil palm biomass. In palm oil mills, the harvested fresh fruit bunch (FFB) from oil palm trees was first heated by boiling water or steam at atmospheric pressure in a sterilizer to inactivate the lipolytic enzymes and loosens the fruits that are attached to bunches (Maycock, 1985). The sterilized bunches was then fed into a rotary drum thresher to separate the fruits from bunches. The empty fruit bunches (EFB) are collected and placed on ground. After that, the sterilized fruits are fed into a digester to loosen pericarp from nuts and prepared for pressing.

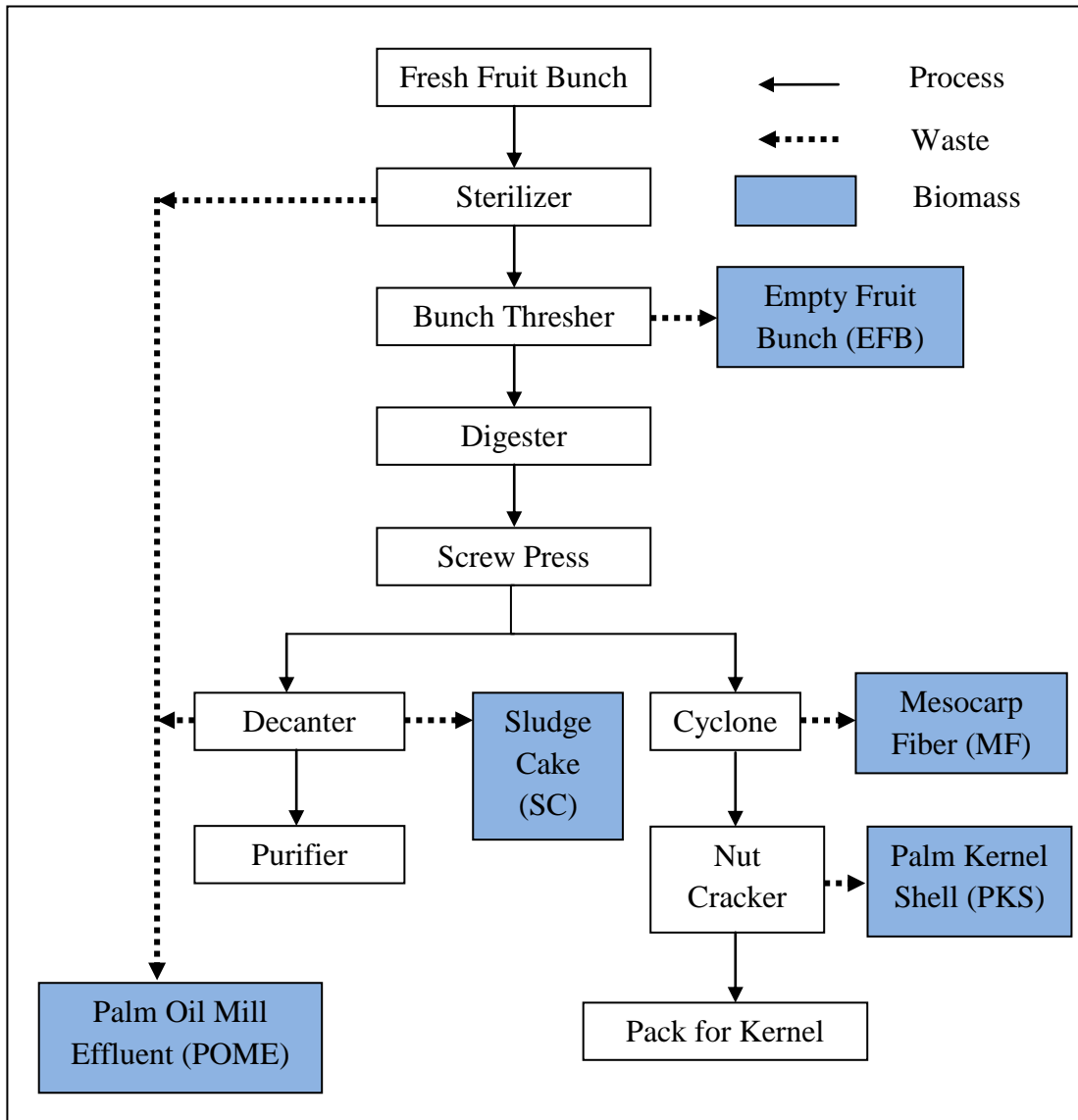


Figure 2.4: Oil extraction and biomass generation process in palm oil mil

The sterilized fruits are stirred and heated to 100 °C in a digester (Maycock, 1985). Homogeneous oil mash from the digester is processed via a screw press, vibrating screen, cyclone and decanters to remove fine solids and water. At the decanter, palm oil mill effluent (POME) and sludge cake (SC) biomass are separated from crude palm oil (CPO), the main product. The crude palm oil is purified via the centrifugal and vacuum driers before keep in a storage tank. Mesocarp fiber (MF)