สำนักงานคณะกรรมการการอุดมศึกษา

สกว
TRF

รายงานวิจัยฉบับสมบูรณ์

โครงการ Study on Heavy Metals Adsorption and Desorption Performances over Activated Carbon Synthesized from Chemical and Physical Activations of Waste Jatropha Oil Cake
(การศึกษาศักยภาพในการดูดซับและคายโลหะหนักของถ่านกัมมันต์ที่ผลิตขึ้นจากกระบวนการกระตุ้นทางเคมีและทางกายภาพของกากสบู่ดำที่เหลือใช้)

โดย ดร. วรพจน์ กนกกันฑพงษ์ และคณะ

มีนาคม 2554

สัญญาเลขที่ MRG5280052

รายงานวิจัยฉบับสมบูรณ์

โครงการ Study on Heavy Metals Adsorption and Desorption Performances over Activated Carbon Synthesized from Chemical and Physical Activations of Waste Jatropha Oil Cake
(การศึกษาศักยภาพในการดูดซับและคายโลหะหนักของถ่านกัมมันต์ที่ผลิตขึ้นจากกระบวนการกระตุ้นทางเคมีและทางกายภาพของกากสบู่ดำที่เหลือใช้)

คณะผู้วิจัย	**สังกัด**
1. ดร.วรพจน์ กนกกันฑพงษ์	มหาวิทยาลัยหัวเฉียวเฉลิมพระเกียรติ
2. รองศาสตราจารย์ ดร.ประเสริฐ ภวสันต์	จุฬาลงกรณ์มหาวิทยาลัย

สนับสนุนโดยสำนักงานกองทุนสนับสนุนการวิจัย

(ความเห็นในรายงานนี้เป็นของผู้วิจัย สกว.ไม่จำเป็นต้องเห็นด้วยเสมอไป)

รหัสโครงการ : MRG5280052

ชื่อโครงการ : การศึกษาศักยภาพในการดูดซับและคายโลหะหนักของถ่านกัมมันต์ที่ผลิตขึ้นจากกระบวนการกระตุ้นทางเคมีและทางกายภาพของกากสบู่ดำที่เหลือใช้

ชื่อนักวิจัย : ดร.วรพจน์ กนกกันฑพงษ์ รองศาสตราจารย์ ดร.ประเสริฐ ภวสันต์ ธัญลักษณ์ เกียรติธนาสกุล และวิชานนท์ วาสนาทิพย์

E-mail Address : xofhcu@gmail.com

ระยะเวลาโครงการ : 2ปี

การเตรียมถ่านกัมมันต์จากกากสบู่ดำเลือกใช้ ถูกนำมากระตุ้นทางเคมีโดยกรดฟอสฟอริก โพแทสเซียมไฮดรอกไซด์ และซิงค์คลอไรด์ที่ต่างสภาวะ ที่อุณหภูมิ 500, 600 และ 700 องศาเซลเซียส เวลาที่ใช้ในการกระตุ้น 60, 120 และ 180 นาที และอัตราส่วนในการเคลือบฝังระหว่างวัตถุดิบกับสารเคมี 1:0.5 ถึง 1:2 รวมทั้งการกระตุ้นทางทางกายภาพโดยไอน้ำ และก๊าซคาร์บอนไดออกไซด์ที่อุณหภูมิ ตั้งแต่ 450 ถึง 1,000 องศาเซลเซียส และเวลาที่ใช้ในการกระตุ้น 45 นาทีถึง 2 ชั่วโมง หลังจากนั้นศึกษาศักยภาพในการดูดซับตะกั่วและทองแดงของถ่านกัมมันต์ที่ได้ค่าพื้นที่ผิวสูงสุดของการกระตุ้นแต่ละวิธีโดยค่าไอโซเทอม และการคายของตะกั่วด้วยกรดไฮโดรคลอริค กรดไนตริก กรดอะซิติก อีดีทีเอ โซเดียมคลอไรด์ และโซเดียมไฮดรอกไซด์ และสารเคมีที่ความเข้มข้น อุณหภูมิ และเวลาต่างกัน

ผลการศึกษาพบว่าสภาวะที่ดีที่สุดในการผลิตถ่านกัมมันต์ โดยการกระตุ้นด้วยวิธีทางเคมีเกิดจากโพแทสเซียมไฮดรอกไซด์ที่อุณหภูมิ 700 องศาเซลเซียส 180 นาที และอัตราส่วนการเคลือบฝัง 1:0.75 ได้ค่าพื้นที่ผิว 666 ตารางเมตรต่อกรัมถ่านกัมมันต์ แต่พื้นที่ผิวสุทธิสูงสุดเกิดจากซิงค์คลอไรด์ที่อุณหภูมิ 700 องศาเซลเซียส 120 นาที และอัตราส่วนการเคลือบฝัง 1:0.75 ได้ค่าพื้นที่ผิว 287 ตารางเมตรต่อกรัมสบู่ดำ โครงสร้างของถ่านกัมมันต์ส่วนใหญ่จะเป็นแบบอสัณฐาน ถ่านกัมมันต์ที่กระตุ้นด้วยซิงค์คลอไรด์อาจจะมีผลึกของ ซิงค์ออกไซด์ และ ซิงค์ทูไฮดรอกไซด์คลอไรด์บนผิวของถ่าน และเกิดหมู่ฟังก์ชันหลากหลายบนพื้นที่ผิว เช่น หมู่อะโรมาติกส์, หมู่ฟังก์ชันที่มีวงเบนซีน และหมู่ไฮดรอกซิล เมื่อคิดค่าพื้นที่ผิวสุทธิพบว่าสภาวะที่ดีที่สุดเกิดจากการใช้ซิงค์คลอไรด์ได้ค่า 289 ตารางเมตรต่อกรัมวัตถุดิบ ในส่วนการกระตุ้นทางกายภาพ พบว่าการกระตุ้นด้วยไอน้ำที่อุณหภูมิ 950 องศาเซลเซียส 60 นาที ได้พื้นที่ผิว 533 ตารางเมตรต่อกรัมถ่านกัมมันต์มากกว่าก๊าซคาร์บอนไดออกไซด์ และได้ค่าพื้นที่ผิวสุทธิ 288 ตารางเมตรต่อกรัมวัตถุดิบ ทั้งไอโซเทอมดูดซับแบบฟรุนดริชและแลงเมียร์สามารถอธิบายการดูดซับได้ที่สุดที่ค่าความเป็นกรด-ด่างเท่ากับ 3 และค่าการคายตะกั่วที่ดีที่สุดจากสารละลายอีดีทีเอ มีค่าการคายสูงสุดร้อยละ 86.22 ที่เวลาการสกัด 60 นาที ความเข้มข้น 0.1 โมลต่อลิตร อุณหภูมิ 35 องศาเซลเซียส

คำหลัก: ถ่านกัมมันต์ การกระตุ้นทางกายภาพ การกระตุ้นทางเคมี การดูดซับ การคายโลหะ

Project Code : MRG5280052

Project Title : Study on Heavy Metals Adsorption and Desorption Performances over Activated Carbon Synthesized from Chemical and Physical Activations of Waste Jatropha Oil Cake.

Investigator : Dr. Vorapot Kanokkantapong, Assoc. Prof. Dr. Prasert Pavasant, Than yalak Kiatthanasakun, and Wichanon Watsanathip

E-mail Address : xofhcu@gmail.com

Project Period : 2 years

The preparation conditions by chemical agents i.e. phosphoric acid, potassium hydroxide, and zinc chloride of activated carbon from jatropha oil waste were determined at various temperatures (500, 600, and 700°C), activation times (60, 120, and 180 min.), and ratios of raw material:chemical agent (1:0.5 – 1:2). The activations by physical agents i.e. steam and carbon dioxide at various temperatures (450 - 1,000°C) and activating time (45 min. – 2 hr.) were also determined. Adsorption isotherm of the maximum surface area of each activation method was revealed. Finally, desorption efficiency via hydrochloric acid, nitric acid, acetic acid, EDTA, sodium chloride and sodium hydroxide solutions at various concentration, temperature and time was performed.

The results found that the best chemical activation condition for the production in term of high surface area of activated carbon from jatropha seed cake occurred with potassium hydroxide at the activation temperature of 700°C, activation time of 180 minutes, and impregnation ratio of 1:0.75. At this optimal condition, the BET surface area was 666 m^2/g activated carbon. However, highest net BET surface area 287 m^2/g raw material occurred from zinc chloride agent at temperature of 700°C, activation time of 120 minutes, and impregnation ratio of 1:0.75. The structure of activated carbon were mainly amorphous, where the activated carbon with zinc chloride might contain the crystals of ZnO and $Zn_5(OH)_8Cl_2 \cdot H_2O$ on the carbon surface. The surface of activated carbon might contain several functional groups including aromatic, benzene derivatives, and hydroxyl groups. Net surface area provided by zinc chloride shown the best at 289 m^2/g raw material. For physical activation, steam activation found the maximum surface area and net surface area at 533 m^2/g activated carbon and 288 m^2/g raw material, respectively, at the activation temperature of 950°C and activation time of 60 minutes. Both Freundlich and Langmuir isotherms were best fitted with this adsorption at pH 3. The maximum desorption efficiency of 86.22% was derived from EDTA solution at concentration of 0.1 mol, time of 60 minutes and temperature of 35 °C

Keywords : Activated carbon, physical activation, chemical activation, adsorption, desorption

Executive Summery

Introduction

Energy crisis is currently one of the most significant global problems, and the seek for alternative energy sources has been set out as an international target for which considerable research efforts have been invested. Agricultural sources have been anticipated as potential options. Jatropha is one of the hopeful plants for serving the biodiesel production in Thailand. However, approx. one liter of biodiesel from Jatropha could generate huge quantity of Jatropha seed waste which is a problem. The application of this waste to be an activated carbon to treat contaminated water should be an interesting option.

In principle, the methods for preparing an activated carbon can be divided into two categories, i.e. chemical and physical activations. For the chemical activation, the raw material is impregnated with activation agents such as phosphoric acid, potassium hydroxide, zinc chloride, etc. and heated at elevated temperature to simultaneously carbonize and activate the carbon. Although this requires lower temperature when compared with the physical means, it suffers from its inherited disadvantages, e.g. the generation of contaminated wastewater (Daifullah, 2004) and impurities derived from the activating agent, which may affect the chemical properties of the activated carbon (Gomez-serrano et al., 2005). For the physical activation, the raw material is carbonized in an inert atmosphere at a temperature below 700°C and then activated by steam or carbon dioxide at temperatures range from 800 to 1000°C. This high temperature requirement is compensated by the elimination of chemical contaminants and shorter production time (Laine and Yunes, 1992), and these make it more environmental attractive.

Experiment

Jatropha seed waste, raw material in this work, was prepared by two methods i.e. chemical and physical activations. Chemical activation using phosphoric acid, potassium hydroxide, and zinc chloride was conducted for various conditions e.g., impregnation ratio, activation temperature, and activation time to determine optimum preparation condition. Physical activation was done by steam and carbon dioxide in various temperature and time. Ash content, apparent (bulk) density, moisture content, volatile matter, functional groups, iodine number, surface area, ultimate analysis, proximate analysis and %yield were analyzed following the standards to reveal the characteristic of activated carbon.

To apply the derived activated carbon, adsorption with heavy metals such as lead and copper was investigated. Famous isotherms e.g., Langmuir and Freundlich equations were used to fit with the result. Finally, desorption efficiency of lead by hydrochloric acid, nitric acid, acetic acid, EDTA, sodium chloride and sodiumhy droxide was experimented to examine the way to reuse activated carbon at various condition.

Result and discussion

1. Preparation of activated carbon from Jatropha seed waste via chemical and physical activations

From the properties of Jatropha seed cake, it was found that the raw material (RM) suitable for the production of activated carbon (AC) which should have a fixed carbon content of more than 30%. Jatropha seed cake was mixed with chemical solutions (phosphoric acid, potassium hydroxide, and zinc chloride) at range of impregnation ratio 1:0.5-1:2, activation temperature 400-700^{o}C and activation time 60-180 minutes. The result found that optimal activation condition by phosphoric acid was occurred at the ratio of 1:0.5, 120 minutes and 700^{o}C with iodine number of 516 mg/g AC. Potassium hydroxide could present maximum iodine number of 696 mg/g AC, among the others, at ratio of 1:0.75, 180 minutes and 700^{o}C. However, at that long period of time, %yield decreased rapidly. Although, activation with zinc chloride might not show utmost iodine number, it could enhance highest net iodine number at 286 mg/g RM.

Physical activation was produced from Jatropha seed cake through the process of carbonization followed by steam and carbon dioxide activations. It was found firstly that the optimum carbonization occurred at temperature of 500°C and time of 60 minutes as shown via the suitable range of fixed carbon. The derived char was then activation with steam and carbon dioxide. Steam activation presented the optimal condition at 950°C 60 minutes, where the net iodine number of obtained activated carbon was 174 mg/g RW and surface area 533 m^2/g. The result from carbon dioxide activation indicated that iodine number increased with an increase in activation temperature. The highest value of the net iodine number from carbon dioxide activation was 166.6 mg/g RM obtained from the activation at 950°C for 120 minutes.

The consideration of the yield and compare the properties of the activated carbon based on the initial weight of the raw material was used in this work as called “Net surface area”. The highest net surface area of 289 mg/g RM was obtained from the activation with zinc chloride with an impregnation ratio of 1:0.5 (raw material:chemical agent) at the activation temperature of 700 ^{o}C for 120 minutes followed by steam activation with temperature of 950 ^{o}C for 60 minutes. It can be seen that, although the best activated carbon with the highest iodine number was obtained from the activation with potassium hydroxide, this method might not be the best as a large quantity of carbon was destroyed during the conversion process (only 16% survived with potassium hydroxide when compared with 64% in the case of zinc chloride).

2. Adsorption and Desorption study

Activated carbon from steam activation was selected to determine the adsorption study because it contained lowest environmental burden for life cycle assessment thinking compared to the others. The isotherm data fitted the Freundlich model relatively well with an R^2 of 0.996 at pH 3. The values of the constants K_F of Pb(II) and Cu(II) ions were calculated to be 6.457 and 9.616 mg/g whereas 1/n of Pb(II) and Cu(II) ions were and 0.931 and 2.867, respectively. Langmuir constants, q_m and b, of Pb(II) and Cu(II) ions at pH 3 were 13.8889 and 2.985 mg/g, and 0.0043 and 0.0138 L/mg, respectively.

For desorption study of lead from activation carbon, 6 solutions, hydrochloric acid, nitric acid, acetic acid, EDTA, sodium chloride, and sodium hydroxide were used as extraction agents. The results showed that maximum desorption efficiency were derived from EDTA solution at 86.22%. The optimum condition was EDTA concentration of 0.1 mol, time of 60 minutes and temperature of 35 ^{o}C.

Conclusion

This work reveals the possibility in the use of Jatropha waste (after oil extraction) in the production of activated carbon. Several options have been tested for the optimality and application. Both chemical and physical conversions were possible and the final product exhibited a reasonably well sorption property. When compared to chemical activation methods, due to the absence of chemical requirements, the physical activation method requires no washing step which not only prevents the generation of wastewater, but also reduces the chemical demands which makes it more attractive in environmental point of view. However, physical treatment requires that the carbon be extensively thermal treated which needs more energy inputs than the chemical activation. The results from this work could be used further to mitigate the disposal problem of excess Jatropha seed waste by converting this waste material to a valuable product such as activated carbon. Although the achievement in this work was still limited to small scale conversion, such information could be useful for the future scale up of the future well defined technology.

CHAPTER I

INTRODUCTION

1.1 Motivations

One of the main recently global problems is energy crisis, which challenge the scientific and engineer knowledge to develop the alternative energy sources. Agricultural sources have been proposed as potential options as they are generally renewable and exert a lower impact on the release of greenhouse gases such as carbon dioxide to the atmosphere when compared to fossil fuels. Among the various energy options, biodiesel has been proposed as one of the most feasible. Biodiesel can be produced from several kinds of raw materials such as coconut oil, palm oil, etc. Jatropha is one of the promising plants for serving the biodiesel production because of its durability to the drought of countries within equator region, including Thailand. Extraction oil from Jatropha seed can be used directly in diesel engines where four kilograms of Jatropha seed could generate approx. one liter of oil, during the biodiesel production, a large quantity of waste from Jatropha seed cake is produced and being a problem to eradicate. Generally, agriculture waste is converted to energy, or fermented in order to produce biogas and fertilizer. Jatropha wastes are no exception, and these can be effectively further processed to fertilizer due to their high nitrogen content. However, this option does not provide value-adding to the wastes as organic fertilizer could, at best, cost at only 10 baht per kilogram.

Activated carbon is one of the favorable treatment approaches using adsorption mechanism. It involves not only in several industrial sectors e.g., air purifier industry, drinking water and tap water industry, metal-plated industry, and food industry, but in domestic sector purposes also, e.g. absorbing odors from refrigerator, wardrobe and closet’s smells, etc. Rate of activated carbon imported from the United State, Japan, Malaysia, and Indonesia to Thailand in the years 2005 to 2008 has continuously increased from 205, 267, 729 and, 1,230 million baht, respectively. Thus, it can be seen that activated carbon market is wide and has potential for consistent demand in the country. It should be conclusively stated that activated carbon can mainly be generated from agriculture waste. The cost of activated carbon is normally over 3 times comparing to fertilizer. Hence, this study aims to investigate the conversion of Jatropha seed cake to activated carbon using chemical treatment. This is a preliminary examination to evaluate the possibility in such conversion.

1.2 **Objectives**

1. To find optimal conditions in the production of activated carbon from Jatropha seed cake by chemical activations.
2. To find optimal conditions in the production of activated carbon from Jatropha seed cake by physical activations.
3. To remove lead and copper from synthetic wastewater by the derived activated carbon.
4. To determine optimum desorption condition from various chemicals.

CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Jatropha

Jatropha curcas L. (Figure 2.1) is a native plant in South America. It has a long history of propagation in Africa and Asia by Portuguese. (Bringi, 1987) Jatropha curcas L. or ‘‘physic nuts,’’ which will be called ‘‘Jatropha’’ below, is a small tree or large shrub that normally reaches a height of 3–5 meters, but can reach a height of 8–10 meters under favorable conditions. (Carels et al., 2009) The productive lifespan of Jatropha is around 50 years. Jatropha produces first time fruit after 6 months and the productivity is stable after 1–3 years old. (Manurung and Satyawati, 2006) Jatropha can be used as traditional medicine and being an essential renewable energy source. The physical properties of Jatropha fruit depend on its moisture content, and this knowledge is essential for the design of harvest and post harvest equipments (e.g., mechanical harvesters, driers, graders, decorticators, and storage bins). (Sahay, 1996) Jatropha oil, produced from seed (Figure 2.2), can be utilized to produce biodiesel fuel by esterification reaction with short chain alcohols, preferably at their super critical conditions without the use of catalysts. (Hawash et al., 2009) This biodiesel from Jatropha can be used in direct or indirect diesel engines, piston ring, and fuel injector choking. As the result, many Jatropha seed cakes (Figure 2.3) are generated as byproduct. Generally, Jatropha produces approx. 1 ton of both of seed cake and shell per 10,000 m^2. A large amount of this seed cake waste will be a huge problem in the near future. The method to manage Jatropha seed cake currently is fermented for fertilizer and biogas production. Some researchers investigated seed cake as a substrate for the industrial production of enzymes such as proteases and lipases. (Carels et al., 2009)

Figure 2.1 Jatropha curcas L.

Figure 2.2 Jatropha seed

Figure 2.3 Jatropha seed cakes

2.2 Activated carbon

Activated carbon, sometimes called activated charcoal, is a form of carbonaceous material that has been processed to highly develop internal surface area and porosity which can be described as solid sponges (Zanzi et al., 2001). Microporosity in the activated carbon is most important for adsorption ability and widely used to indicate the quality of activated carbon. Generally, one gram of activated carbon achieves a surface area of over 500 m^2, as determined typically by nitrogen gas adsorption. Activated carbon can be classified based on its physical characteristics as follows.

2.2.1 Powdered activated carbon (PAC)

Traditionally, activated carbons are made in a powder form with a size range between 0.15 and 0.25 mm. PAC is not commonly used in a dedicated vessel, owing to the high head-loss that would occur. It is beneficial to reduce the concentration of trace organics in drinking water such as pesticides (Humbert et al., 2008). One of the main advantages of PAC is low capital cost, however, its applicability is limited to the low concentration of organic materials due to the short contact time (Kim et al., 2008).

Additionally, handling and disposal of PAC could be difficult (Areerachakul et al., 2007).

2.2.2 Granular activated carbon (GAC)

Granular activated carbon (GAC) is generally associated with small pore diameter and large internal surface area. This forms irregular shaped particles with size ranging from 0.2-5.0 mm and they are considered more versatile and command a larger percentage of the carbon market (Activated Carbon Markets, 1994). About 80% of the GAC produced worldwide is used in liquid-phase purifications, and the rest is used in gas-phase applications (Usmani et al., 1994).

2.2.3 Pellets or extruded activated carbon

The shape of extruded and cylindrical activated carbon appears with diameters from 0.8 to 45 mm. It is mainly required for gas phase applications because of their low pressure drop, high mechanical strength and low dust content.

2.3 Raw materials for the production of activated carbon

Activated carbons can be prepared from several raw materials, which should be abundant and cheap, with high carbon content and low volatile content like wood, coal, lignite, and coconut shells. The properties of manufactured activated carbon depend on the type and properties of the raw material used. Some of the properties of raw materials suitable for the production of activated carbon are summarized below:

- low organic volatile content
- high carbon content
- high lignin content
- inexpensive and efficient use of resources
- high and stable properties

Several raw materials were attractive to produce activated carbon as illustrates in Table 2.1. It can be seen that these materials have high content of fixed carbon and low content of ash, nitrogen and sulfur, which is interesting with respect to their applications in gasification and pyrolysis processes (Gonzalez et al., 2009).

In the recent years, many agricultural by-products have been used as sources for activated carbons production such as cherry tree (Ioannidou et al., 2007), Coconut shells (Li et al., 2009), Coffee endocarp (Nabais et al., 2008), olive stones (Gonzalez et al., 2009), oil palm stones (Cagnon et al., 2009), and eucalyptus wood (Ngernyen et al., 2006). They are suited for activated carbon manufacture due to their pyrolytic transformation into porous coke which produces an economically justifiable yield. Suitable adsorbent properties (adsorption capacity, hardness, and granularity) require the use of mechanically stable cokes with a small fraction of macropores (Bouchelta et al., 2008).

Table 2.1 Properties of raw materials for the production of activated carbon

Raw materials	Moisture (%)	Ash (%)	Volatiles (%)	C (%)	H (%)	N (%)	S (%)	References
Almond tree	10.60	1.20	72.20	51.30	6.50	0.80	0.04	Gonzalez et al., 2009
Corn cobs	-	0.9	80.2	48.89	6.38	0.18	0.00	Aworn et al., 2009
Eucalyptus bark	10.50	1.35	76.05	41.36	4.67	-	-	Patnukao et al., 2007
Eucalyptus wood	4.1	1.2	76.4	-	-	-	-	Ngernyen et al., 2006
Olive stone	10.40	1.40	74.40	44.80	6.00	0.10	0.01	Gonzalez et al., 2009
Plum stones	3.8	0.9	-	50.7	6.3	2.1	<0.3	Cagnon et al., 2009

2.4 Production of activated carbon

The preparation of activated carbon can be mainly classified into two processes: chemical activation and physical activation. The nature of the precursor, activation method, and activation conditions determine the characteristics of porosity in activated carbons, including pore size distribution, shapes of pores, and surface chemistry (Sentorun-Shalaby et al., 2006). The detail of chemical and physical activation is presented below:

2.4.1 Chemical activation

Chemical activation is usually limited to woody precursors. This process involves carbonizing the parent materials after impregnation with, e.g., phosphoric acid (Castro et al., 2000), sulphuric acid, potassium carbonate (Hameed et al., 2008), potassium hydroxide

(Tseng et al., 2008), sodium chloride (Khuysangaain, 2001), and zinc chloride (Aravindhan et al., 2009). Chemical activation is usually carried out at temperature ranging from 400-600°C. The advantages of chemical activation are lower energy cost, shorter activation time, and higher product yield and surface area as compared to the method of physical activation (Ngernyen et al., 2006). However, chemical activation poses problems such as lack of adequate control over porosity development. The activation agents are considered hazardous chemicals and the recovery of these chemical from the products or off gas results in multiple operations. Non-recovery of chemicals not only makes the process uneconomical but also contributes to environmental pollution (Patrick, 1995).

2.4.2 Physical activation

Physical activation is the development of porosity by gasification with an oxidizing gas at 700-1100 °C. Commonly used gases are carbon dioxide (Aworn et al., 2009; Bello et al., 2002; Fukuyama et al., 2008; Gonzalez et al., 2009; Ngernyen et al., 2006; Suzuki et al., 2007), steam (Achaw et al., 2008; Arriagada et al., 1994; Aworn et al., 2008; Bouchelta et al., 2008; Gonzalez et al., 2009; Jindaphunphairoth, 2000; Li et al., 2008; Nabais et al., 2008; Tancredi et al., 1996; Sentorun-Shalaby et al., 2006; Zanzi et al., 2001) and air (Ahmad et al., 2007). They can be used singly or in combination. Physical activation can be divided into two steps as follows:

2.4.2.1 Carbonization

Carbonization or pyrolysis is one of the most important steps in the production process of activated carbon. The pyrolysis consists of slow heating of the raw materials at temperature usually below 700^{o}C in the absence of air. The raw materials are carbonized to obtain the char or carbonaceous material, which is activated to yield the highly porous final products (Suzuki et al., 2007). However, the char produced in the pyrolysis step is highly dependent on the initial biomass pyrolyzed. Three steps of the carbonization process are follows:

1. The mass loss is verified by heating the materials up to 200 °C, for moisture content elimination.

2. The mass is greater loss at temperature between 200 and 450 °C at the primary carbonization process. This stage presents a considerably greater weight loss for the raw biomass due to the elimination of volatile matters and tars.

3. The decomposition of a structure with higher stability occurs under the temperature range from 497 to 847 °C. At the temperature above 800 °C, the weight loss is small (less than 10%) with indicates basic structure.

2.4.2.2 Activation

The purposes of activation are to develop the porosity, to create some ordering of the structure and to generate a highly porous solid as the final product. There are usually three stages in the pore development during the activation process: (i) opening of previously inaccessible pores; (ii) creation of new pores by selective activation; and (iii) widening of the existing pores (Li et al., 2008).

Steam and carbon dioxide are commonly used as activating agents. The activating agent must penetrate into the interior of the particle to remove a carbon atom from that position. Thus, many carbon atoms within the porous carbon are bypassed during penetration without undergoing reaction or gasification. There are at least two reasons for this: the sensitivity of carbon atom ‘reactivity’ to relative position within the carbon network is critical; also of importance are stereo-effect, i.e. the steam, carbon dioxide or oxygen molecule needs appropriate space to orientate itself for the reaction which leads to gasification. Thus, the extent of development of porosity and the characteristics of this porosity are a function of:

- The structure of the initial carbon
- The presence of catalytic inorganic impurities in the carbon
- The activating agent
- Temperature of gasification
- Pressure of the gas
- Duration of gasification
- Particle size of the carbon

Details of the mechanism by which carbon reacts with steam and carbon dioxide are shown below:

1) Activation with steam

Steam is the preferred activation gas because the water molecule has smaller dimension than the carbon dioxide molecule, and consequently the use of steam leads to faster diffusion into the porous network and easier access into the micropores. A faster reaction rate is approximately three times faster than the carbon dioxide reaction at temperature of 800 °C and a pressure of 10 kPa (Patrick, 1995). Gasification with steam produces a more noticeable widening of microporosity to mesoporosity with the increasing effect of activation compared to that obtained by carbon dioxide, which control the competition between the rates of diffusion and gasification reactions (Sentorun-Shalaby et al., 2006). In the steam activation, an oxygen atom has to be transferred and bonded to the carbon atom of the network, and the resultant carbon monoxide has subsequently to be "desorbed" from the network, so creating a wider range of porosities in carbons (Patrick, 1995).

The reactions of carbon with steam to remove carbon atoms from the network within solid carbon are as follows:

$$C + H_2O \quad = \quad CO + H_2 \qquad \Delta H = +117 \text{ kJ mol}^{-1} \tag{2.1}$$

The rate of gasification of carbon by a mixture of steam and hydrogen is given by the formula:

$$V = \frac{k_1 P_{H2O}}{1 + k_2 P_{H2O} + k_3 P_{H2}} \tag{2.2}$$

where:

P_{H2O} = the partial pressure of steam

P_{H2} = the partial pressure of hydrogen

k_1, k_2, k_3 = the experimentally determined rate constants

The following reaction scheme is accepted as highly probable:

$$C + H_2O \leftrightarrow C\square\ (H_2O) \tag{2.3}$$

$$C\square\ (H_2O) \leftrightarrow C\square\ (O) + H_2(g) \tag{2.4}$$

$$C + C\square\ (O) \leftrightarrow C\square\ (CO) \tag{2.5}$$

The steam reaction is product-inhibited; hydrogen is strongly adsorbed on the active centres of the carbon surface and this reduces the reaction rate (Patrick, 1995)

$$C + H_2 \longleftrightarrow C\square\ (H_2) \tag{2.6}$$

It was assumed that the first step of the reaction is the dissociated adsorption of water molecules according to the scheme:

$$2C + H_2O \rightarrow C\ (H) + C\ (OH) \tag{2.7}$$

$$C\ (H) + C\ (H) \rightarrow C\ (H_2) + C\ (O) \tag{2.8}$$

Hydrogen and oxygen are adsorbed at neighboring active sites, which account for about 2 percent of the surface area.

The reaction of steam with carbon is accompanied by the secondary reaction of water-gas formation, which is catalyzed by the carbon surface:

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \Delta H = -42 \text{ kJ mol}^{-1} \qquad (2.9)$$

Activation with steam is carried out at temperatures from 750 to 950°C with the exclusion of oxygen. These temperatures aggressively attack carbon and decrease the yield by surface burn-off. It is catalyzed by the oxides and carbonates of alkali metals, iron, copper and other metals; the activation catalysts usually employed in practice are carbonates of alkali metals, which are added in small amounts to the material to be activated.

2) Activation with carbon dioxide

The activation gas is usually carbon dioxide, since it is clean, easy to handle and it facilitates control of the activation process due to the slow reaction rate at temperatures around 800 °C (Ioannidou et al., 2007).

The reaction of carbon dioxide with carbon is endothermic and a stoichiometric equation has the form:

$$C + CO_2 = 2CO \qquad \Delta H = +159 \text{ kJmol}^{-1} \qquad (2.10)$$

$$C + CO_2 \Leftrightarrow C\square\ (O) + CO \qquad (2.11)$$

$$C\square\ (O) = C\square + CO \qquad (2.12)$$

The rate of gasification of carbon by carbon dioxide an equation analogous to that for the reaction with steam has been derived:

$$V = \frac{k_1 P_{co2}}{1 + k_2 P_{CO} + k_3 P_{CO2}} \qquad (2.13)$$

where:

P_{CO2} = the partial pressures of carbon dioxide

P_{CO} = the partial pressures of carbon monoxide

k_1, k_2, k_3 = the experimentally determined rate constants

Activation with carbon dioxide is inhibited by hydrogen and carbon monoxide. The carbon monoxide acts by increasing the rate of the back reaction [C□ (O) + CO = C□ + CO_2]. Rand and Marsh (2006) showed that the addition of carbon monoxide to the reacting gas resulted in the development of a better microporous structure in addition to decreasing the rate of gasification.

Activation with carbon dioxide involves a less energetic reaction than that with steam and requires a higher temperature 850-1000°C. The activation agent used in technical practice is flue gas which a certain amount of steam is usually added. The catalysts for the reaction with carbon dioxide are carbonates of alkali metals (Patrick, 1995).

The activation by steam is faster than by carbon dioxide due to the mechanisms of gasification reaction that the rate of dissociation and adsorption of intermediate of steam (i.e., H_2O) to gasifiable active site C*, ($C^* + H_2O \leftrightarrow C(O) + H_2$), is faster than that of CO_2, ($C^* + CO_2 \leftrightarrow C(O) + CO$) and CO inhibits further reaction. For further difference between the reaction with steam and carbon dioxide, the larger carbon dioxide molecule compared to steam restricts the ability of carbon dioxide to diffuse through the pores in the carbon and to access the gasificable sites of inner pore, which results in slower gasification by carbon dioxide than by steam (Fukuyama et al., 2008). Although pore development is dependent on temperature and concentration of reactant gas, the carbon precursor also determines the characteristics of the activated carbon produced.

2.5 Estimation of the properties of activated carbon

Activated carbon has certain chemical (bulk density, surface area) and physical (ash, moisture content, volatile matter, pore volume, iodine number) properties depending on the basic material source, precursor and activation. These are delineated below.

2.5.1 Iodine Number

Many carbons preferentially adsorb small molecules. Iodine number is the most fundamental parameter used to characterize activated carbon performance. It is a measure of activity level (higher number indicates higher degree of activation), often reported in mg g^{-1} (typical range 500-1200 mg g^{-1}). It is a measure of the micropore content of the activated carbon by adsorption of iodine from solution. Iodine number can be up to 1,300 mg g^{-1}.

2.5.2 Moisture content

This is the amount of water on the activated carbon under normal condition. High moisture content indicates poor quality and a normal value varies between 1 to 5%.

2.5.3 Ash content

Ash reduces the overall activity of activated carbon and the efficiency of reactivation. This ash consists mostly of calcium salts and metal oxides and comes initially from the basic material. In general, good activated carbon should have low ash content.

2.5.4 Apparent density

Higher density provides greater volume activity and normally indicates better quality activated carbon.

2.5.5 Particle size distribution

The finer the particle size of an activated carbon introduces the better access to the surface area and the faster rate of adsorption kinetics. In vapor phase systems, this needs to be considered against pressure drop which affects energy cost. Careful consideration of particle size distribution can provide significant operating benefits.

2.5.6 Surface area

A range of techniques is available for estimating porosity and surface area. Comparisons are made between results obtained from isotherms and those from other methods. A good activated carbon should have the following characteristics: high porous (microporous structure), large internal surface area, high total surface area (usually, the surface areas of activated carbon are ranging from 500-1400 m^2 g^{-1}). Large pore volume is significant for adsorption and is also used to indicate the quality of activated carbon.

2.6 Adsorption isotherm

To quantify the adsorption process, extents of adsorption (mg g^{-1}) is related to the equilibrium partial pressure p/p^0 at constant temperature to create the isotherm. Adsorption isotherms are studied to obtain information about the followings:

- Estimates of surface areas
- Estimates of pore volumes in the porosities present, e.g. pore-size of potential energy distributions
- Assessments of the surface chemistry of the adsorbent
- The fundamentals of adsorption process, e.g. the nature of the adsorbed phase

Interpretation of isotherms is not straightforward and this causes considerable debate among surface chemists. Adsorption processes in microporosity are the most difficult to describe accurately. The adsorption process occurring within mesopores are more easily understood. Macroporosity behaves in the same way as an open surface to adsorption, and accounts for less than 1% of the adsorption processes compared to microporous adsorption.

Figure 2.4 sets out the six major classes of isotherm shape obtained from adsorption experiments. Knowledge of adsorption mechanisms in different sizes of porosity is necessary to explain the isotherm shapes.

Type I isotherm is typical of microporous solid in that micropore filling occurs significantly at relatively low partial pressures less than 0.1 p/p^0, the adsorption process being complete at approx. 0.5 p/p^0. Examples include the adsorption of nitrogen on microporous carbon at 77 K and of ammonia on charcoal at 273 K.

Type II isotherm describes physical adsorption of gases by non-porous solids. Monolayer coverage is succeeded by multilayer adsorption at higher p/p^0 values. Type II isotherm can also be obtained from carbons with mixed micro- and mesoporosity.

Type III and Type V isotherms are convex towards the relative pressure axis. These isotherms are characteristic of weak gas-solid interactions. Type III isotherm originates from both non-porous and microporous solids and Type V isotherm is from microporous or mesoporous solids. The weakness of the adsorbent-adsorbate interactions causes the uptakes at low relative pressures to be small; however, once a molecule has become adsorbed at a primary site. The adsorbate-adsorbate forces promote further adsorption in a cooperative of water molecules on oxides of carbon surfaces. An example is the adsorption of water vapor on graphitized carbon black.

Type IV isotherm possesses a hysteresis loop, the shape of which varies from one adsorption system to another. Hysteresis loops are associated with mesoporous solids, where capillary condensation occurs.

Type VI isotherm is of surfaces with an extremely homogeneous structure (e.g. pyrolytic graphite) using, for example, argon and methane as adsorbates (but not nitrogen).

The term “surface area” does not describe a carbon unequivocally. Carbons with similar effective surface areas (ESA) can be very different from each other structurally. Furthermore, values obtained using one adsorbate at a certain temperature can differ when other adsorbates at other temperatures are used. When quoting surface areas, it is important to qualify them by including the technique, adsorbate and temperature used.

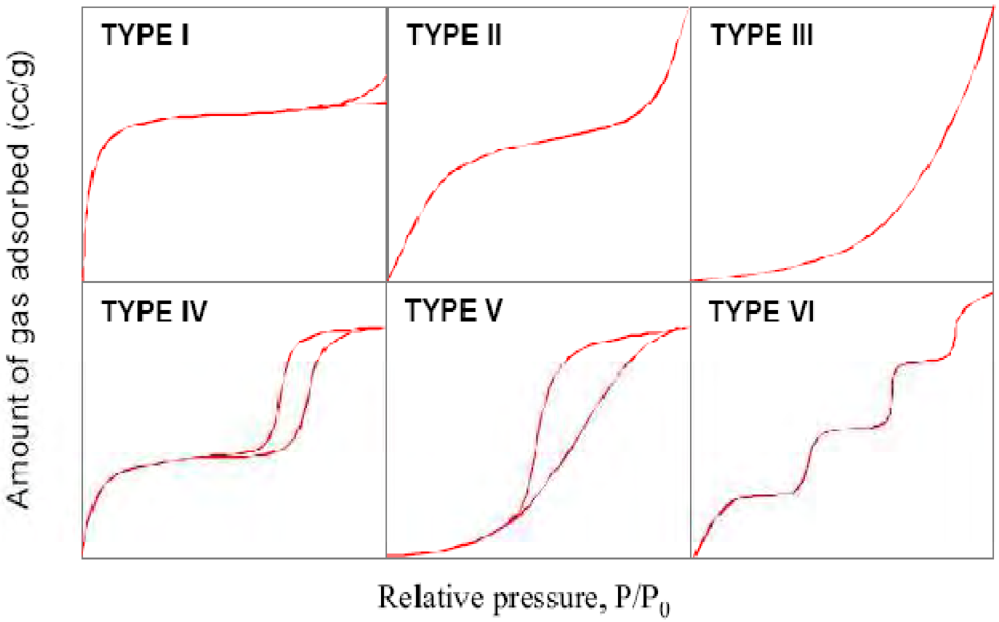

Figure 2.4 Isotherm patterns for the activated carbon (Sing, 1998)

2.6.1 Langmuir Isotherm

Langmuir isotherm is based on the following assumptions:

- Only monolayer adsorption can occur;
- Adsorption is localized, with no adsorbate-adsorbate interactions;
- The heat of adsorption is independent of surface coverage, i.e. the adsorbent has a homogeneous surface.

The expression of this isotherm can be described by Equation (2.14)

$$q_e = \frac{q_m b C_e}{1+bC_e} \tag{2.14}$$

where;

q_e = the amount of adsorbed at equilibrium (mg g^{-1})

q_m = the total number of surface sites per mass of sorbent

C_e = the remaining concentration of solution after equilibrium (mg L^{-1})

b = Langmuir constant or capacity factor (mg g-1).

The linear form of equation (2.14) can be written as:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{bq_m} \tag{2.15}$$

2.6.2 Freundlich isotherm

The Freundlich model is a mathematical approach for fitting the experimental data of adjustable parameter to account for the variation in adsorption heat on an energetic heterogeneity of surface with the concentration of adsorbate. The relationship can be described by Equation (2.16):

$$q_e = K_F C_e^{(1/n)} \tag{2.16}$$

where;

q_e = the amount of adsorbed at equilibrium (mg g^{-1})

C_e = the remaining concentration of solution after equilibrium (mg L^{-1})

K_F = Freundlich adsorption constant

n = Freundlich exponent

The Freundlich isotherm has been derived by assuming an exponentially decaying sorption site energy distribution. The linear form of Equation (2.16) can be written as:

$$\log q_e = \log K_F + (\frac{1}{n})\log C_e \tag{2.17}$$

The Freundlich isotherm is based on the following assumption: (i) there are many layers (multilayer) of adsorbate on the adsorbent surface; and (ii) adsorbent surfaces are heterogeneous surface. If this isotherm does not match the experimental data, the assumption behind Freundlich isotherm might not hold true. Nevertheless, there is no total capacity term in the Freundlish isotherm equation, so there is no upper limit on adsorption. This condition is less likely to be true for any specific case, and hence, Freundlich isotherm is often used for a specific range of concentration of adsorbate, which is most of the time at the low concentration range.

2.7 Applications

Activated carbons concern on many industries as diverse as food processing, pharmaceuticals, chemical, petroleum, mining, nuclear, automobile and vacuum manufacturing. Because of their adsorptive properties, they have a high available area which is presented in their extensive internal pore structure. Such high porosity is a function of both the precursor as well as the scheme of activation.

The chemical nature of activated carbons significantly influences its adsorptive, electrochemical, catalytic, and other properties. Generally speaking, activated carbons with acidic surface chemical properties are favorable for basic gas adsorption such as ammonia while activated carbons with basic surface chemical properties are suitable for acidic gas adsorption such as sulfur dioxide. The uses of the activated carbon produced by agricultural residues are summarized in Table 2.3 (Ioannidou et al., 2006).

Table 2.3 Uses of activated carbons produced by agricultural residues (Ioannidou et al., 2006)

Raw material	**Uses**
Peanut hulls, rice straw	Treat industrial gas, indoor air (air pollution control) Adsorption of mathylene blue (liquid purification) Trace metals
Rice husk, orange peal Palm kernel fibre	Adsorption of acid dyes Removal of ions Removal of Arsenic
Pitch-based carbons Activated carbons membranes Wheat straw	Clean-up of fruits and vegetables Removal of nitrate and pesticides Adsorption of atrazine
Rice husks Jordanian olive stones	Wastewater treatment Groundwater treatment Purification of drinking water Removal of heavy metals Purification of effluent gas streams Removal of mercury vapors Removal of volatile organic compounds Removal of NO_x and SO_x Removal of phenols and phenolic compounds

2.8 Literature review

Activated carbon is most widely produced from agricultural waste such as coconut shell, eucalyptus bark, hazelnut shell, rubber wood, rice-husk, palm stems, coffee husk, soybean oil cake, and coconut shell as this is generally low cost, using renewable source, and is one way of enhancing waste value. Activated carbons are generally produced using two activation methods. The first method is the physical or gas activation (Savova et al., 2001; Lua et al., 2004; Namasivayam et al., 2007; Ncibi et al., 2009), using steam, nitrogen, and carbon dioxide at high temperature in order to increase adsorptive capacity and surface area. This physical means usually involves two steps: carbonization and activation. Recent research, Savova et al. (2001) used steam activation to convert almond shell to activated carbon. The condition was: carbonization temperature 800°C 60 minutes, activation temperature 800°C 60 minutes. The resulting activated carbon had the surface area of 998 m^2/g. Recent works on the production of activated carbon with physical activation are demonstrated in Table 2.5. The second method is the chemical activation, using chemical agent to activate raw material in order to produce activated carbon with high surface area and high adsorptive capacity. Chemical agents most widely used can be categorized into three types: (i) acid such as phosphoric acid (H_3PO_4) (Srinivasakannan et al., 2004; Daifullah et al.,2004; Temmink and Grolle, 2005; Haimour and Emeish, 2006; Patnukao and Pavasant, 2008; Demirbas, 2008; Gratuito et al., 2008; Jibril et al., 2008; Yagmur et al., 2008; Baccar et al., 2009; Rosas et al., 2009), hydrochloric acid (HCl), and sulfuric acid (H_2SO_4) Demirbas, 2008 (ii) base such as sodium hydroxide (NaOH), potassium hydroxide (KOH) (Jibril et al., 2008; Wang et al., 2008; El-Hendawy, 2009), and potassium carbonate (K_2CO_3) (Budinova et al., 2008 ; Cabal et al., 2009 ;Tay et al., 2009) (iii) salt such as zinc chloride ($ZnCl_2$). (Aygun et al., 2003; Gurses et al., 2006; Kalderis et al., 2008; Alhamed et al., 2009; Aravindhan et al., 2009; Olivares-Marin et al., 2006; Oliveira et al., 2009) In case of phosphoric acid as chemical agent, Srinivasakannan et al. (2009) used phosphoric acid activation to convert rubber wood sawdust to activated carbon using the best condition at 500°C and 45 min. The resulting iodine number was 1096 mg/g and the surface area of 1496 m^2/g. Sutcu and Demiral et al. (2009) used potassium hydroxide activation to loquat stones convert to activated carbon, with the following conditions: activation temperature 1000°C and 120 min. The activated carbon had the surface area of 2915 m^2/g. A successful example of using salt as chemical agent can be seen from the work of Olivares-Marin et al. who employed zinc chloride to convert cherry stone to activated carbon with the activation temperature of 550°C at 120 min. The resulting activated carbon had the surface area of as much as 1971 m^2/g. In summary, chemical agents that require low activation temperature can be ordered according to its superiority as: zinc chloride, phosphoric acid, and potassium hydroxide, whereas the order of chemical agents which reduce the activation time is phosphoric acid, potassium hydroxide, and zinc chloride. Some recent works on the production of activated carbon with chemical activation are given in Table 2.4 and 2.5.

Heavy metals are recognized as dangerous contaminants because of their high toxicity, accumulation, and retention in human body. Lead, which is a remarkably toxic and non-biodegradable metal, can be generated by several sources, resulting in contamination of wastewater and soil. Adsorption has been shown to be one of the most favourable technique for the removal of lead from wastewater. The activated carbon is a unique and effective adsorbent because of their highly developed porosity, large surface area, changeable characteristics of surface chemistry, and high degree of surface reactivity. Table 2.6 summarizes literature reviews of lead adsorption by activated carbon. The percentage removal of lead increases with the increasing in adsorbent dosage and decreases with increasing in initial lead concentration and increasing temperature. The optimal solution pH range for the removal of lead was determined to be around 4 - 6 and the adsorption isotherm often follows the Langmuir type with a maximum adsorption capacity of more than 10 mg g^{-1}.

Table 2.4 Recent works on the production of activated carbon with chemical activation

Type of raw material	**Condition**						**Activated carbon properties**		**reference**
	Type of activation	**Ratio**	**Carbonization**		**Activation**		**Iodine number (mg/g)**	**Surface area (m^2/g)**	
			Temperature (°C)	**Time (min.)**	**Temperature (°C)**	**Time (min.)**			
Hazelnut shell	Chemical/$ZnCl_2$				800	120	965	793	(Aygun et al., 2003)
Rubber wood sawdust	Chemical/H_3PO_4	1:1.5			500	45	1,096	1,496	(Srinivasakannan et al., 2004)
Rice-husk	Chemical/H_3PO_4	1:0.7			500	150		376	(Daifullah et al., 2004)
Wastewater (papper)	Chemical/H_3PO_4							1,400	(Temmink and Grolle, 2005)
Rosa canina fruits	Chemical/$ZnCl_2$	1:5			500	60	495	800	(Gurses et al., 2006)
Date stone wastes	Chemical/H_3PO_4	1:0.4	RT	1440	800	60	495		(Haimour and Emeish, 2006)

Type of raw material	Condition						Activated carbon properties		reference
	Type of activation	Ratio	Carbonization		Activation		Iodine number (mg/g)	Surface area (m^2/g)	
			Temperature (°C)	Time (min.)	Temperature (°C)	Time (min.)			
Eucalyptus dehn bark	Chemical/H_3PO_4	1:1			500	60	1,043	1,239	(Patnukao and Pavasant, 2008)
Antibiotic production	Chemical/K_2CO_3	1:1	60	120	900	120	1,170	1,260	(Budinova et al., 2008)
Hazelnut shell	Chemical/H_2SO_4				200	1440	204	441	(Demirbas, 2008)
Coconut shell	Chemical/H_3PO_4	1:1.725	RT	720	416	19.5		1,151	(Gratuito et al., 2008)
Palm stems	H_3PO_4		85	180	500	120		1,100	(Jibril et al., 2008)
	KOH				600	120		947	
Sugarcane bagasse	Chemical/$ZnCl_2$	1:0.75	150	1440	700	30		674	(Kalderis et al., 2008)
Rice husk	Chemical/$ZnCl_2$	1:1	150	1440	700	30		750	(Kalderis et al., 2008)

Type of raw material	Condition						Activated carbon properties		reference
	Type of activation	Ratio	Carbonization		Activation		Iodine number (mg/g)	Surface area (m^2/g)	
			Temperature (°C)	Time (min.)	Temperature (°C)	Time (min.)			
Jackfruit peel waste	Chemical/H_3PO_4			1440	550			1,260	(Prahas et al., 2008)
Activated sludge	Chemical/KOH	1:2.5	RT	1440	600	60	563	382	(Wang et al., 2008)
Waste tea	Chemical/H_3PO_4	1:3		4320	350	60		1,157	(Yagmur et al., 2008)
Dates stones	Chemical/$ZnCl_2$	1:0.5			500	180		1,270	(Alhamed et al., 2009)
S.longifolium	Chemical/$ZnCl_2$	1:0.3			800	120	1,041	802	(Aravindhan et al., 2009)
H. valentiae	Chemical/$ZnCl_2$	1:0.3			800	120	962	783	(Aravindhan et al., 2009)
Olive-waste cakes,	Chemical/H_3PO_4	1:1.75	104	120	450	120	583	1,020	(Baccar et al., 2009)

Type of raw material	Condition						Activated carbon properties		reference
	Type of activation	Ratio	Carbonization		Activation		Iodine number (mg/g)	Surface area (m^2/g)	
			Temperature (°C)	Time (min.)	Temperature (°C)	Time (min.)			
Maize stalks	Chemical/KOH	1:1			700 (N_2)	60		1,684	(El-Hendawy, 2009)
Bean pods	Chemical/K_2CO_3	6:4	RT	720	950 (N_2)	10		1,580	(Cabal et al., 2009)
Cherry stones	Chemical/$ZnCl_2$	1:4	RT	1440	500	120		1,971	(Olivares-Marin et al., 2006)
Hemp fibers	Chemical/H_3PO_4	3:1			550	120		1,350	(Rosas et al., 2009)
Loquat stones	Chemical/KOH	1:2			1000	120		2,915	(Sutcu and Demiral, 2009)
Coffee husk	Chemical/$ZnCl_2$	1:1			550 (N_2)	180		900	(Oliveira et al., 2009)
Soybean oil cake	Chemical/K_2CO_3	1:1		1440	800	60		1,352	(Tay et al., 2009)

Table 2.5 Recent works on the production of activated carbon with physical activation.

Type of raw material	**Type of activation**	**Condition**				**Activated carbon properties**		**reference**
		Carbonization		**Activation**		**Iodine number (mg/g)**	**Surface area (m^2/g)**	
		Temperature (°C)	**Time (min.)**	**Temperature (°C)**	**Time (min.)**			
Jatropha curcus	Physical/Steam			700	60	70	1	(Namasivayam et al., 2007)
P.oceanica leaf sheaths	Physical			600	60		111	(Ncibi et al., 2009)
Almond Shells	Physical/Steam	800	60	800	60		998	(Savova et al., 2001)
Grape seeds	Physical/Steam	800	60	800	60		497	(Savova et al., 2001)
Nut Shells	Physical/Steam	800	60	800	60		743	(Savova et al., 2001)
Pistachio-nut shell	Physical/CO_2	500	120	900	30		778	(Lua et al., 2004)

Table 2.6 Literature reviews on the adsorption of lead by activated carbon

Adsorbent	Condition				Efficiency (%)	Isotherm	References
	pH	Initial lead concentration (mg L^{-1})	Adsorbent (g L^{-1})	Time (hr)			
Cladophora fascicularis	5	100	2.5	6	90	Langmuir: q_m = 198.5 mg g^{-1}, b = 0.0357 $(mg/L)^{-1}$ Freundlich: K_F = 37.46 mg g^{-1}, 1/n = 3.621	Deng et al., 2007
Coffee residue	5.8	10	63 mg g^{-1}	-	-	Langmuir: q_m = 63.291 mg g^{-1}, b = 0.396 $(mg/L)^{-1}$ Freundlich: K_F = 27.495 mg g^{-1}, 1/n = 0.244 Temkin: q_e = 13.123 mg g^{-1}, b = 4.1334	Boudrahem et al., 2009
Crab and Arca shell	5.5	100	2.5	24	99.1	Langmuir: q_m = 33.89, 30.39 mg g^{-1}, b = 0.056, 0.069 $(mg/L)^{-1}$ Freundlich: K_F = 8.194, 1.848 mg g^{-1}, 1/n = 0.246, 0.353 Lagergren: q_e = 26.63, 18.63 mg g^{-1}, K_L = 0.02, 0.013	Dahiya et al., 2008
meranti sawdust	6	100	5	2	-	Langmuir: q_m = 34.246 mg g^{-1}, b = 0.016 $(mg/L)^{-1}$ Freundlich: K_F = 1.504 mg g^{-1}, 1/n = 1.046 Dubinin–Radushkevich: C_m= 0.410 mg g^{-1}, R^2 = 0.998	Rafatullah et al., 2009
Pomegranate peel	5.6	-	-	2	-	Langmuir: q_m = 17.637 mg g^{-1}, b = 0.260 $(mg/L)^{-1}$ Freundlich: K_F = 8.422 mg g^{-1}, 1/n = 0.463 Temkin: q_e = 9.39 mg g^{-1}, b = 3.753	El-Ashtoukhy et al., 2008
Spartina alterniflora	5-6	46.9-69.8	0.5	0.33		Langmuir: q_m = 99.5 mg g^{-1}, b = 0.222 $(mg/L)^{-1}$ Freundlich: K_F = 31.57 mg g^{-1}, 1/n = 0.270	Li and Wang, 2009
Tea waste	5-6	-	0.25-1.5		37-94	Langmuir: q_m = 65 mg g^{-1}, b = 0.0494 $(mg/L)^{-1}$	Amarasinghe

Adsorbent	**Condition**				**Efficiency (%)**	**Isotherm**	**References**
	pH	**Initial lead concentration (mg L^{-1})**	**Adsorbent (g L^{-1})**	**Time (hr)**			
						Freundlich: K_F = 9.65 mg g^{-1}, 1/n = 0.3885	and Williams, 2007
Tamarind wood	-	10-50	-	-	99	Langmuir: q_m = 43.859 mg g^{-1}, b = 0.274 $(mg/L)^{-1}$ Freundlich: K_F = 9.321 mg g^{-1}, 1/n = 0.668	Acharya et al., 2009
Viscum album L.	5	50	0.8	1.5	99	Langmuir: q_m = 769.23 mg g^{-1}, b = 0.0.34 $(mg/L)^{-1}$ Freundlich: K_F = 101.86 mg g^{-1}, 1/n = 0.3748 Temkin: B = 138.24 A = 0.653 L mg^{-1} Harkins-Jura: A = 50,000, B = 2.0	Erenturk and Malkoc, 2007

CHAPTER III

RESEARCH METHODOLOGY

3.1 Preparation of raw material

Raw material, Jatropha seed waste, was prepared by washing with tap water, drying in oven, sieving pass through mesh number 10 (2 mm), and storing in closed dessicator.

3.2 Optimum preparation condition of activated carbon via chemical activation

Jatropha seed cake was impregnated into various chemical agents i.e. phosphoric acid (85 wt%), potassium hydroxide (55 wt%), and zinc chloride (55 wt%) via the condition below:

- weight ratio of raw material and chemical agents (impregnation ratio): 1:0.5 – 1:2
- activation temperature in a muffle furnace in range 400 and 700°C
- activation time of 0.5 – 3 hours
- final pH of the char after washing with hot distilled water of 6-8.

3.3 Optimum preparation condition of activated carbon via physical activation

Jatropha seed cake was placed in the middle of tubular reactor and put the reactor in the horizontal tubular furnace as shown in Figure 3.1. The furnace system consists of horizontal tubular furnace (8), tubular reactor (6), gas cylinder (N_2, air and CO_2) (1, 2, 3) and steam generator (4, 5). The horizontal tubular reactor was made of SS304 steel with a minimum volume of 150cc. This tubular reactor had the flange with an outside diameter of 40 mm and internal diameter of 35 mm and was placed in the horizontal tubular furnace. The horizontal tubular furnace could be heated up to 1100°C with a fixed heating rate of 10°C min^{-1}. The steam was generated by pumping DI water with peristaltic pump through the heater at 140°C and carried into the tubular reactor by N_2 carrier gas through the piping network made of stainless steel (SS316L size 1/4").

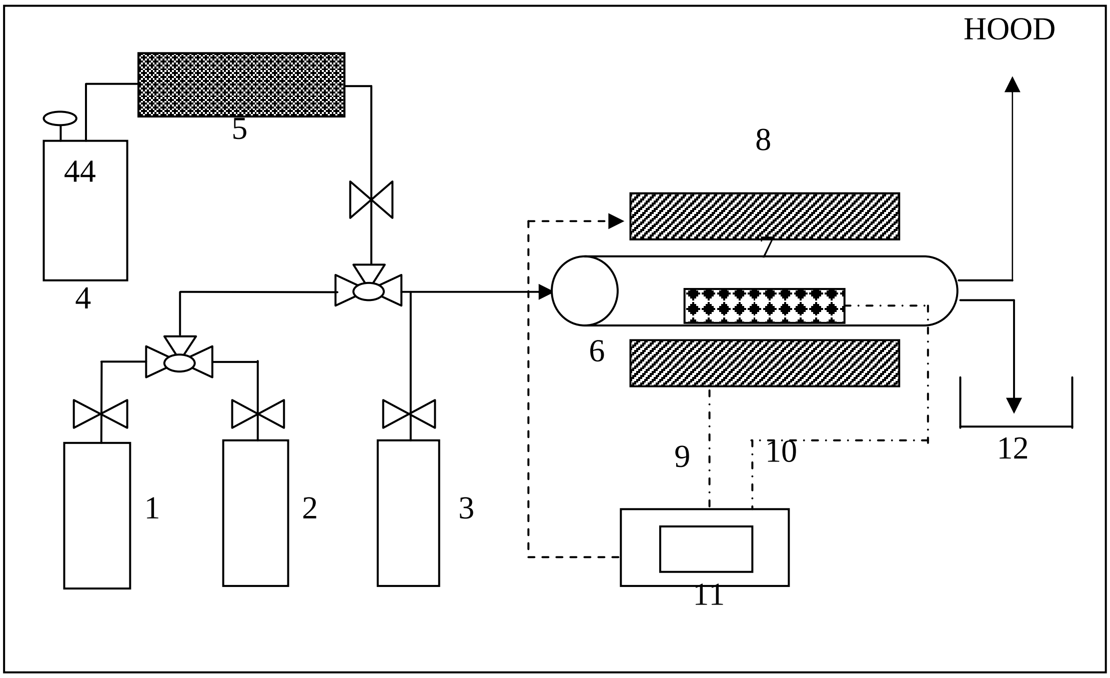

Figure 3.1 Schematic diagram of the experimental set up: (1) nitrogen gas cylinder; (2) air cylinder; (3) carbon dioxide cylinder; (4) peristaltic pump; (5) heater; (6) tubular reactor; (7) sample; (8) tubular furnace; (9) furnace thermocouple; (10) sample thermocouple; (11) temperature controller; (12) beaker (liquid product collectors)

First step is carbonization at the various condition of temperatures (450-600°C) and times (30-120 minutes) to determine the range proximate analysis. The second step is to determine the optimal condition for activation by set experiment as below:

- flow of N_2 gas at 200 cm^3 min^{-1}

- heating rate controlled at 10°C min^{-1} starting from room temperature (30°C) to final temperature of 850, 900, 950°C, respectively

- Activate by switching N_2 to steam or CO_2 at various times 60, 90 and 120, and then, cool down by switching the gas flow to N_2.

3.4 Analysis of activated carbon properties

1. Ash content: determined by standard method ASTM D 2866-94.
2. Apparent (bulk) density: calculated as the ratio between weight and volume of packed dry material.

3. Chemical analysis of wood charcoal: determined according to the standard method ASTM D 1762-84. This method covers the determination of moisture, volatile matter, and ash in charcoal made from wood.

4. Fourier Transform Infrared Spectrometer (FT-IR): determined functional groups attached in activated carbon.

5. Iodine number: determined according to the standard method ASTM D 4607-94.

6. Moisture content of activated carbon: determined according to the standard method ASTM D 2867-95.

7. Surface area: calculated from adsorption isotherms using the method of Brunauer, Emmet and Teller (BET method).

8. Ultimate analysis of material: performed by CHNS/O analyzer (Perkin Elmer PE2400 Series II), using gaseous products feed by pyrolysis in high purity oxygen and were chromatographically detected with a thermal conductivity detector. The proximate analysis was developed following ASTM standards for chemical analysis of wood charcoal (ASTM D 1762-84).

9. Yield of activated carbon: the yield is defined as the ratio of the weight of the resultant activated carbon to that of the original eucalyptus bark with both weight on a dry basis, i.e.

$$\%\text{Yield} = \frac{W_1}{W_0} \times 100 \tag{3.1}$$

where W_0 is the original mass of the precursor on a dry basis and W_1 is the mass of the carbon after activation, washing and drying.

Adsorption isotherm

Lead and Copper in form of $Pb(NO_3)_2$ and $Cu(SO)_4$, respectively, were prepared and mixed with activated carbon to determine kinetic and isotherm at various condition as follow:

- stirring rate of 200 rpm
- stirring time range from 5 to 120 minutes
- temperature of 30°C
- pH range from 1 to 3.

Initial and final of lead and copper concentrations were analyzed by Flame & Graphite Furnace Atomic Absorption Spectrophotometer (AAS) and then fitted with Langmuir and Freundlich isotherms.

3.6 Desorption efficiency

Desorption efficiency of lead was experimented as the condition below:

- chemical solutions: hydrochloric acid (HCl), nitric acid (HNO_3), acetic acid (CH_3COOH), Ethylene Diamine Tetraacetic Acid (EDTA), sodium chloride (NaCl) and sodium hydroxide (NaOH)
- chemical concentrations: acids 0.05 – 2.0 N and other chemicals 0.01 – 0.40 mol
- stirring rate of 200 rpm
- stirring time range from 5 to 120 minutes
- temperature of 30°C.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Properties of Jatropha seed cake

The properties of Jatropha seed cake were analyzed by several methods such as proximate analysis, ultimate analysis, bulk density and SEM etc. in order to compare the differences of raw materials. Table 4.1 displays results from the proximate analysis and ultimate of Jatropha seed cake. The raw material suitable for the production of activated carbon should have a fixed carbon content of more than 30%. The carbon contents of Jatropha seed cake fell in this range and therefore it was considered suitable for the production of activated carbon.

Table 4.1 Proximate analysis and ultimate analysis of Jatropha seed cake (dry basis)

Properties	Value
Volatile (%)	59.16
Ash (%)	6.99
Fixed carbon (%)	33.85
C (%)	37.2
H (%)	4.36
N (%)	0.23
S (%)	0.67
Bulk density (g/cm^3)	0.73

4.2 Characteristics of activated carbon from Jatropha seed cake

4.2.1 Chemical activation

100 grams of each seed cake from Jatropha were washed with distilled water and dried at 100±10°C. The dried material was milled, sieved and then mixed with chemical solutions (phosphoric acid, potassium hydroxide, and zinc chloride) at impregnation ratio of 1:0.5-1:2. The activated carbon was produced from those materials after pyrolyzed in furnace at activation temperature in range of 400-700°C and activation time in range of 60-180 minutes. The efficiency of activated carbon was evaluated via iodine number. This number can be indicated their relative activation level and the surface area available for micropores. Usually adsorbents with high iodine number have a high surface area and

suitable for adsorbing small compound (Bestani et al., 2008). The detail of each activation agent is described as follows.

1. **Activation with phosphoric acid**

Table 4.2 displays the properties of the activation carbon from the seed cake. It illustrates that, at the impregnation ratio of 1:0.5 and preparation period of 60 minutes, iodine number increased with increasing temperature from 500-700°C. Higher activation temperature reduced the volatile matter, which raised the fixed carbon content. However, too high temperature could impose adverse effect on the activated carbon property, e.g. iodine number was found to decrease at 800°C possibly due to the destruction of porous structure and network at extremely high temperature. The optimal activation time was found at 120 minutes and 700°C. A further increase in activation time resulted in a lower %yield because a long activation also promoted a more burn-off of carbonaceous matter and increased fixed carbon content. At 700°C and 120 min, %yield decreased from 32 to 19 when the impregnation ratio increased from 1:0.5 to 1:1. This is because an excess amount of agent promoted the gasification of char, increasing the total weight loss of carbon. Bulk density of the activated carbon of Jatropha seed cake varied in the range of 0.48 – 0.57 g/cm^3.

Table 4.2 Properties of activated carbon from Jatropha seed cake with phosphoric acid activation

Temp (°C)	Time (min.)	Impregnation ratio (Raw material: H_3PO_4)	Yield (%)	Volatile matter (%)	Ash (%)	Fixed carbon (%)	Iodine number (mg/g)	Net Iodine number (mg/g)
500	60	1:0.5	50	32.55	4.06	63.40	201	100.5
600	60	1:0.5	36	18.76	3.73	77.50	360	129.6
700	60	1:0.5	33	14.28	4.23	81.49	423	139.6
700	120	1:0.5	32	15.17	4.93	79.90	516	165.1
700	120	1:1	19	13.24	9.63	77.12	409	77.7
800	60	1:0.5	31	14.56	6.88	78.56	344	106.6

2. Activation with potassium hydroxide

Table 4.3 illustrates that, as activation temperature increased from 600-700°C, the iodine number of the activated carbon derived from the Jatropha seed cake increased from 354-609 mg/g. This was due to a better disengagement of chemical agent from the pore of the activated carbon at high temperature. In addition, increasing activation time extended the contact time between chemical agent and raw material resulted in development of pore structure and porous network, however, a longer activation time played an important role in lowering the yield as it caused more burn-off of the carbon creating a combination of micro-pores which led to a formation of meso-pore or macro-pore. Therefore the activation time should be long enough for the potassium hydroxide to contact the raw material in order to create sophisticating pore structure and high surface area but not too long to prevent the pore collapse. Increasing the impregnation ratio from 1:0.5 to 1:0.75 led to an increase in the iodine number from 636-696 mg/g. Bulk density of activated carbon for this case was around 0.3-0.4 g/cm^3.

Table 4.3 Properties of activated carbon from Jatropha seed cake with potassium hydroxide activation

Temp (°C)	Time (min.)	Impregnation ratio (Raw material: KOH)	Yield (%)	Volatile matter (%)	Ash (%)	Fixed carbon (%)	Iodine number (mg/g)	Net Iodine number (mg/g)
600	60	1:0.5	25	22.06	22.58	55.35	354	88.5
700	60	1:0.5	20	16.82	21.54	61.64	558	111.6
700	120	1:0.5	21	1.04	13.79	85.17	609	127.9
700	180	1:0.75	16	26.94	17.09	55.97	696	111.4

3. Activation with zinc chloride

Table 4.4 illustrates that increasing the temperature enhanced the iodine number because high activation temperature supported the development of pore structure but decreased %yield. An increase in activation time decreased %yield of the activated carbon due to a greater release of volatile matter and moisture. A shorter activation time might not be enough for the release of volatile matter, and therefore it remained in the activated carbon leading to a higher %yield than that at a longer activation time. %yield of zinc chloride activation was the highest compared with the other chemical agents. This was because activated carbon from zinc chloride did not require intensive washing, resulting in a lesser loss of activated carbon. An increase in impregnation ratio from 1:0.5–1:0.75 increased iodine number from 446–525 mg/g because at high impregnation ratio, an excess chemical agent could penetrate deep into the structure of carbon generating tiny pore, but this reduced %yield from 64 – 51 due to a more intensified reaction that removed the carbon content and created high porosity structure. Bulk density of activated carbon with zinc chloride activation was the highest in the range of 0.77-1.23 g/cm^3 (Jatropha seed cake). It is noted that zinc is a heavy metal and when mixed with Jatropha seed cake could increase the weight of the final activated carbon product.

Table 4.4 Properties of activated carbon from Jatropha seed cake with zinc chloride activation

Temp (^{o}C)	Time (min.)	Impregnation ratio (Raw material: $ZnCl_2$)	Yield (%)	Volatile matter (%)	Ash (%)	Fixed carbon (%)	Iodine number (mg/g)	Net Iodine number (mg/g)
500	60	1:0.5	44	32.69	22.50	44.80	95	41.8
600	60	1:0.5	50	27.71	23.12	49.17	82	41.0
700	60	1:0.5	53	11.36	27.67	60.97	413	218.9
700	120	1:0.5	64	13.58	27.36	59.06	446	285.4
700	120	1:0.75	51	11.87	23.74	64.39	525	267.8
700	120	1:1	44	14.96	22.28	62.76	495	217.8
700	180	1:0.5	45	18.95	18.82	62.23	350	157.5

4.2.2 Physical activation

Activated carbons were produced from Jatropha seed cake through the process of carbonization followed by steam and carbon dioxide activations. During the carbonization process, Jatropha seed cake was carbonized in the absence of air at various temperatures (450, 500, 550 and 600°C) and various times (30, 45, 60, 90 and 120 minutes). The optimum carbonization occurred at temperature of 500°C and time of 60 minutes as shown via the suitable range of fixed carbon. The derived char was then activation with steam and carbon dioxide.

1. Steam activation

The activation step is designed to develop the porosity in the material to generate a highly porous solid as the final product due to the removal of some components, e.g. tar like matter, and disorganized carbon deposited in pore. The effect of activation temperature and time were carried out at various temperatures: 750, 850, 900 and 950°C and various times: 60 and 120 minutes using steam as an activating agent.

The optimal condition for production of activated carbon is indicated using the following parameters: i.e. iodine number, yield and bulk density. The best activated carbon was produced by steam activation at 950°C 60 minutes, where the iodine number of obtained activated carbon was 328 mg/g activated carbon and surface area 533 m^2/g as illustrated in Table 4.5. The carbon content from activated carbon was higher than the charcoal (53.01%) owing to a decrease in amount of volatile matter and an increase in fixed carbon at higher temperature.

Table 4.5 Properties of activated carbon from Jatropha seed cake with steam activation

Temp (^{o}C)	Time (min.)	Yield (%)	Ash (%)	Iodine number (mg/g)	Net Iodine number (mg/g)
750	120	58	13.16	260	150.8
850	120	26	18.83	336	87.4
900	60	56	22.42	300	168.0
900	120	28	26.13	261	73.4
950	60	54	35.10	328	173.8
950	120	18	36.11	441	79.2

The overall yield on dry basis was 58% which was higher than the %yield resulted from all chemical activation methods. This was because in chemical activation processes, washing is required in order to remove any residual of dehydrating agents and this consequently resulted in the loss of a large amount of carbon mass. This washing step is not necessary for the physical activation process and therefore a high carbon yield could be achieved.

2. Carbon dioxide activation

The result from carbon dioxide activation indicated that iodine number increased with an increase in activation temperature. This was because, at high temperature, the reaction of carbon dioxide as the activating agent with carbon structure did not only result in the development of micropore and the opening of blocked pores by devolatilization process leading to the formation of new micropores, but did also cause the widening of existing micropore by gasification reaction and possibly by the collapse of neighboring pore walls. Therefore, with high temperature, the activating agent could be easily diffuse to the carbon structure, resulting in the carbon product with high iodine number.

Similar to the activation temperature, the activation time was also an important factor controlling the property of the activated carbon such as the iodine number. Iodine number increased from 226 to 347 mg/g with an increasing holding time from 60 to 120 minutes as shown in table 4.6. This was a consequence of increasing rate of reaction between carbon and carbon dioxide which led to the enhancement of the devolatilization and thermal degradation. This then resulted in the opening of pores and even the loss of some walls among the pores. The highest value of the net iodine number (166.6 mg/g raw material) was obtained from the activation at 950°C for 120 minutes.

Table 4.6 Properties of activated carbon from Jatropha seed cake with carbon dioxide activation

Temp (°C)	Time (min.)	Yield (%)	Ash (%)	Iodine number (mg/g)	Net Iodine number (mg/g)
900	60	56	20.89	226	126.6
900	120	52	22.54	342	177.8
950	60	55	21.10	231	127.1
950	120	48	23.84	347	166.6
950	180	38	25.73	324	123.1

4.3 Ultimate assessment of the effectiveness of activation techniques

The evaluation thus far only looked at the properties of the final activated carbons and did not consider the yield of the activated carbon which represents the quantity of the raw materials that could be converted to the useful product. The assessment in this section was designed to consider the yield and compare the properties of the activated carbon based on the initial weight of the raw material used in each case.

To be able to do this assessment, the following calculations have to be carried out:

Net iodine number:

$$\text{net iodine number} = \text{iodine number} \times \text{yield of activated carbon} \quad (4.1)$$

$$\left(\frac{\text{mg iodine of activated carbon}}{\text{g of raw material}}\right)\left(\frac{\text{mg iodine of activated carbon}}{\text{g of activated carbon}}\right)\left(\frac{\text{g of activated carbon}}{\text{g of raw material}}\right)$$

Net surface area:

$$\text{net surface area} = \text{surface area} \times \text{yield of activated carbon} \quad (4.2)$$

$$\left(\frac{\text{m}^2\text{of activated carbon}}{\text{g of raw material}}\right)\left(\frac{\text{m}^2\text{of activated carbon}}{\text{g of activated carbon}}\right)\left(\frac{\text{g of activated carbon}}{\text{g of raw material}}\right)$$

Tables 4.7 displays the results of these calculations. The highest net surface area of 289 mg/g of raw material seed cake was obtained from the activation with zinc chloride with an impregnation ratio of 1:0.5 (raw material:chemical agent) at the activation temperature of 700°C for 120 minutes followed by steam activation with temperature of 950°C for 60 minutes. It can be seen that, although the best activated carbon with the highest iodine number was obtained from the activation with potassium hydroxide, this method might not be the best as a large quantity of carbon was destroyed during the conversion process (only 16% survived with potassium hydroxide when compared with 64% in the case of zinc chloride). The activation with zinc chloride, despite of its lower effectiveness in creating high surface (for iodine adsorption), was considered better as the initial carbon could still be retained in the product and the total iodine adsorption was greater than those obtained from other methods.

Table 4.7 Net surface area from chemical and physical activations

Activating agent	Temp (°C)	Time (min.)	Impregnation ratio	Surface area (m^2/g)	Yield (%)	Net surface area (m^2/g)
H_3PO_4	700	120	1:0.5	507	32	162.24
KOH	700	120	1:0.75	666	21	139.86
$ZnCl_2$	700	120	1:0.75	567	51	289.17
Steam	950	60		533	54	287.82
CO_2	950	120		328	52	170.56

4.4 FTIR

The existence of functional groups determines the acid-base character of activated carbons. The electrical charge of the surface groups may increase or decrease to adsorb target molecules. Generally, adsorbate has opposite electrostatic charge as the carbon surface or target molecule attracted with carbon surface resulting in increasing adsorption capacity. Figure 4.1 illustrates the functional groups in seed cakes and activated carbon from seed cake. These are described in detail below.

4.4.1 FTIR of Jatropha seed cake

Fig 4.1 shows the FTIR of Jatropha seed cake. The broad band at 600 cm^{-1} was ascribed to the O-H band. The C-H out of plane bending in benzene derivative vibrations existed as apparent in the bands at 800 and 875 cm^{-1}. The band located at 1100 cm^{-1} corresponded to C-O vibration in alcohol. The band located at 1320, 1540, 1650 cm^{-1} were ascribed to C-O vibrations of carboxylate group, C=C vibrations of aromatic, and C=C of the olifinic, respectively. The sharp band located at 2850 and 2910 cm^{-1} corresponded to C-H vibration in methyl and methylene group. The strong broad band at 3400 cm^{-1} was ascribed to O-H stretching vibration in hydroxyl group involved in hydrogen bonds.

4.4.2 FTIR of activated carbon with phosphoric acid activation

The absorption at 1190 cm^{-1} was tentatively assigned to the following phosphorous species: P-O, O–C stretching vibrations in P-O-C of aromatics and P-OOH. (Budinova et al., 2006) The band located at 1700 cm^{-1} was ascribed to phosphoric acid. This indicated that traces of phosphatic species remained in carbon matrix even after repeated washing. The band located at 750-890 cm^{-1} was ascribed to out-of-plane bending in benzene derivative vibrations which remained on surface after increasing activation temperature. (El-Hendawy. 2009; Girgis et al., 2009) The broad band located between 1080 cm^{-1} was attributable to C-O vibration. The band located at 500 cm^{-1} may be attributed to alphatic C-H species vibrations. A band appear in the spectra at 1590 cm^{-1} most likely was the C=C vibrations in aromatic rings after carbonization/activation. The strong band at 3400 cm^{-1} was ascribed to –OH streaching vibration in hydroxyl groups (El-Hendawy. 2009)

4.4.3 FTIR of activated carbon with potassium hydroxide activation

The strong band at 3400 cm^{-1} was ascribed to –OH stretching vibration in hydroxyl groups and mostly attributed to hydrogen bond participating in adsorbing water molecules. The hydroxyl groups maybe occurred from reaction of potassium hydroxide and raw material. The band located at 1600 cm^{-1} could be ascribed to olifinic C=C vibration. The band located between 1100 cm^{-1} and 1050 cm^{-1} were ascribed to C-O vibrations and R-OH groups in alcohol. The small band at 895 cm^{-1} was ascribed to C-H out of plane bending in benzene derivative vibration. The broad band at 600 cm^{-1} was ascribed to the O-H band (El-Hendawy. 2009).

4.4.4 FTIR of activated carbon with zinc chloride activation

The small band at 870 cm^{-1} was ascribed to the C-H out of plane bending in benzene derivative vibration but this band disappeared after 120 minutes of activation at 700^{o}C. The intense band at 1050 cm^{-1} could be assigned to alcohol R-OH group. The band located at 1600 cm^{-1} was ascribed to the presence of olefin C=C vibration. (Alhamed et al., 2009; El-Hendawy. 2009) The strong broad band located at 3420 cm^{-1} was ascribed to –OH stretching vibration in hydroxyl groups but this band disappeared when increasing activation time from 60 to 120 minutes.

4.4.5 FTIR of activated carbon with steam and carbon dioxide

The assignment of absorption bands shows that functional groups like alkene, aromatic, ketone, alcohol, hydroxyl and carboxyl were present in the carbonized products. These functional groups could be derived from the Jatropha raw material, which are essentially composed of cellulose, hemicellulose and lignin. After activation by steam, the band at 3642.83 cm^{-1} appeared which indicated that the reaction between steam and carbon atom in charcoal led to a formation of non-bonded OH groups. The IR absorption bands of steam activation carbon exhibited a lower intensity than carbonization product. This change in intensity was a consequence of the activating reaction of steam where oxygen and hydrogen groups were decomposed and extracted from the surface. The IR spectra obtained for carbon dioxide activated carbon exhibited a similar shape, which shows that the same functional groups were present in the carbon dioxide activated carbon product.

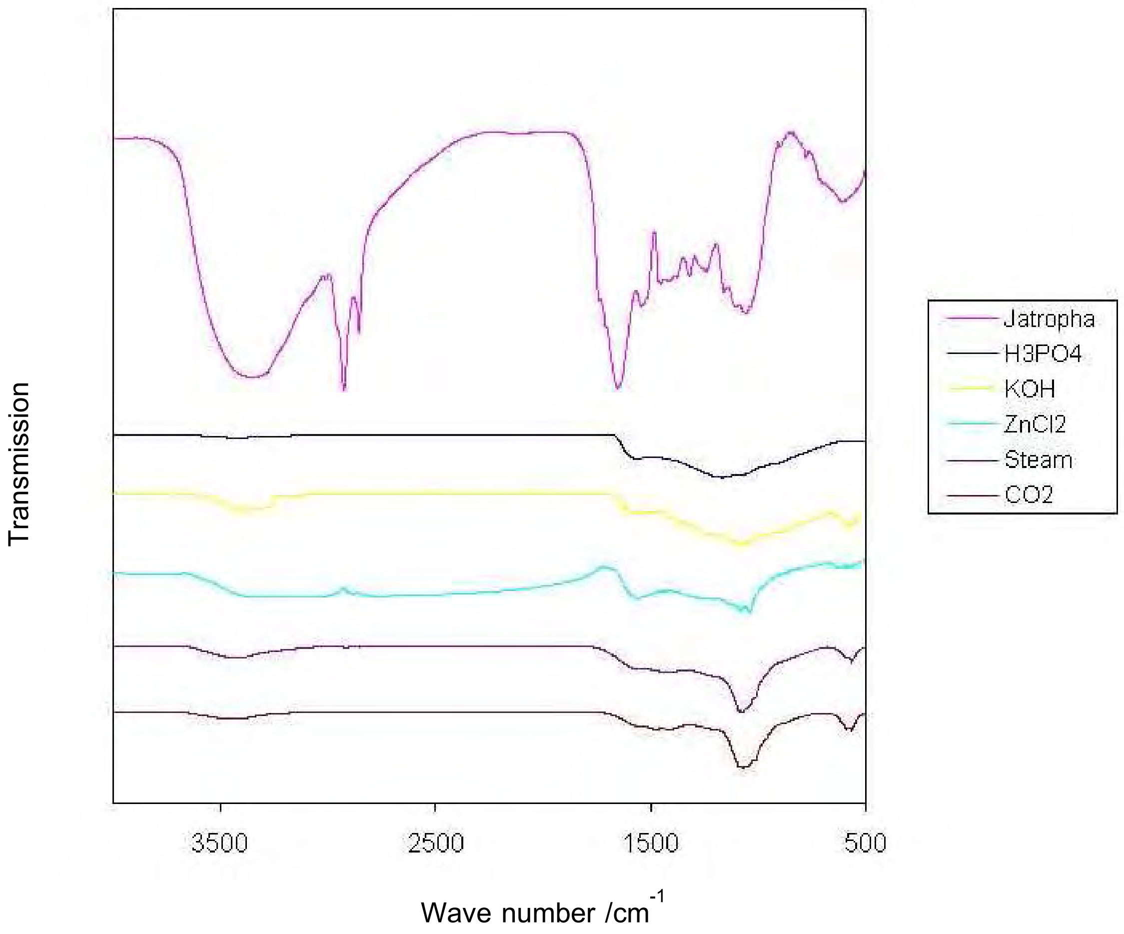

Figure 4.1 FTIR spectra of raw material and activated carbons

4.5 Adsorption study

Activated carbon from steam activation was selected to determine the adsorption study because it contained lowest environmental burden for life cycle assessment thinking compared to the others.

The adsorption isotherms reveal the specific relation between adsorption capacity and concentration of the remaining adsorbate at constant temperature. Several models have been used in the literature to describe experimental adsorption data. Freundlich and Langmuir models are the two most frequent used. In this work both models were used to quantify the adsorption capacity of steam activated carbon for the removal of Pb(II) and Cu(II) ions from synthetic wastewater.

Freundlich isotherm describes the heterogeneous surface energies by multilayer sorption and is expressed by the following equation:

$$q_e = K_F C_e^{1/n} \tag{4.4}$$

where K_F and n are constants of Freundlich isotherm incorporating adsorption capacity (mg g^{-1}) and intensity. The isotherm data fitted the Freundlich model relatively well with an R^2 of 0.996 at pH 3. The values of the constants K_F of Pb(II) and Cu(II) ions were calculated to be 6.457 and 9.616 mg/g whereas 1/n of Pb(II) and Cu(II) ions were and 0.931 and 2.867, respectively. The value of 1/n of less than 1 indicates a favorable adsorption.

Langmuir isotherm is based on the monolayer sorption of lead ions on the surface of carbon sites and is represented by the following equation:

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + (\frac{1}{q_m})C_e \tag{4.3}$$

where C_e and q_e are the remaining concentration of Pb(II) ions after eguilibrium (mg L^{-1}) and the amount of adsorbed lead at equilibrium, respectively, q_m and b the total number of surface sites per mass of sorbent (mg/g) and Langmuir constant or capacity factor. The plots of Pb(II) and Cu(II) ions at pH 3 which shows that a straight line could be well observed between $1/q_m$ and $1/C_e$. This implies that the isotherm data fitted the Langmuir equation quite well (R^2 = 0.983 and 0.996 for Pb(II) and Cu(II), respectively). The values of q_m and b determined from the Langmuir plot of Pb(II) and Cu(II) at pH 3 were 13.8889 and 2.985 mg/g, and 0.0043 and 0.0138 L/mg, respectively.

Table 4.8 Adsorption constant for lead and copper with activated carbon

Heavy metals	pH	Freundlich equation			Langmuir equation		
		K	1/n	R^2	q_m	b	R^2
Pb	1	0.238	6.487	0.989	1.0810	0.0081	0.954
	2	6.295	3.060	0.990	11.7643	0.0045	0.954
	3	6.457	0.931	0.906	13.8889	0.0043	0.983
Cu	1	2.296	9.081	0.950	0.6016	0.0268	0.942
	2	2.512	5.753	0.955	1.1547	0.0174	0.922
	3	9.616	2.867	0.996	2.9850	0.0138	0.996

The pH of solution has been identified as the most important variable governing metal adsorption on the adsorbent (Wang et al., 2009). This is because hydrogen ion is competing with the positively charged metal ions on the active sites of the adsorbent. The effect of pH on adsorption of Pb (II) and Cu(II) ions on steam activated carbon has been examined by allowing the adsorption in the controlled environment with different pH levels (range from 1–3) and the results are shown in Table 4.8. This pH range was chosen in order to avoid metal solid hydroxide precipitation. The results indicate that the maximum adsorptions of Pb(II) and Cu(II) in terms of both Freundlich and Langmuir isotherms were obtained at pH 3 (k = 6.457 and 9.616 mg/g, and q_m = 13.8889 and 2.9850 mg/g respectively). The equilibrium adsorption amount of both heavy metals on steam activated carbon increased with increasing pH as a result of a decrease in competition between protons (H^+) and positively charged metal ions at the surface sites (Boudrahem et al., 2009). The sorption decreased at higher pH (pH > 4.0) which was possibly due to the metal hydrolysis and potential precipitation. Subsequent studies are thereafter conducted at pH 3.

4.6 Desorption study

For the study of desorption of lead from activation carbon, 6 solutions, i.e., 3 acidic agents: hydrochloric acid (HCl), nitric acid (HNO_3) and acetic acid (CH_3COOH), and 3 other chemicals: ethylene diamine tetraacetic acid (EDTA), sodium chloride (NaCl), and sodium hydroxide (NaOH) were used as extraction agents. The desorption efficiency was conducted by varying concentration of acids in the range of 0.05 - 2.0 N, whereas EDTA, NaCl, and NaOH solutions at 0.01 – 0.40 mol, respectively, time in the range of 5 minutes to 2 hours and various temperature at 25, 30 and 35 C^o.

For the group of acidic solutions, the results showed that the maximum extraction efficiency was occurred from Nitric acid at the concentration of 2.0 N, extraction time of 120 minutes and extraction temperature of 35^{o}C. The extraction efficiency of Nitric acid was in the range from 56.32 - 82.04%. Hydrochloric acid presented the following efficiency of 42.52 - 67.16 % at concentration of 0.4 N, extraction time of 60 minutes and extraction temperature of 35^{o}C. Acetic acid was found the lowest efficiency of 30.76 - 54.33 % at concentration of 0.4 N, extraction time of 60 minutes and extraction temperature of 35^{o}C.

For the group of other chemicals, the result found that maximum desorption efficiency were derived from EDTA solution at 86.22%. The optimum condition was EDTA concentration of 0.1 mol, time of 60 minutes and temperature of 35 ^{o}C. NaCl solution showed the second desorption efficiency of 77.95% at NaCl concentration of 0.2 mol/L, time of 60 minutes and temperature of 35°C. NaOH solution performed the lowest desorption efficiency of 73.24% at NaOH concentration if 0.4 mol, time of 60 minutes and temperature of 35 °C.

CHAPTER V

CONCLUSION

1. Activated carbon prepared from both Jatropha seed cake by KOH as an activating agent exhibited the highest surface area. However, if yield was to be considered for the net iodine number, activated carbon prepared from Jatropha seed cake with zinc chloride activation exhibited the greatest adsorption properties.

2. The best conditions for production of high surface area activated carbon from Jatropha seed cake are the activation with potassium hydroxide; activation temperature of 700^{o}C, activation time of 180 minutes, and impregnation ratio between raw material:chemical agent of 1:0.75. At this optimal condition, the BET surface areas are 666 m^2/g and iodine numbers are 696 mg/g.

3. The best condition for production of net iodine number from Jatropha seed cake is the activation with zinc chloride; activation temperature 700^{o}C, activation time of 120 minutes, and impregnation ratio of 0.5. At this optimal condition, the net iodine number is 285 mg/g.

4. The optimal carbonization condition for the production of charcoal from Jatropha seed cake was 500°C for 45 minutes. This condition yielded a suitable amount of volatile matter of 25.0%.

5. The best condition of steam activation was at 950°C for 60 minutes. This condition gave the highest net BET surface area (288 m^2/g).

6. FTIR results revealed that several functional groups were disappeared at higher temperature.

7. The sorption of lead and copper onto steam-activated carbon depended on solution pH, contact time and initial concentration of Pb (II) and CU(II). The maximum sorption uptake of both was achieved at pH 3 for 30 minutes.

8. Adsorption of Pb (II) and CU(II) was fitted with Freundlich and Langmuir isotherms via k = 6.457 and 9.616 mg/g, and q_m = 13.8889 and 2.9850 mg/g, respectively.

9. Maximum desorption of lead derived from EDTA solution at 86.22% at concentration of 0.1 mol, time of 60 minutes and temperature of 35 ^{o}C.

REFERENCES

Acharya, J., Sahu, J.N., Mohanty, C.R., and Meikap, B.C. 2009. Removal of lead (II) from wastewater by activated carbon developed from Tamarind wood by zinc chloride activation. Journal of Chemical Engineering 149: 249–262.

Achaw, O-W., and Afrane, G. 2008. The evolution of the pore structure of coconut shells during the preparation of coconut shell-based activated carbons. Journal of Microporous and Mesoporous Materials 112: 284–290.

Ahmad, A.L., Loh, M.M., and Aziz, J.A. 2007. Preparation and characterization of activated carbon from oil palm wood and its evaluation on Methylene blue adsorption. Journal of Dyes and Pigments 75: 263-272

Alhamed et al. 2009. Sulfur removal from model diesel fuel using granular activated carbon from dates' stones activated by $ZnCl_2$. Fuel 88 (1):87-94.

Amarasinghe P.K and Williams RA. 2007. Tea waste as a low cost adsorbent for the removal of Cu and Pb from wastewater. Journal of Chem Eng 132: 299–309.

Aravindhan, R., J. Raghava Rao, and B. Unni Nair. 2009. Preparation and characterization of activated carbon from marine macro-algal biomass. Journal of Hazardous Materials 162 (2-3):688-694.

Aravindhan, R., J. Raghava Rao, and B. Unni Nair. 2009. Preparation and characterization of activated carbon from marine macro-algal biomass. Journal of Hazardous Materials 162 (2-3):688-694.

Areerachakul, N., Vigneswaran, S., Ngo, H.H., and Kandasamy, J. 2007. Granular activated carbon (GAC) adsorption-photocatalysis hybrid system in the removal of herbicide from water. Separation and Purification Technology 55: 206–211

Arriagada, R., Gercia, R., and Reyes, P. 1994. Steam and carbon dioxide activation of *Eucalyptus globulus* charcoal. Journal of Chemical Technology Biotechnology 60: 427-345.

Aworn, A., Thiravetyan, P., and Nakbanpote, W.2008. Preparation and characteristics of agricultural waste activated carbon by physical activation having micro- and mesopores. Journal of Anal. Appl. Pyrolysis 82: 279–285.

Aworn, A., Thiravetyan, P., and Nakbanpote, W.2009. Preparation of CO_2 activated carbon from corncob for monoethylene glycol adsorption. Journal of Eng. Aspects 333: 19-25.

Aygun et al. 2003. Production of granular activated carbon from fruit stones and nutshells and evaluation of their physical, chemical and adsorption properties. Microporous and Mesoporous Materials 66 (2-3):189-195.

Baaoui, A., A. Yaacoubi, A. Dahbi, C. Bennouna, R. Phan Tan Luu, F. J. Maldonado-Hodar, J. Rivera-Utrilla, and C. Moreno-Castilla. 2001. Optimization of conditions for the preparation of activated carbons from olive-waste cakes. Carbon 39 (3):425-432.

Baccar et al. 2009. Preparation of activated carbon from Tunisian olive-waste cakes and its application for adsorption of heavy metal ions. Journal of Hazardous Materials 162 (2-3):1522-1529.

Bestani, B., N. Benderdouche, B. Benstaali, M. Belhakem, and A. Addou. 2008. Methylene blue and iodine adsorption onto an activated desert plant. Bioresource Technology 99 (17):8441-8444.

Bouchelta, C., Medjram, M.S., Bertrand, O., and Bellat, J-P. 2008. Preparation and characterization of activated carbon from date stones by physical activation with steam. Journal of Anal. Appl. Pyrolysis 82: 70–77.

Bringi, N. V. 1987. Non-Traditional Oilseeds and Oils in India.Oxford & IBH Publishing Co. Pvt. Ltd., New Delhi.

Budinova et al. 2006. Characterization and application of activated carbon produced by H_3PO_4 and water vapor activation. Fuel Processing Technology 87 (10):899-905.

Budinova, T., N. Petrov, J. Parra, and V. Baloutzov. 2008. Use of an activated carbon from antibiotic waste for the removal of Hg(II) from aqueous solution. Journal of Environmental Management 88 (1):165-172.

Cabal, B., T. Budinova, C. O. Ania, B. Tsyntsarski, J. B. Parra, and B. Petrova. 2009. Adsorption of naphthalene from aqueous solution on activated carbons obtained from bean pods. Journal of Hazardous Materials 161 (2-3):1150-1156.

Carels, N., K. Jean-Claude, and D. Michel. 2009. Chapter 2 Jatropha curcas: A Review. In Advances in Botanical Research: Academic Press, 39-86.

Castro, J.B., Bonelli, P.R., Cerrella, E.G., and Cukierman, A.L. 2000. Phosphoric acid activation of agricultural residues and bagasse from sugar cane: Influence of the experimental conditions on adsorption characteristics of activated carbons. Industrial and Engineering Chemical Research 39: 4166-4172.

Chandra, T. C., M. M. Mirna, J. Sunarso, Y. Sudaryanto, and S. Ismadji. 2009. Activated carbon from durian shell: Preparation and characterization. Journal of the Taiwan Institute of Chemical Engineers 40 (4):457-462.

Dahiya S, Tripathi R.M, Hegde AG. 2008. Biosorption of lead and copper from aqueous solutions by pre-treated crab and arca shell biomass. Journal of Bioresource Technol 99: 179–187.

Daifullah, A. A. M., B. S. Girgis, and H. M. H. Gad. 2004. A study of the factors affecting the removal of humic acid by activated carbon prepared from biomass material. Colloids and Surfaces A: Physicochemical and Engineering Aspects 235 (1-3):1-10.

Daifullah, A.A.M., Girgis, B.S., and Gada, H.M.H. 2004. A study of the factors affecting the removal of humic acid by activated carbon prepared from biomass material. Colloids and Surfaces A: Physicochemical and Engineering Aspects 235: 1-10.

Demirbas, e. a. 2008. Adsorption kinetics of a basic dye from aqueous solutions onto apricot stone activated carbon. Bioresource Technology 99 (13):5368-5373.

Diao, Y., W. P. Walawender, and L. T. Fan. 2002. Activated carbons prepared from phosphoric acid activation of grain sorghum. Bioresource Technology 81 (1):45-52.

El-Ashtoukhya E.S.Z, Amina N.K, and Abdelwahabb O. 2008. Removal of lead (II) and copper (II) from aqueous solution using pomegranate peel as a new adsorbent. Desalination 223: 162–173.

El-Hendawy, A.-N. A. 2009. An insight into the KOH activation mechanism through the production of microporous activated carbon for the removal of Pb2+ cations. Applied Surface Science 255 (6):3723-3730.

Erenturk S, and Malkoc E. 2007. Removal of lead (II) by adsorption onto Viscum album L.: Effect of temperature and equilibrium isotherm analyses. Applied Surface Sci 253: 4727– 4733.

Ganan-Gomez, J., A. Mac̊ias-Garc̊ia, M. A. Diaz-Diez, C. Gonzolez-Garcia, and E. Sabio-Rey. 2006. Preparation and characterization of activated carbons from impregnation pitch by $ZnCl_2$. Applied Surface Science 252 (17):5976-5979.

Gergova, K., Petrov, N., Eser, S., 1994. Adsorption properties and microstructure of activated carbons produced from agricultural byproducts by steam pyrolysis. Journal of Carbon 32, 693–702.

Girgis, B. S., E. Smith, M. M. Louis, and A.-N. A. El-Hendawy. 2009. Pilot production of activated carbon from cotton stalks using H_3PO_4. Journal of Analytical and Applied Pyrolysis 86 (1):180-184.

Gomez-Serrano, V., Cuerda-Correa, E.M., Fernandez-Gonzalez, M.C., Alexandre-Franco, M.F., and Macias-Garcia, A. 2005. Preparation of activated carbons from chestnut wood by phosphoric acid-chemical activation. Study of microporosity and fractal dimension. Materials Letters 59: 846-853.

Gonzalez, J.F., Roman, S., Encinar, J.M., and Martınez, G.2009. Pyrolysis of various biomass residues and char utilization for the production of activated carbons. Journal of Anal. Appl. Pyrolysis 2289: 8-15.

Gratuito, M. K. B., T. Panyathanmaporn, R. A. Chumnanklang, N. Sirinuntawittaya, and A. Dutta. 2008. Production of activated carbon from coconut shell: Optimization using response surface methodology. Bioresource Technology 99 (11):4887-4895.

Guerrero, M., Ruiz, M.P., Alzueta, M.U., Bilbao, R., and Millera, A. 2005. Pyrolysis of eucalyptus at different heating rate: studies of char characterization and oxidative reactivity. Journal of Anal. Appl. Pyrolysis 74: 307-314

Guo, J., and A. C. Lua. 2003. Surface Functional Groups on Oil-Palm-Shell Adsorbents Prepared by H_3PO_4 and KOH Activation and their Effects on Adsorptive Capacity. Chemical Engineering Research and Design 81 (5):585-590.

Gurses, A., Dogar, S. Karaca, M. Aikyildiz, and R. Bayrak. 2006. Production of granular activated carbon from waste Rosa canina sp. seeds and its adsorption characteristics for dye. Journal of Hazardous Materials 131 (1-3):254-259.

Haimour, N. M., and S. Emeish. 2006. Utilization of date stones for production of activated carbon using phosphoric acid. Waste Management 26 (6):651-660.

Hameed, B.H., Tan, I.A.W., and Ahmad, A.L. 2008. Preparation of oil palm empty fruit bunch-based activated carbon for removal of 2,4,6-trichlorophenol: Optimization using response surface methodology. Journal of Hazardous Materials 164: 1316-1324

Hawash, S., N. Kamal, F. Zaher, O. Kenawi, and G. E. Diwani. 2009. Biodiesel fuel from Jatropha oil via non-catalytic supercritical methanol transesterification. Fuel 88 (3):579-582.

Jibril, B., O. Houache, R. Al-Maamari, and B. Al-Rashidi. 2008. Effects of H_3PO_4 and KOH in carbonization of lignocellulosic material. Journal of Analytical and Applied Pyrolysis 83 (2):151-156.

Kalderis, D., S. Bethanis, P. Paraskeva, and E. Diamadopoulos. 2008. Production of activated carbon from bagasse and rice husk by a single-stage chemical activation method at low retention times. Bioresource Technology 99 (15):6809-6816.

Khezami, L., Chetouani, A., Taouk, B., and Capart, R., 2005. Production and characterisation of activated carbon from wood components in powder: cellulose, lignin, xylan. Powder Technol. 157: 48–56.

Kumar, B.G. P., Shivakamy, K., Miranda, L.R., and Velan, M. 2006. Preparation of steam activated carbon from rubberwood sawdust (*Hevea brasiliensis*) and its adsorption kinetics. Journal of Hazardous Materials B136: 922–929

Laine, J., and S. Yunes, 1992. Effect of the Preparation Method on the Pore Size Distribution of Activated Carbon from Coconut Shell. Carbon 30: 601-604.

Li, W., and Wang, X. 2009. Adsorptive removal of Pb (II) by activated carbon prepared from Spartina alterniflora: Equilibrium, kinetics and thermodynamics. Journal of Bioresource Technology 100 : 2810–2815.

Li, W., J. Peng, L. Zhang, K. Yang, H. Xia, S. Zhang, and S.-h. Guo. 2009. Preparation of activated carbon from coconut shell chars in pilot-scale microwave heating equipment at 60 kW. Waste Management 29 (2):756-760.

Lillo Rodenas, Cazorla-Amor๓s, and Linares-Solano. 2003. Understanding chemical reactions between carbons and NaOH and KOH: An insight into the chemical activation mechanism. Carbon 41 (2):267-275.

Lua, A. C., T. Yang, and J. Guo. 2004. Effects of pyrolysis conditions on the properties of activated carbons prepared from pistachio-nut shells. Journal of Analytical and Applied Pyrolysis 72 (2):279-287.

Manurung, R., Heeres, H.J., Ratnaningsih, E., Suryatmana, P.,, and M. R. Satyawati, Junistia, L., Daniel, L. 2006. Initial Stage on the Volarisation of Jatropha curcas Using Biorefinery. International Symposium on Volarisation of Indonesian Renewable Resources and Particularly Jatropha curcas Using the Biorefinery Concept, The Agency for the Assessment and Application of Technology, Jakarta November:20-21.

Marsh, H., and F. Rodriguez-Reinoso. 2006. Activated Carbon. In Activated Carbon. Oxford: Elsevier Science Ltd.

Marsh, H., D. S. Yan, T. M. O'Grady, and A. Wennerberg. 1984. Formation of active carbons from cokes using potassium hydroxide. Carbon 22 (6):603-611.

Martin-Gullon, I., J. P. Marco-Lozar, D. Cazorla-Amor๓s, and A. Linares-Solano. 2004. Analysis of the microporosity shrinkage upon thermal post-treatment of H_3PO_4 activated carbons. Carbon 42 (7):1339-1343.

Mozammel, H. M., O. Masahiro, and B. Sc. 2002. Activated charcoal from coconut shell using $ZnCl_2$ activation. Biomass and Bioenergy 22 (5):397-400.

Nakagawa, Y., M. Molina-Sabio, and F. Rodrํguez-Reinoso. 2007. Modification of the porous structure along the preparation of activated carbon monoliths with H_3PO_4 and $ZnCl_2$. Microporous and Mesoporous Materials 103 (1-3):29-34.

Namasivayam, C., D. Sangeetha, and R. Gunasekaran. 2007. Removal of Anions, Heavy Metals, Organics and Dyes from Water by Adsorption onto a New Activated Carbon from Jatropha Husk, an Agro-Industrial Solid Waste. Process Safety and Environmental Protection 85 (2):181-184.

Nasser, A.A., El-Hendawy, Samra, S.E., and Girgis, B.S. 2001. Adsorption characteristics of activated carbons obtained from corncobs. Colloids and Surfaces A: Physicochemical and Engineering Aspects 180: 209-221.

Ncibi, M. C., V. Jeanne-Rose, B. Mahjoub, C. Jean-Marius, J. Lambert, J. J. Ehrhardt, Y. Bercion, M. Seffen, and S. Gaspard. 2009. Preparation and characterisation of raw chars and physically activated carbons derived from marine Posidonia oceanica (L.) fibres. Journal of Hazardous Materials 165 (1-3):240-249.

Okay, O. 2000. Macroporous copolymer networks. Progress in Polymer Science 25 (6):711-779.

Olivares-Marin, M., C. Fernandez-Gonzolez, A. Macias-Garcia, and V. Gomez-Serrano. 2006. Preparation of activated carbon from cherry stones by chemical activation with $ZnCl_2$. Applied Surface Science 252 (17):5967-5971.

Olivares-Marํn, M., J. A. Fernแndez, M. J. Lแzaro, C. Fernundez-Gonzแlez, A. Macํas-Garcia, V. Gomez-Serrano, F. Stoeckli, and T. A. Centeno. 2009. Cherry stones as precursor of activated carbons for supercapacitors. Materials Chemistry and Physics 114 (1):323-327.

Oliveira, L. C. A., E. Pereira, I. R. Guimaraes, A. Vallone, M. Pereira, J. P. Mesquita, and K. Sapag. 2009. Preparation of activated carbons from coffee husks utilizing $FeCl_3$ and $ZnCl_2$ as activating agents. Journal of Hazardous Materials 165 (1-3):87-94.

Patnukao, P., and P. Pavasant. 2008. Activated carbon from Eucalyptus camaldulensis Dehn bark using phosphoric acid activation. Bioresource Technology 99 (17):8540-8543.

Prahas, D., Y. Kartika, N. Indraswati, and S. Ismadji. 2008. Activated carbon from jackfruit peel waste by H_3PO_4 chemical activation: Pore structure and surface chemistry characterization. Chemical Engineering Journal 140 (1-3):32-42.

Qian, Q., M. Machida, and H. Tatsumoto. 2007. Preparation of activated carbons from cattle-manure compost by zinc chloride activation. Bioresource Technology 98 (2):353-360.

Rafatullah, M., Sulaiman, O., Hashim, R., and Ahmad, A. 2009. Adsorption of copper (II), chromium (III), nickel (II) and lead (II) ions from aqueous solutions by meranti sawdust. Journal of Hazardous Materials

Reed, A.R., and Williams, P.T. 2004. Thermal processing of biomass natural fibre wastes by pyrolysis. Int. Journal of Energy Res. 28, 131–145.

Rosas, J. M., J. Bedia, J. Rodr̊guez-Mirasol, and T. Cordero. 2009. HEMP-derived activated carbon fibers by chemical activation with phosphoric acid. Fuel 88 (1):19-26.

Sahay, K. M., Singh, K.K. 1996. Unit Operation of Agricultural Processing. Vikas Publishing House Pvt. Ltd., New Delhi, India.

Savova, D., E. Apak, E. Ekinci, F. Yardim, N. Petrov, T. Budinova, M. Razvigorova, and V. Minkova. 2001. Biomass conversion to carbon adsorbents and gas. Biomass and Bioenergy 21 (2):133-142.

Sentorun-Shalaby, C., Ucak-Astarlıoglu, M.G., Artok, L., and Sarıcı, C. 2006. Preparation and characterization of activated carbons by one-step steam pyrolysis/activation from apricot stones. Journal of Microporous and Mesoporous Materials 88 : 126–134

Sing, K.S.W. 1998. Adsorption methods for the characterization of porous materials. Advances in Colloid and Interface Science 76-77: 3-11.

Srinivasakannan et al. 2004. Production of activated carbon from rubber wood sawdust. Biomass and Bioenergy 27 (1):89-96.

Suhas, P.J.M.C., and Ribeiro, M.M.L.C. 2007. Lignin – from natural adsorbent to activated carbon: A review. Journal of Bioresource Technology 98: 2301–2312

Sutcu, H., and H. Demiral. 2009. Production of granular activated carbons from loquat stones by chemical activation. Journal of Analytical and Applied Pyrolysis 84 (1):47-52.

Suzuki, R.M., Andrade, A.D., Sousa, J.C., and Rollemberg, M.C. 2007. Preparation and characterization of activated carbon from rice bran. Journal of Bioresource Technology 98:1985–1991

Tay, T., S. Ucar, and S. Karagoz. 2009. Preparation and characterization of activated carbon from waste biomass. Journal of Hazardous Materials 165 (1-3):481-485.

Temmink, H., and K. Grolle. 2005. Tertiary activated carbon treatment of paper and board industry wastewater. Bioresource Technology 96 (15):1683-1689.

Tseng, R-L., Tseng, S-K., Wu, F-C., Hu, C-C., and Wang, C-C. 2008. Effects of micropore development on the physicochemical properties of KOH-activated carbons. Journal of the Chinese Institute of Chemical Engineers 39: 37–47.

Ucar, S., M. Erdem, T. Tay, and S. Karagaz. 2009. Preparation and characterization of activated carbon produced from pomegranate seeds by $ZnCl_2$ activation. Applied Surface Science 255 (21):8890-8896.

Usmani, T. H., T. W. Ahmad, and A. H. K. Yousufzai. 1994. Preparation and liquid-phase characterization of granular activated-carbon from rice husk. Bioresource Technology 48 (1):31-35.

Usmani, T. H., T. W. Ahmad, and A. H. K. Yousufzai. 1994. Preparation and liquid-phase characterization of granular activated-carbon from rice husk. Journal of Bioresource Technology 48 (1):31-35.

Wang, X., N. Zhu, and B. Yin. 2008. Preparation of sludge-based activated carbon and its application in dye wastewater treatment. Journal of Hazardous Materials 153 (1-2):22-27.

Yagmur, E., M. Ozmak, and Z. Aktas. 2008. A novel method for production of activated carbon from waste tea by chemical activation with microwave energy. Fuel 87 (15-16):3278-3285.

Yorgun, S., N. Vural, and H. Demiral. 2009. Preparation of high-surface area activated carbons from Paulownia wood by $ZnCl_2$ activation. Microporous and Mesoporous Materials 122 (1-3):189-194.

Youssef, A. M., N. R. E. Radwan, I. Abdel-Gawad, and G. A. A. Singer. 2005. Textural properties of activated carbons from apricot stones. Colloids and Surfaces A: Physicochemical and Engineering Aspects 252 (2-3):143-151.

Zabaniotou, A., Stavropoulos, G., and Skoulou, V.2008. Activated carbon from olive kernels in a two-stage process: Industrial improvement. Journal of Bioresource Technology 99: 320–326.

Zanzi, R., Bai, X., Capdevila, P., and Bjornbom, E. Pyrolysis of Biomass in Presence of Steam for Preparation of Activated Carbon, Liquid and Gaseous Products, 6th World Congress of Chemical Engineering Melbourne, pp.1-8. Australia, 2001

Zhu, J., Yang, J., and Deng, B. 2009. Enhanced mercury ion adsorption by amine-modified activated carbon. Journal of Hazardous Materials 166: 866–872.

Output จากโครงการวิจัยที่ได้รับทุนจาก สกว.

การนำเสนอผลงานในการประชุมวิชาการระดับชาติ

1. Wichanon Watsanathip, Vorapot Kanokkantapong and Prasert Pavasant. Preparation of activated carbon from Jatropha wastes via phosphoric acid chemical activation. การประชุมวิชาการวิศวกรรมเคมีและเคมีประยุกต์แห่งประเทศไทย ครั้งที่ 19, 26 - 27 ต.ค. 52 ณ เฟลิกซ์ ริเวอร์แคว รีสอร์ท จ.กาญจนบุรี
2. Activated carbon from Eucalyptus bark with carbon dioxide activation. Thanyalak Kiatthanasakun, Vorapot Kanokkantapong, Prasert Pavasant. การประชุมวิชาการวิศวกรรมเคมีและเคมีประยุกต์แห่งประเทศไทย ครั้งที่ 19, 26 - 27 ตุลาคม 2552 ณ เฟลิกซ์ ริเวอร์แคว รีสอร์ท จ.กาญจนบุรี

อยู่ระหว่างการเขียนเพื่อตีพิมพ์

Vorapot Kanokkantapong and Prasert Pavasant, Comparison between physical and chemical activations of activated carbon from Jatropha seed waste involving life cycle thinking approach. คาดว่าจะส่งตีพิมพ์ในวารสาร Hazardous Materials

ภาคผนวก

Preparation of activated carbon from Jatropha wastes via phosphoric acid chemical activation

Wichanon Watsanathip[1], Vorapot Kanokkantapong[2] and Prasert Pavasant[1,3,*]
1) Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University
Chulalongkorn University, Bangkok 10330
2) Department of Environmental Health, Faculty of Public and Environmental Health,
Huachiew Chalermprakiet University, Samutprakarn 10540
3) Center of Excellence for Environmental and Hazardous Waste Management,
Chulalongkorn University, Bangkok 10330, e-mail: prasert.p@chula.ac.th

Abstract

The preparation conditions of activated carbon from waste of jatropha seed cake and shell were determined at various temperatures (500, 600, and 700 °C), activation times (60, 120 and 180 min.), and ratios of raw material: phosphoric acid (1:0.5, 1:1, and 1:1.5). The derived activated carbon was analyzed for its the Brunauer–Emmett–Teller (BET) specific surface area, Scanning electron microscopy (SEM), ash content, particle size, bulk density, yield, and weight loss. The yield of product decreased with an increase in activation temperature. Surface area also increased from 193 to 507 m^2/g as the activation temperature increased from 500 to 700°C. Increasing activation time from 60 to 120 min. enhanced the surface area from 379 to 507 m^2/g but reduced the iodine number from approx. 900 to 500 mg/g. For activated carbon produced from jatropha shell, surface area slightly improved from 492 to 533 m^2/g and iodine number from 338 to 461 mg/g with activation temperature increased from 500 to 600°C.

1. Introduction

Activated carbon is one of the favorable treatment approaches using adsorption mechanism. It involves in several industrial sectors e.g., air purifier industry, drinking water and tap water industry, metal-plated industry, and food industry[4], and in domestic sector purposes e.g., odors removal from refrigerator, wardrobe and closet's smells, etc. Rate of activated carbon imported to Thailand in the years 2005 to 2008 has continuously increased from 205, 267, 729 and, 1,230 million Bahts, respectively. Thus, it can be seen that activated carbon market is quite broad and has potential for consistent demand in the country. Activated carbon can mainly be generated from agriculture waste e.g. eucalyptus, sugarcane, etc. Jatropha has been promoted as an energy plant in Thailand. However, the remaining waste from this bio-diesel production should also be regarded as a considerate problem because 10,000 m^2 of jatropha to diesel production produces over 2,000 kg of shell and seed cake.

Normally, activated carbon can be produced from physical or chemical activation. For chemical activation, it uses chemical agent to impregnate raw material at range of temperature 450-900°C. The activated carbons obtained by chemical activation are with high surface area and with well-developed microporosity, which can be controlled and maintained narrow[3]. All chemical agents used are dehydrating agent that influence pyrolytic decomposition and inhibit formation or tar, thus enhancing the yield of carbon[1]. The most widely used chemicals are acids such as phosphoric acid (H_3PO_4)[2,5,7,10,11], or bases such as potassium carbonate (K_2CO_3)[3], potassium hydroxide (KOH)[7] and salts such as sodium chloride (NaCl) and zinc chloride ($ZnCl_2$)[6]. This study aims to examine the potential of producing activated carbon from Jatropha wastes by acid activation (phosphoric acid).

2. Experimental methods

2.1 Preparation of activated carbon using phosphoric acid an potassium hydroxide as activating agents

Jatropha seed waste obtained from Jatropha school in Kasetsart University, Kamphaeng Saen Campus, was mixed with 85% phosphoric acid at various ratio 1:0.5, 1:1, and 1:1.5 and stirred thoroughly until well mixed at room temperature. Carbonization and activation processes were then carried out in a muffle furnace at targeted temperatures (500, 600, and 700°C) and various times (60, 120 and 180 min.). Derived activated carbon was washed with hot distilled water until the final pH reaches approx. 6-8, then dry in oven at 105°C for 4 h. Finally, activated carbon was crushed and sieved in the size ranged between mesh number 100 (0.150 mm) and 325 (0.045 mm) and stored in dessicator before further analysis.

2.2 Analysis of activated carbon

The analysis of activated carbon included the surface area of activated carbon was Brunauer–Emmett–Teller (BET), The surface morphology of activated carbon was visualized via scanning electron microscopy (SEM). The ultimate analysis of Jatropha seed cake and shell was performed by CHNS/O analyzer (Perkin Elmer PE2400 Series II), X-ray diffraction (XRD). Functional group was analyzed by Fourier Transform Infrared Spectroscopy (FTIR). Characterization of activated carbon i.e., moisture content, ash content, particle size, bulk density, yield of activated carbon and weight loss, and volatile matter, and adsorption ability of activated carbon i.e., iodine number, methylene blue number were investigated.

3. Results and discussion

3.1 Optimal activation temperature

Higher carbonization temperature played an important role in increasing surface area of activated carbon from jatropha seed from 193 m^2/g at 500°C to 507 m^2/g at 700°C. However, this high temperature tended to reduce the yield. In the case of jatropha shell, increasing carbonization temperature resulted in an increase in the surface area from 492 m^2/g (500°C) to 533 m^2/g (600°C) and iodine number from 338 to 461 mg/g.

3.2 Optimal activation time

For Jatropha seed cake, an increase in activation time from 60 to 120 min enhanced the surface area from 379 to 507 m^2/g but decreased the iodine number from approx. 900 to 500 mg/g.

3.3 Optimal weight ratio of raw material and phosphoric acid

Iodine number of Jatropha shell rose from 338 to 380 mg/g but surface area decreased from 493 to 175 m^2/g when changing the weight ratio of raw material and phosphoric acid from 1:0.5 to 1:1.

4. Conclusion

- The effective conditions for the preparation of activated carbon from jatropha seed cake were carbonization at 700 °C 60 min. and weight ratio of raw material and phosphoric acid of 1:1.

- The effective conditions for the preparation of activated carbon from jatropha shell are carbonization at 600 °C 60 min. and weight ratio of raw material and phosphoric acid is 1:0.5.

5. Reference

[1] Aravindhan R. Preparation and characterization of activated carbon from marine macro-algal biomass. J. Hazardous Meterial 162(2009) p.688-694

[2] Baccar R. Preparation of activated carbon from Tunisian olive-waste cakes and its application for adsorption of heavy metal ions. J. Hazardous Meterial 162 (2009) p.1522-1529

[3] Budinova T. Characterization and application of activated carbon produced by H_3PO_4 and water vapor activation. Fuel Processing Technology 87 (2006) p.899-905

[4] CARELS N. Jatropha curcas: Review. Advances in Botanical Research, 50 (2009)

[5] Girgis B.S. Pilot production of activated carbon from cotton stalks using H_3PO_4. J. Anal. Appl. Pyrolysis (2009)

[6] Gurses A. Production of granular activated carbon from waste *Rosa canina* sp. seeds and its adsorption characteristics for dye. J. Hazardous Meterial B131 (2006) p.254-259

[7] Haimour N.H. Utilization of date stones for production of activated carbon using phosphoric acid. Waste Management 26(2006) 651-660

[8] Jibril B. Effects of H_3PO_4 and KOH in carbonization of lignocellulosic material. J. Anal. Appl. Pyrolysis 83(2008) p.151-156

[9] Namasivayam C. Removal of anions, heavy metals, organics and dye from water by adsorption onto a new activated carbon from jatropha husk, an agro-industrial solid waste. Process Safety and Environmental Protection. 85(B2)(2007) p.181–184

[10] Pavasant P. Activated carbon from *Eucalyptus camaldulensis Dehn* bark using phosphoric acid activation. Bioresource Technology 99 (2008) p.8540-8543

[11] Prahas D. Activated carbon from jackfruit peel waste by H_3PO_4 chemical activation: Pore structure and surface chemistry characterization. Chemical Engineering J. 140 (2008) p.32-42

Activated carbon from Eucalyptus bark with carbon dioxide activation

Thanyalak Kiatthanasakun[1, 2], Vorapot Kanokkantapong[3] and Prasert Pavasant[4,*]
1) International Postgraduate Programs in Environmental Management,
Graduate School, Chulalongkorn University, Bangkok, 10330
2) National Center of Excellence for Environmental and Hazardous Waste Management
(NCE-EHWM), Chulalongkorn University, Bangkok, 10330
2) Department of Environmental Health, Faculty of Public and Environmental Health,
Huachiew Chalermprakiet University, Samutprakarn 10540
3) Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University/
Center of Excellence for Environmental and Hazardous Waste Management,
Chulalongkorn University, Bangkok 10330, e-mail: prasert.p@chula.ac.th

Abstract

Activated carbon was produced from eucalyptus bark using CO_2 activation process. The preparation process consisted of carbonization under the N_2 flow at various temperatures (400, 450, 500 and 550 °C) and various times (45, 60, 90 and 120 min.) followed by activating the derived chars with activating agents (CO_2). The activation temperature was varied from 700 to 900 °C and activation time from 60 to 150 min. The derived activated carbon was characterized for its Brunauer-Emmett-Teller (BET) surface area test, total pore volume, mesopore volume, micropore volume and average pore diameter. Preliminary results revealed that the optimal temperature and time for the carbonization process and optimal temperature for activation process were 450 °C and 45 min, and 900 °C, respectively.

1. Introduction

Urbanization and industrialization inevitably cause wastewater pollution, including wastewater contaminated with heavy metals. Several treatment processes can be used for removing heavy metals from wastewater, e.g. metal coagulation, ion exchange and adsorption. Activated carbon is one of the most widely used processes for waste streams containing low level of heavy metals due to its durability and cost effectiveness [3].

In principle, the methods for preparing activated carbon can be divided into two categories, i.e. chemical and physical activations. For the physical activation, the raw material is carbonized in an inert atmosphere at a temperature below 700°C and then activated by steam or carbon dioxide (CO_2) at temperatures range from 800 to 1000°C. This high temperature requirement is compensated by the elimination of chemical contaminants and shorter production time [6].

The pulp mill has generated a large quantity of eucalyptus bark which needs to be dealt with before being disposed of. The conversion of eucalyptus bark into activated carbon has been shown to be feasible and can be treated as one alternative for the management of pulp waste. Previous study revealed that eucalyptus bark has relatively high carbon and low inorganic content which makes it suitable for preparing activated carbon [4]. Thus, this study aims to extend the research finding to cover the mechanism of physical technique in the preparation of activated carbon. The activation with CO_2 will therefore be investigated.

2. Experimental methods

The schematic of the experimental set up is shown in Fig. 1.

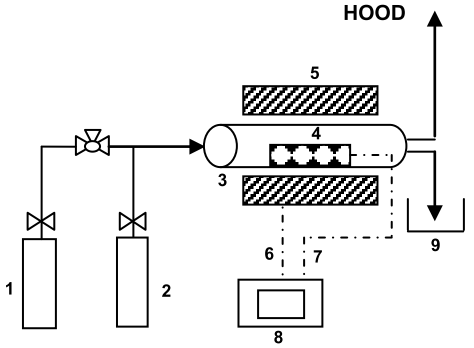

Figure 1. Schematic diagram of the experimental set up: (1) nitrogen gas cylinder; (2) carbondioxide cylinder; (3) tubular reactor; (4) sample; (5) tubular furnace; (6) furnace thermocouple; (7) sample thermocouple; (8) temperature controller; (9) beaker (liquid product collectors).

2.1 Carbonization process

A stainless steel tube reactor filled with 20 g of eucalyptus bark was carbonized in a Horizontal tubular furnace at various times (45, 60, 90 and 120) and various temperatures (400, 450, 500 and 550˚C) under the flow of N_2 gas at 200 $cm^3 min^{-1}$. The heating rate was controlled at 10˚C min^{-1}, and in all cases, the initial temperature was at room condition (30˚C). Then the resulting char was allowed to cool to room temperature in the furnace. The chars were analyzed by proximate analysis and BET.

2.2 Activation process

Activation process was carried out in a Horizontal tubular furnace using CO_2 as activating agent. In order to investigate the optimal activation condition, 3 temperatures (700, 800 and 900 °C), 4 activation times (60, 90, 120 and 150) and 3 activating agents flow rates (100, 150 and 200 $cm^3 min^{-1}$) were investigated. Characteristics of activated carbon were analyzed by proximate analysis, iodine number, and BET.

3 Results and discussion

3.1 Proximate analysis of materials

Eucalyptus bark as the precursor material was procured from the actual pulp mill in Prachinburi province. The proximate analysis shows that this bark constitutes of fixed carbon, volatile matters, ash, and moisture at 14%, 74 %, 7% and 5%, respectively.

3.2 Optimal carbonization temperature

Higher carbonization temperature (550 to 400 °C) caused a decrease in amount of volatile matter from 28% to 18% due to devolatilization and thermal degradation of extractives as well as high-molecular weight hydrocarbons [5]. Charcoal yield decreased from 40% to 35% while fixed carbon and ash content increased from 56% to 64% and 15% to 18%, respectively. Higher temperature obtained by prolonging pyrolysis period caused the carboxylic and phenolic structures in charcoal to decompose, leaving it with porous structure [1]. The optimal temperature for production of eucarlyptus bark activated carbon was 450°C.

3.3 Optimal carbonization time

Increasing carbonization time from 45 to 120 min suggested decreasing of both volatile matters in charcoal, charcoal yield and moisture content from 30% to 25%, 40% to 38 % and 1% to 0.5%, respectively. On the other hand, fixed carbon increased from 53 to 58, whereas ash content remained almost constant at 16-17%. The optimal carbonizing time for the production of eucarlyptus bark activated carbon was 45 min.

3.4 Optimal activation temperature

The activated carbon yield was seen to decrease from 34 to 26% as activation temperatures increased from 700 to 900 °C. During these temperatures, there was a combination of continual devolatilization of volatile matters and carbon. Activation temperature from 700 to 900 °C caused an increase in iodine number from 330 to 656 mg/l due to an increasing rate of reaction between carbon and CO_2, which resulted in the development of internal surface area and porosity. However, during pyrolysis, some of the pores might have been blocked by deposition of carbonaceous tar materials during the cooling period after pyrolysis [2].

4 Conclusion

The best conditions for the preparation of activated carbon from eucalyptus bark using CO_2 activation were found at carbonization temperature of 450°C, a carbonization time of 45 min and activation temperature of 900°C.

5 References

[1] Ahmad MA. Carbonization of low rank coal. MSc Thesis, Universiti Sains Malaysia (2002) p. 1-91.

[2] A.L. Ahmad, M.M. Loh, J.A. Aziz, Preparation and characterization of activated carbon from oil palm wood and its evaluation on Methylene blue adsorption, *J. Dyes and Pigments* 75 (2007) p. 263-272

[3] Department of industrial works, *Textbook water pollution treatment systems* (2006)

[4] J.F. Gonzalez, S. Roman, J.M. Encinar, G. Martinez, Pyrolysis of various biomass residues and char utilization for the production of activated carbons, *J. Anal. Appl. Pyrolysis* 2289 (2009)

[5] Khalik MS. Studies on the production of charcoal by carbonization using mangrove wood in Malaysia. MSc Thesis, Universiti Sains Malaysia (2000) p. 1-141.

[6] Laine, J., and S. Yunes, Effect of the Preparation Method on the Pore Size Distribution of Activated Carbon from Coconut Shell. *J. Carbon* 30, (1992) p.601-604.