UNIVERSITI PUTRA MALAYSIA

PREPARATION AND CHARACTERIZATION OF GELAM WOOD AND RICE HUSK ACTIVATED CARBONS FOR THIN LAYER CHROMATOGRAPHY STATIONARY PHASE

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By

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Chairman : Associate Professor Anuar Kassim , Ph.D.

Faculty : Science and Environmental Studies

Gelam wood (*Meleuca Cajiputi*) was used as a precusor for the preparation of activated carbon. Potassium orthophosphate, potassium hydroxide , phosphoric acid and carbon-dioxide were used as chemical and physical activating agents. The industrial activated carbons AC (7080 and 4050) were used as comparison. In addition physically activated carbon of rice husk was also used in this study. Thirty grams of shredded gelam wood were impregnated with 9% w/w K_3PO_4, for the potassium hydroxide impregnation 9% w/w KOH was impregnated with thirty grams of wood. 2.2 M H_3PO_4 concentration of phosphoric acid was used for the impregnation of thirty grams of gelam wood.Then the impregnated wood was carbonized in a horizontal electric furnace. The activated carbons were washed using 1.0 M nitric acid followed by distilled water using reflux method.

Surface area, functional group analysis, elemental analysis, pH effect, moisture and ash content are some of the characterization methods done on the activated carbons. The study of the surface morphology was done using the scanning electron microscope. Elemental constituents of the activated carbons was done using atomic absorption analysis. The atomic absorption spectra showed that Ca, K, Mg, Zn, Pb and Fe were present in the activated carbons.

Thin layer chromatography was done to show the separation and selective retention of the amino acids used in this research. Namely thyroxine, isoleucine and leucine. Solvents used for separation methanol, ethanol, butanol, propanon, acetone, acetic acid and ethanol : butanol (9:1, 8:2, 7:3) v/v, butanol : propanol (9:1, 8:2, 7:3) v/v, acetic acid : water (9:1, 8:2, 7:3) v/v, acetone : water (9:1, 8:2, 7:3) v/v. Three factors which played a important role in the separation and selective retention are (i) polarity of the solvent (ii) characteristic of the activated carbon and (iii) characteristic of the amino acids used. Whereby the methanol, butanol and propanol showed that the amino acids can be separated effectively compared to that of propanon, and acetone. Wherelase the AC 7080 showed it was the most effective activated carbon for the separation and the lowest being rice husk (Phy). For the combination solvent system, the ethanol:butanol (7:3)v/v showed most effective combination for the separation of the amino acids the lowest being acetone:water for all its volume per volume ratio. Amongst the three amino acids, isoleucine and leucine showed it can be separated compared to that of thyroxine for the single solvent system and combination solvent system.

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

PENYEDIAAN DAN PENCIRIAN KARBON TERAKTIF KAYU GELAM DAN HAMPAS PADI SEBAGAI FASA PEGUN UNTUK KROMATOGRAFI TURUS NIPIS

Oleh

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Kayu gelam (*Meleuca Cajiputi*) diguna sebagai prekusor dalam penyediaan karbon teraktif. Kalium ortofosfat, kalium hidroksida, asid fosforik dan gas karbon dioksida bertindak sebagai agen fizikal dan kimia. AC 7080 dan AC 4050 karbon teraktif dibeli untuk tujuan perbandingan. Karbon teraktif hampas padi yang telah diaktifkan secara fizikal juga telah digunakkan di dalam kajian ini. Tiga puluh gram kayu gelam yang dipotong nipis telah dimpregnasikan dengan 9 % w/w K_3PO_4. Untuk impregnasi kalium hidroksida , 9 % w/w telah digunakan dicampur bersama tiga puluh gram kayu gelam. Asid fosforik 2.2 M telah ditambah dengan tiga puluh gram kayu gelam untuk impregnasi asid fosforik. Kayu gelam yang dimpregnasi dibakar dengan kebuk pemanasan elektrik. Karbon teraktif yang terhasil dibasuh dengan menggunakkan 1.0 M asid nitric dan air suling.

Analisis kumpulan berfungsi, kandungan logam, kesan pH, kandungan kelembapan, dan kandungan abu adalah diantara kaedah pencirian yang dilakukan ke atas karbon teraktif. Kajian morfologi permukaan karbon teraktif dilakukan dengan menggunakkan elektron mikroskop. Untuk menentukan kandungan logam di dalam karbon teraktif ditentukan melalui spektroskopi penyerapan atom. Melalui kaedah tersebut dapat ditentukan kewujudan logam kalsium, magnesium, zink, plumbum dan ferum wujud di dalam karbon teraktif.

Proses pemisahan asid amino telah dilakukan melalui kaedah kromatografi turus nipis. Asid amino yang digunakan adalah tyroxine, isoleucine dan leucine. Pelarut – pelarut yang digunakan adalah metanol, butanol, propanon, asetone, asid asetik dan etanol : butanol (9:1, 8:2, 7:3) v/v, butanol : propanol (9:1, 8:2, 7:3) v/v, asid asetik : air (9:1, 8:2, 7:3) v/v dan asetone : air (9:1, 8:2, 7:3) v/v. Tiga factor utama yang memainkan peranan yang penting dalam pemisahan dan penahanan selektif asid amino adalah (i) kepolaran pelarut (ii) sifat karbon teraktif (iii) sifat asid amino. Pelarut metanol, butanol dan propanol berjaya memisahkan asid amino berbanding pelarut propanon dan asetone. Manakala AC 7080 merupakan karbon teraktif yang paling efektif yang dapat memisahkan asid amino berbanding karbon teraktif hampas padi yang kurang berkesan dalam pemisahan asid amino. Untuk pelarut campuran, kombinasi etanol : butanol (7:3) v/v merupakan yang paling efektif dalam pemisahan asid amino berbanding pelarut asetone : air. Kalangan ketiga- tiga asid amino isoleucine dan leucine menunjukkan ia dapat dipisahkan dengan berkesan berbanding tyroxine bagi semua pelarut dan kombinasi pelarut yang digunakkan.

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Gelam (PHY)	physically activated carbon of gelam wood
Gelam (K_3PO_4)	potassium orthophosphate impregnated activated carbon of gelam wood
Gelam(H_3PO_4)	phosphoric acid impregnated activated carbon of gelam wood
Gelam (KOH)	potassium hydroxide impregnated activated carbon of gelam wood
Rice husk(PHY)	physically activated carbon of rice husk
AC 7080	industrial activated carbon purchased from a local factory
AC 4050	industrial activated carbon purchased from a local factory
Bef wash	before wash
Aft wash	after wash
v/v	volume per volume
w/w	weight per weight
$R_{(f)}$	retention factor value
TLC	thin layer chromatography
TI solution	combination of two amino acids in a solution (thyroxine and isoleucine)
TL solution	combination of two amino acids in a solution (thyroxine and isoleucine)

CHAPTER 1

INTRODUCTION

Activated carbon is a crude form of graphite and is commonly made from wood, coal, lignite, and coconut shell. The imperfect structure of activated carbon, which is highly porous is what differentiates it from graphite. These pores range in size from visible cracks and crevices to microscopic dimensions. This structure gives the carbon its very large surface area, which allows the carbon to adsorb such a wide range of components. Activated carbon has the strongest physical adsorbent force or the highest volume of adsorbing porosity of any substance known to mankind.

Coals and ligno-cellulosic materials are commonly used as a starting material, for preparing activated carbon. Recently, numerous attempts to prepare activated carbon from solid wastes have also been made. The development of methods to re-use waste materials is greatly desired and production of activated carbons from wastes is an interesting possibility. Lignin is a waste which generally used only for its fuel value. Therefore, it was of interest to prepare a higher value product such as an activated carbon from lignin.

A substance is first subjected to a heating process called carbonisation. This forms a fixed carbon mass that is full of tiny pores. It is then activated by a second heat/steam treatment (200-1600) °C while regulating oxygen level. This is what creates the huge internal pore network and imparts surface chemistries that gives carbon its unique characteristics. Three forms of activated carbon: (1) granular – irregular shaped particles ranging in size from 0.2 to 5 mm. (2) powder – pulverized carbon (3) extruded and cylindrical in shape. Many studies preparing activated carbon by chemical activation have been done. Recently, activated carbons with very high surface area have been prepared by chemical activation. Gas storage is a potential application for such a high surface area materials. However, the purpose of most of these studies was to prepare the activated carbon, and little attention has been given to the influence of the activating reagent on the pore structure and to mechanism of activation.

Proper utilisation of agroindustrial by-products is very important for the national economy. It would not only help in solving the disposal problem but would also help in reducing the shortages with respect to several materials. A large quantity of husk available as waste from rice-miling. Dry husks contains (70-85)% organic matter (lignin, cellulose, sugars) and the inorganic content consists of mainly silica.

Activated carbons are carbons which generally have a high surface area and complex pore structure resulting from physical or chemical activation processes. The structure of an activated carbon is composed of pores classified into three groups namely micropores, mesopores and macropores. Micropores usually account for over 95% of the total surface area of activated carbons. The volumes of the micropores range from 0.15 up to 0.6 $cm^3 g^{-1}$. Conventional activated carbons are tridisperse having all three types of pores present within the structure. Adsorbents molecules penetrate through the wider pores and into the micropore structure. Activated carbons are made by carbonising and then activating a material rich in carbon. Different activated carbons obtained from agricultural by products has also been studied. Activated carbons are highly effective adsorbents partly because of their large specific surface area. Activated carbon is predominantly an amorphous solid with a large internal surface area and pore volume. Several models have been proposed to describe its structure. The main feature common to all activated carbons are graphite-like planes, which show varying degrees of disorientation and the resulting spaces between these planes which constitute porosity. The units built of condensed aromatic rings are referred to as Basic Structural Units (BSU). Activated carbons adsorb molecules from both liquid and gaseous phases depending upon the pore size distribution of the adsorbent (and also upon the geometry and size distribution of the adsorbate molecule). In adsorption from gas phase mainly microporous carbon is used whereas mesoporous carbon is applied in liquid phase processes. Application of mesoporous activated carbons include drinking water purification, waste water treatment, sweetener discolouration, food and chemical processing. On the other hand, microporous carbons are used for solvent recovery, gasoline emission control, cigarette filters and industrial emission gas treatment. The usage of carbon adsorbents depends on their surface area, pore size distribution and chemical surface characteristics.

(a) Surface area – used as primary indicator of the activity level, based on the principle that the greater the surface area, the higher the number of adsorption sites available.

(b) Pore size distribution- determination of the pore size distribution of an activated carbon is an extremely useful way of understanding the performance character of the material. The macropores are used as the entrance to the activated carbon, mesopores for the transportation and micropores for adsorption.

(c) Carbon tetrachloride activity- measurement of the porosity of an activated carbon by the adsorption of saturated carbon tetrachloride vapor.

(d) Hardness – an important factor in system design, filter life and product handling. There are large differences in the hardness of activated carbon, depending on the raw material and activation level.

(e) Bulk density- should be carefully considered when filling fixed volume as it can have considerable commercial implications.

(f) Particle size distribution- the finer particles size of an activated carbon the better access to the surface area and faster the rate of adsorption kinetics. In vapor phase systems this needs to be considered against pressure adsorption, which will affect energy cost. Careful consideration of particle size distribution can provide significant operating benefits.

1.1 History

The adsorptive properties of activated carbon made activated carbon an adsorbent even in the centuries before Christ. It has been used in purifying water with charcoal by ancient Hindus . The medical use of charcoal was recommended by Hippocrates in 1550 B.C to dust wounds with powdered charcoal in order to remove the unpleasant odour. At the end of 18th century. Scheese discovered the adsorption of gasses on charcoal and Lovits found that charcoal decolorized tartaric acid (Ruthven, 1984). The discovery lead to the industrial application of charcoal in the sugar industry in England and this actually initiated research on adsorption from liquid phase

In the years 1900-1901, R V Ostrejko was granted two patents which opened new prospects for the manufacturing technology of activated carbons. The essence of the invention described in the first patent consisted in heating vegetable material with metal chlorides and that of the second patent in activating charcoal with CO_2 and steam at red heat (Biscoe and Warren 1942).

In 1911 in Netherlands, scientist named Norit NV began manufacturing activated carbon in commercial scale by using activation of peat with steam. According to Bansal *et al*, 1998 chemical activation of sawdust with $ZnCl_2$ was described in a patent and operated in Aussig, Czechslovakia and Bayer in 1915

During World War 1, Nikolai Zelinski was the first to suggest the use of activated carbon as the adsorption medium in masks (Gerhatz 1986).

1.2 Adsorption

Adsorption is the process by which activated carbon removes substances from water Defined adsorption is the collection of a substance onto the surface of adsorbent solids It is a removal process where carbon particles are bond to an adsorbent particle surface by either chemical or physical attraction Adsorption is often confused with absorption where the substance being