การไฮโดรเทอร์มอลคาร์บอนไนเซชันของผักตบชวาเพื่อผลิตวัสดุขั้วไฟฟ้าคาร์บอน

นางสาวธัญธร วนาวนิชย์กุล

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Hydrothermal carbonization of water hyacinth for producing carbon electrode materials

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ธัญธร วนาวนิชย์กุล : การไฮโดรเทอร์มอลคาร์บอนไนเซชันของผักตบชวาเพื่อผลิตวัสดุขั้วไฟฟ้าคาร์บอน (Hydrothermal carbonization of water hyacinth for producing carbon electrode materials) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: รศ. ดร.ธวัชชัย ชรินพาณิชกุล, อ.ที่ปรึกษาวิทยานิพนธ์ร่วม: ดร. ขจรศักดิ์ เฟื่องนวกิจ, ดร. นาวิน วิริยะเอี่ยมพิกุล, 91 หน้า.

ท่ามกลางปัญหาการจัดการทรัพยากรน้ำ การควบคุมปัจจัยทางสิ่งแวดล้อมโดยเฉพาะอย่างยิ่งปัญหามลภาวะทางสิ่งแวดล้อมของผักตบชวา ผักตบชวาได้กลายเป็นหัวข้อที่น่าสนใจในการศึกษาในงานวิจัยหลายประเทศ ด้วยเหตุผลที่ว่าผักตบชวาเป็นหนึ่งในพืชรุกรานชนิดหนึ่ง ซึ่งก่อให้เกิดปัญหาทางสังคมและสิ่งแวดล้อมซึ่งในงานวิจัยนี้จึงได้นำผักตบชวามาใช้เป็นแหล่งวัสดุคาร์บอน เพื่อเพิ่มมูลค่าให้เพิ่มสูงขึ้นกับวัสดุ ซึ่งงานวิจัยนี้เลือกใช้วิธีการไฮโดรเทอร์มอลทรีเมนทำมาเป็นขั้นตอนในการใช้สำหรับการแปลงผักตบชวา โดยใช้ช่วงที่อุณหภูมิ 160-220 องศาเซลเซียส เป็นเวลา 4-12 ชั่วโมง โดยการไฮโดรเทอรมอลทรีเมนที่อุณหภูมิ 220 องศาเซลเซียส เป็นเวลา 8 ชั่วโมง ได้แสดงปริมาณของคาร์บอนที่สูงที่สุด คือ 57.27% โดยน้ำหนัก ผลิตภัณฑ์จากกระบวนการไฮโดรเทอรมอลทรีเมนหรือไฮโดรชาร์จะแสดงหมู่ฟังชั่นของออกซิเจนต่างๆ และองค์ประกอบสารซึ่งอยู่บนพื้นผิว ดังนั้นจึงส่งผลให้คุณสมบัติและปริมาณคาร์บอนในไฮโดรชาร์มีปริมาณที่สูงขึ้น หลังจากนั้นไฮโดรชาร์ถูกนำไปคาร์บอนไนเซชั่นที่อุณหภูมิ 900 องศาเซลเซียส พบว่าการไฮโดรเทอรมอลทรีเมนส่งผลต่อผลิตภัณฑ์ของการคาร์บอนไนเซชั่น โดยที่อุณหภูมิในการไฮโดรเทอรมอลทรีเมนที่ 180 องศาเซลเซียส เป็นเวลา 8 ชั่วโมง ส่งผลให้ได้พื้นที่ผิวจำเพาะสูงสุด คือ 635.8 ตางรางเมตรต่อกรัม และการไฮโดรเทอรมอลทรีเมนที่ 220 องศาเซลเซียส เป็นเวลา 8 ชั่วโมง ส่งผลให้ได้ค่าการนำไฟฟ้าสูงสุดและปริมาณคาร์บอนสูงสุด คือ 73.10 % โดยน้ำหนัก นอกจากนี้ยังได้มีการสังเคราะห์วัสดุไฮบริดของอนุภาคคาร์บอนกับเหล็ก ซึ่งพบว่าการไฮโดรเทอรมอลทรีเมนที่ 180 องศาเซลเซียส เป็นเวลา 8 ชั่วโมง และคาร์บอนไนเซชั่นที่อุณหภูมิ 900 องศาเซลเซียส ได้วัสดุไฮบริดที่มีสัดส่วนเหล็กออกไซด์ต่อตัวอย่าง 28.2% โดยน้ำหนัก หลังจากนั้นวัสดุดังกล่าวถูกนำไปใช้เป็นแท่งอิเล็กโทรดเพื่อผลิตคาร์บอนระดับนาโนเมตรในการอาร์ดิสชาร์ตในน้ำ

ภาควิชา วิศวกรรมเคมี ลายมือชื่อนิสิต .....

สาขาวิชา วิศวกรรมเคมี ลายมือชื่อ อ.ที่ปรึกษาหลัก .....

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5770200721 : MAJOR CHEMICAL ENGINEERING
KEYWORDS: WATER HYACINTH / HYDROTHERMAL TREATMENT / CARBONIZATION / ARC DISCHARGE IN WATER / CARBONACEOUS MATERIALS

THANTORN VANAVANICHKUL: Hydrothermal carbonization of water hyacinth for producing carbon electrode materials. ADVISOR: ASSOC. PROF. TAWATCHAI CHARINPANITKUL, Ph.D., CO-ADVISOR: KAJORNSAK FAUNGNAWAKIJ, Ph.D., NAWIN VIRIYA-EMPIKUL, Ph.D., 91 pp.

Among various issues of water resource management, control of environmental nuisances, especially water hyacinth has become an important research topic in many countries because it is one of the invasive plants which resulted in social and environmental problems. This research studied conversion of water hyacinth into high value-added carbonaceous materials. Hydrothermal treatment was utilized for converting water hyacinth in temperature range 160-220 °C for 4-12 hours. It was found that the water hyacinth treated hydrothermally at 220 °C for 8 hours showed highest carbon content of 57.27 w/w%. Hydro-chars were carbonized for removing oxygen contained contents of hydrogen, oxygen, and other constituents. The carbonized hydro-char would possess a higher carbon and improved surface properties. It was found that the carbonized hydro-char at 900 °C sample which was hydrothermally treated at 180 °C for 8 hours possessed the highest specific surface area of 635.8 m^2/g. Meanwhile, carbonized hydro-char at 900 °C sample which was hydrothermally treated at 220 °C for 8 hours possessed highest electric conductivity and carbon content of 73.1 w/w%. Moreover, the Fe-hybridized carbonaceous particle was successful synthesized by hydrothermal treatment and carbonization. Fe-hybridized carbonaceous was shown iron oxide 28.2 %w/w of the sample. Carbonized hydro-char was utilized as carbonaceous rods for fabricating electrode by conducting arc discharge in water

Department:	Chemical Engineering	Student's Signature	.....
Field of Study:	Chemical Engineering	Advisor's Signature	.....
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		Co-Advisor's Signature	.....

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CONTENTS

Page

Page

LIST OF FIGURES

LIST OF TABLES

Page

CHAPTER I

INTRODUCTION

1.1 Motivation for this research

Because of the growth population, a fuel and fossil material is high demand. Decreasing of fuel and fossil material has becomes seriously environmental problems. The fuel and fossil material is main a source of gas pollution especially carbon dioxide gas. The Carbon dioxide (CO_2) is one of greenhouse gas which impact on climate change. Climate change has been caused an increasing in the atmosphere temperature. Therefore, biomass has been used as a precursor leading to a decrease of releasing carbon dioxide gas [1, 2]. The biomass has attracted to utilize it as renewable resource. They can be a sustainable source instead of the fossil and fuel material. The biomass is presented on waste, wood agricultural and agricultural residuals. The biomass is an organic compound which is mainly a lignocellulosic material. The lignocelloulosic material is mainly consists of cellulose, hemicellulose, and lignin. They are significantly found elementary compound such as carbon, hydrogen and oxygen. Because of easy decompose compound, they could be used as the precursor which could convert to high value added. The biomass has attracted many attentions to utilize it as renewable material resources.

Water hyacinth is an interesting of renewable resources. The water hyacinth is one of an invasive plant which results in environmental problems, such as obstructing water transportation, decreasing oxygen content in water resource. Because of fast growing, water hyacinth causes water pollution. In the past, water hyacinth was removed by burning with oxygen which affected of clime change. However, water hyacinth consists of lignocellulosic materials. The water hyacinth has become an important topic in much kind of researches. The water hyacinth was utilized as feedstock for producing bio-fuel, fertilizer, catalyst [3, 4].

In many technologies for converting biomass into higher value-added products, hydrothermal treatment has been interested technology because it could convert biomass to high value-added 3 phase materials such as gas, liquid and carbonaceous material. Gas products were produced such as carbon dioxide, methane, hydrogen gas which was used for generating energy. However, generating gas products significantly treats high temperature and pressure for converting lignocellulosic materials. Liquid phase product composed of organic and acid compound materials which were used as a raw material for producing biodiesel. Solid product shows high carbon content and specific surface area. Converting biomass mainly gives carbonaceous product by using hydrothermal treatment. It was called hydrothermal carbonization [5]. Hydrothermal carbonization usually uses conditions in a temperature range 160 to 350 °C under autogenic pressure. Because of the addition of water, the water could react with biomass to generate products [6]. The water was decried by sub-critical water depending on processing temperature and time. This research focused on treatment temperature and reaction time on hydrothermal carbonization technology. In addition, a presence of $Fe(NO_3)_3 \bullet 9H_2O$ into dried water hyacinth powder was examined in hydrothermal carbonization for producing metal-hybridized material. However, hydro-char product showed functional groups compound on the surface. Functional groups helped to combine compound for making a rod. Then, the hydro-char was carbonized for removing radical on surface. Finally carbonized hydro-char was examined for exploring the possibility to produce carbonaceous rod which would be utilized as electrode materials of gas-injected arc-in-water technique.

1.2 Objectives

This thesis sets its aim to investigate the effects of temperature and time in hydrothermal carbonization of dried water hyacinth and an addition of $Fe(NO_3)_3 \cdot 9H_2O$ on characteristics of carbonaceous powders through comprehensive experiments and analyses. In addition, exploring on usage of producing electrode materials which would be utilized in gas-injected arc-in-water technique

1.3 Scope of this research

In order to achieve the objective described above, the following scope of experimental works would be taken into account.

1. Effect of hydrothermal treatment conditions of water hyacinth (leaf and trunk) on the properties of carbonaceous powder

1.1. 1:2 amount of dried water hyacinth and de-ionize water ratio

1.2. 160, 180, 200 and 220 °C of hydrothermal treatment temperature

1.3. 4, 8, and 12 hours of hydrothermal treatment time

1.4. 4, 8 and 12 g of Fe content filler on microscopic properties of Fe-hybridized hydro-char powder

2. Effect of carbonization temperature within nitrogen atmosphere on characteristics of final carbonaceous powder

2.1. 100 ml/min of nitrogen gas flow rate

2.2. 5 °C/min of heating rate

2.3. 500, 700, 900 °C of carbonization temperature

2.4. 2 hours of carbonization time

3. Effect of using synthesized Fe-hybridized carbonaceous rods and carbonaceous rods obtained carbonized water hyacinth treated hydrothermally as electrode material which would be employed in gas-injected arc-in-water technique. Testing condition of the gas-injected arc-in-water technique is determined with respects to an optimal condition reported by Poojarernsilp C.,at al.[21].

3.1 80 A of DC current supply

3.2 10 l/min of nitrogen flow rate inside cathode electrode

3.3 20 mm of cathode graphite rod diameter

3.3.1 2 mm of diameter and 25 lengths of diameter on 4 of hole upper

3.3.2 12 mm of diameter and 25 lengths of diameter on 1 of hole lower

3.4 1.5 mm/s of velocity of anode electrode

3.5 1 mm of distance of two electrodes by arc discharge

CHAPTER II

FUNDAMENTAL THEORY AND LITERATURE REVIEW

2.1 Biomass

Nowadays, environmental problems increased because energy consumption has demanded. Effect of reduction of energy resource significantly developed industry and technology. For researching energy material, many countries developed many materials. Fossil fuels are high-value materials which are competitive on the market for converting energy applications. The fossil and fuel importantly released excess carbon dioxide into the atmosphere. Biomass is a one of interesting material. Because biomass can use for power, fuel, production materials. In the past, biomass material was produced by burning with oxygen for conducting energy material. Effect of gas pollution mainly causes of increasing temperature. Recently, utilizing biomass material has used much technology and decreased greenhouse effect obtained from gas carbon dioxide. Biomass has regarded materials such as wood, food waste, crop, agricultural crop, and byproducts obtained from agricultural processes. Biomass is an organic material which has utilized the material in the form of the chemical structure [7]. Generally, biomass composed of a lignocellulosic material which represented chemical composition. The lignocellulosic material is mainly consists of cellulose, hemicellulose, and lignin as shown in **Fig.** 2.1

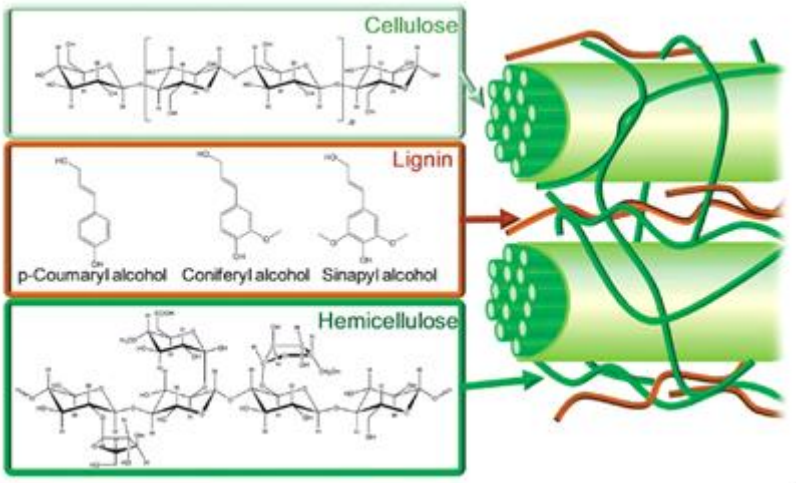


Fig. 2.1 Structure of lignocellulosic material with cellulose, hemicelluloses and building block of lignin [7]

A lignocellulosic material has utilized in many applications. Typically biomass showed the different of the chemical composition as shown in **Table** 2.1. It should be noted that a cellulose and hemicellulose showed high effectively for producing gas, liquid, and solid products because the cellulose and hemicellulose are easy decomposed. On the other hand, lignin has hindered decomposed lignocellulosic material [9].

Table 2.1 lignocellulosic composition on biomass

Lignocellulosic material	Cellulose (%)	Hemi-cellulose (%)	Lignin (%)
Hardwood	18-25	24-40	40-55
Softwood	25-35	25-35	45-50
Corn cabs	15	35	45
Wheat straw	16-21	26-32	29-35
Bagasse	23.33	16.52	54.87
Rice straw	16-21	26-32	29-35

2.1.1 Cellulose

In general, a lignocellulosic material mainly presented origin compound of cellulose which a homo-polymer compound. The cellulose is found in starch, glycogen, and other carbohydrates. The cellulose is composed of D-glucose ($C_6H_{10}O_5$) units linked by β-1,4 glycosidic bond via hydrogen bonds and van der Waals forces [7]. The structure of cellulose showed in **Fig**. 2.2. The amount of glucose is liked 3,000-10,000 units which presented fibrous structure both crystalline and amorphous. The amorphous structure is easy decomposed more than the crystalline structure by subcritical water. However, acid and base solution could improve hydrolysis reaction of cellulose. It should be noted that the cellulose could be hydrolyzed with de-ionized water at temperature of 180 °C

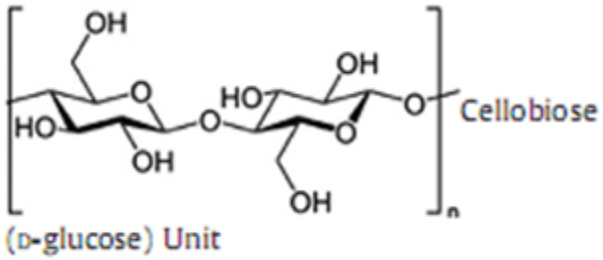


Fig. 2.2 Chemical structure of cellulose [7]

2.1.2 Hemi-cellulose

A hemicellulose is one of a lignocellulosic material. The hemicellulose was lowest decomposed treatment temperature to compare with a cellulose and lignin. Because of low molecular weight polymer, the hemicellulose consists of five and six carbon compound which presented in polymers such as pentose, hexoses, mannose, glucose, and sugar acids [8] The hemicellulose linked by (1→4)-glycosidic or α(1→2)-bonded 4-O-methylglucoronic acids as shown in **Fig** 2.3. The hemicellulose is a random amorphous structure which composed of shorter chains 500-3,000 sugar units. The hemicellulos was hydrolyzed bond at a temperature of 160 °C by using

hydrothermal treatment. Hydronium ions obtained from water could break hydrocarbon compound bond to xylose.

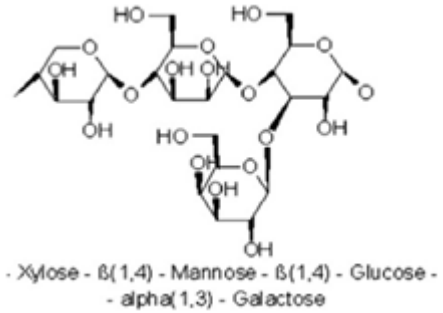


Fig. 2.3 Chemical structure of hemi-celluloses [7]

2.1.3 Lignin

A lignin is complex hydrocarbon structure as shown in **Fig.** 2.4. Normally, the lignin presented in the cell wall of biomass. The lignin is an amorphous structure which was cross-linked 10,000 units of a macromolecule. It showed highest hydrophobic interaction and aromatic structure. The lignin is the most thermally stable polymer and hard degradation. The lignin was decomposed at a temperature of 600 ºC under atmospheric conditions [7].

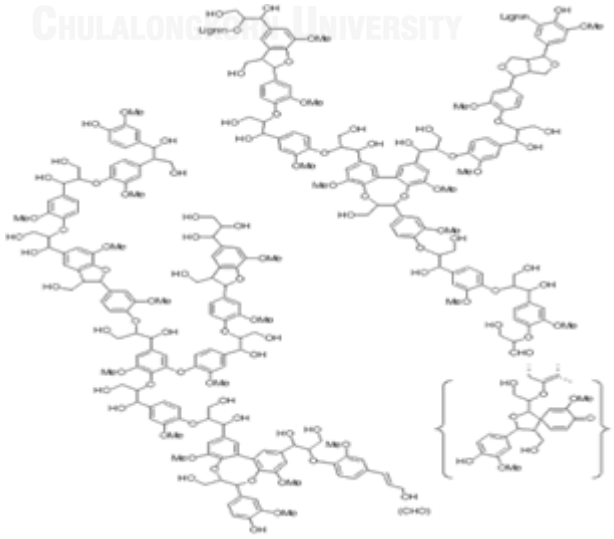


Fig. 2.4 Chemical structure of lignin [7]

By using the indigenous source of a biomass was converted to high value added. The biomass was not a problem on market. The biomass could be effectively developed for the production of fuel, energy and material. Meanwhile, water hyacinth is a one of lignocellulosic material which could be converted into valuable carbonaceous products with some promising applications.

2.2 Water hyacinth

Because of fossil fuel exhaustion, much research has to developed new materials. The factor of development such as low cost, high effectively, environment-friendly and sustainable resources are important. A lignocellulosic material is a performance converted to high value added. Among of various lignocellulosic, water hyacinth, a harmful aquatic weed, has been found in many countries. Therefore, the technological development for production from water hyacinth has recognized in many countries [10].

Water hyacinth (Eichhornia crassipes) is a floating plant on water which is recognized invasive species. The water hyacinth presented on 1 m of a trunk and 10-20 cm of leave. The water hyacinth propagates rapidly growth rate. The water hyacinth results in environmental problems such as decreasing water quality and obstructing water transport. In previous, the water hyacinth was eliminated by burning with oxygen. Products obtained burning with oxygen affected releasing carbon dioxide gas. Carbon dioxide impacts on climate change and increasing a temperature in the atmosphere. It was found that the water hyacinth is compared with another typically biomass. The water content of water hyacinth is up to 95% w/w. The drying process results in increasing cost and decreasing of efficiency [11]. However, the water hyacinth has many plant nutrients such as carbon, hydrogen, nitrogen, phosphorus and potassium. Utilizing of water hyacinth as a raw material was suitable and environment-friendly for produce some materials.

So far there are many methods which have been developed for converting water hyacinth into valuable compounds including carbonaceous products because of a high amount of hemicelluloses and cellulose as a carbon source [12, 13].

2.3 Hydrothermal Carbonization

Hydrothermal carbonization is a thermo-chemical process for converting organic feedstock into a high carbonaceous. During the process, a biomass and water were treated in temperature range 150-350 ºC with several times [6]. Usually, the reaction pressure is not controlled in the process. The process depends on an autogenously step with the saturation vapor pressure of subcritical water corresponding to the reaction temperature.

Hydrothermal carbonization eliminates the pre-drying requirements of a biomass which requires energy consumption when processed with thermal pre-treatment like slow pyrolysis. The resultant product was formed of three main products 3 phases 1) solid product (hydro-char), 2) liquid products (bio-oil in water) and 3) gas products (mainly CO_2) [14]. Generally, the biomass treated hydrothermally was used as raw material for producing glucose, xylose and acid solution. They have using feedstock for conducting bio-diesel or energy consumption. The solid product was neglected. However, the solid product is high carbon content and specific surface area. The carbonaceous particle was utilized in many applications, such as catalyst, energy storage and electrode material [15, 16].

In hydrothermal treatment, the raw material is decomposed to oligomers and monomer as water medium. Based and acid solution has corresponded to decompose on pressure, temperature and chemical treatment [17]. The hydrothermal carbonization is an exothermal process involving with a high degree of aromatization with a large number of oxygen and hydrogen content containing groups. The hydrothermal treatment could covert to higher oxygen functional groups. Both quantity and quality of those products depend on the composition of biomass and operating condition [18].

At time same time, the metal-hybridized carbonaceous particle could be synthesized by using hydrothermal treatment. Metal-hybridized carbonaceous with glucose were successfully synthesized homogeneously and highly crystalline. Metal-hybridized carbonaceous are high effectively for using as electrode materials. Water hyacinth is consists of high cellulose content, for this reason the water hyacinth could be converted into metal- hybridized carbonaceous materials [19].

2.4 Carbonization

Carbonization processes is a one of a process for producing a carbonaceous product which was burned under low oxygen or an inert gas such as N_2, He and CO_2. Because of adding inert gas, carbonaceous could not burn with functional combustion and radical sample for releasing carbon dioxide gas. During the carbonization processes, an elemental compound such oxygen, hydrogen, nitrogen and other compound was removed by thermal decomposition. The solid resultant product created carbon bond which produced aromatic ring carbon structure. Carbon arranged crystallite and amorphous structure. Because of operating low cost and excessive material as feedstock into processes, a biomass was used as feedstock by the carbonization process. The carbonized biomass presented high purity carbon content and specific surface area. However, the carbonization process employed high temperature for producing carbonaceous particle.

A parameter was significantly observed the quantity and quality such as temperature, heating rate, time and raw material. This research used biomass as raw material because biomass is high carbon organic compound. Carbonization processes could divide 4 steps 1) removing water and moisture content 2) removing cellulose and hemi-cellulose content 3) converting carbonaceous product 4) increasing purity carbon and graphitic crystallites. A temperature carbonization is a most important parameter. The temperature could break radical bonds on raw material and decompose volatile product. An increasing the temperature enhanced a mechanical and chemical properties of the carbonaceous product.

Carbonaceous product obtained from carbonized biomass was utilized in many applications such as catalyze, absorption, binder especially electrode material. The carbonized products have utilized as the carbonaceous powder for fabricating electrode because of its high specific surface area and electric conductivity. This research carbonized hydro-char rod was investigated as an anode for conducting arc discharge in water.

2.5 Arc discharge

Many techniques can provide synthesizing carbon material such as chemical vapor deposition, arc discharge, and laser ablation. Each of technique can control condition let to different structure and size distribution of a product.

Arc discharge is a one of technique which can provide carbonaceous materials. Two graphite electrodes as carbon sources were conducted by injecting inert gas into arc zone within a hollow cavity of a cathode submerged in water. The anode graphite material was consumed to carbon vapor because heat temperature in an arcing zone was presented highly temperature. Carbon vapor self-assembly organized new carbonaceous structure. In arc zone, liquid solution or water would quench the carbon vapor emitted from the anode and the gas bubbles. Gas-inject arc-in-water (GI-AW) is a one in arc discharge for providing single wall carbon nano-horn and carbonaceous particle under nitrogen gas. The two electrodes were submerged in water between arcing carbons. In many technologies was utilized producing carbonaceous and metal-hybridized carbonaceous material. Conducting arc discharge is a one of technology for producing material because it is easy and simple technologies. As a modified arc-in-liquid method, the GI-AIW method has a benefit about its efficacy for synthesizing various materials including metal hybridized carbonaceous particles. The experimental apparatus for conducting arc discharge in water for synthesized carbonaceous was shown in **Fig**. 2.5.

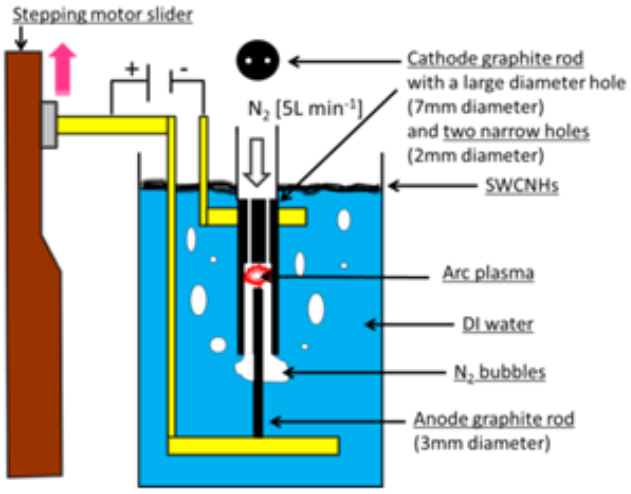


Fig. 2.5 Experimental apparatus for conducting arc discharge in water [21]

2.6 Literature reviews

2.6.1 Treating hydrothermal

Sevilla et al. (2009a) reported producing of hydro-char by hydrothermal carbonization of cellulose which was synthesized in a temperature range 210-250 ºC for 2-4 hours. The cellulose was changed from sponge to a spherical morphology. The spherical particles showed particle size of 0.4-0.6 μm. The spherical morphology presented in core-shell shape. The cellulose treated hydrothermally shown several functional groups on the surface of resultant products. The oxygen functional groups of the inner part of the microspheres consist of less reactive groups such as ether, quinone, pyrone. The shell of the microsphere mainly contains more reactive hydrophilic such as hydroxyl, carbonyl, carboxylic, ester as shown in **Fig.** 2.6 [22].

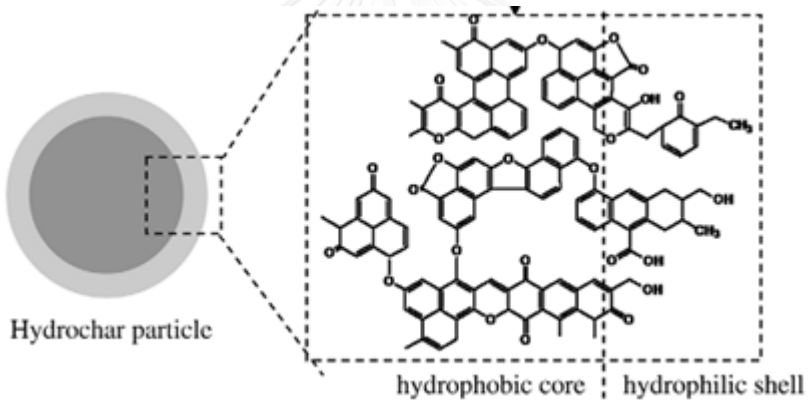


Fig. 2.6 Formation of hydro-char particles from cellulose by hydrothermal carbonization [22]

Sevilla et al. (2009b) reported hydrothermal treatment of saccharides for producing a carbonaceous particle. The saccharides were treated hydrothermally in temperatures range 170-240 ºC. It was found that water could hydrolyze by thermal decomposition for producing of hydronium and hydroxide ions. Both of acid and base ions could hydrolyze saccharides for producing oligomer and monomers such as cellobiose, cellohexaose, cellopentaose, cellotetraose, cellotriose and glucose. Then, the oligomers are dehydrated into monomers such as 1,6-anhydroglucose, erythrose, furfural-like compounds. The decomposed monomers and oligomers provided soluble

organic acids in the liquid phase. The hydroniums ions obtained from acid solutions could catalyze increasing intermediate and other product via degradation reaction. Then, the resultant product of dehydration was polymerized or condensed reactions which resulted conducting the carbonaceous particle. The carbonaceous particle was formed. The growth carbonaceous particle was described by diffusion chemical in the liquid phase. The carbonaceous surface presented on hydroxyl, carbonyl, and carboxylic group of the particle [23].

Geo et al. (2013) reported hydrothermal carbonization of water hyacinth at temperate of 240 ºC for 0.5-24 hours. It was found that 45.21 wt% of a SiO_2 content of ash which showed in the water hyacinth. Base on TGA, the thermal decomposition of lignocellulosic material was volatilized hemicellulose and cellulose in the temperature range 200-400 °C. Lignin was volatilized in the temperature range 400-700 °C. The hydrothermal carbonization caused decreasing H/C and O/C ratio because, hydro-char product related by dehydration and carboxylation reaction. It should be noted that 6 hours of hydrothermal carbonization showed stable origin content. For SEM image, 6 hours of hydrothermal treatment showed small microsphere. At the same time, the lignocelulosic material was importantly decomposed water hyacinth. 24 hours treated water hyacinth corresponded with surface morphology. Hydrothermal carbonization could increase higher a heating value of the water hyacinth (HHVs) from 16.83 MJ/kg of the water hyacinth to 20.63 MJ/kg of hydro-char [24].

Hu et al. (2009) studied differently in temperatures range 280-365 ºC and reaction time 2 hours. From SEM, It was found that lignin was decomposed with an increasing hydrothermal treatment temperature. At temperature 330 °C, the hydro-char presented a largest specific surface area at 2.5536 m^2/g and pore volume 0.0189 cm^3/g. Base on XRD, lignin was high treated hydrothermally temperature. Hydro-char significantly showed crystalline structure. However, an increase treatment temperature could decrease hydroxyl group [25].

Kalderis et al. (2014) reported producing hydrothermal carbonization of rice hunk at different temperature and time. 1:5 of rice husk and water ratio was treated hydrothermally in a temperature range 200-300 °C for 2-16 hours. It should be noted that after 6 hours of hydrothermal treatment showed constable hydro-char yield. At 6

hours of treatment different temperature was compared pH value and electrical conductivity. Acid could increase 4.4 to 3.4 in the temperature range 200-300 °C. An increasing temperature caused high electrical conductivity [26].

2.6.2 Carbonizing biomass

Han et al. (2014) reported at different pyrolysis in a temperature range 700-900 °C. The green tea was removed some impurity by a hydrothermal treatment at 100 °C for 5 min. Then, green tea was carbonized with nitrogen gas. At different carbonization temperature samples were analyzed by using an FT-IR analyzer. The resultant product showed –OH, C-H and C-O functional groups on a surface. It was found that C-H and C-O group was decreased when carbonization temperature was increased. At the same time, the increasing temperature increased the graphitic structure. It should be noted that the high temperature causes small particle size and porous diameters size. However, large pore diameter was shown high effective adsorption lithium ions [27].

Laginhas et al. (2016) reported activated a chitosan treated hydrothermally by carbonization. The hydro-char was activated under CO_2 gas at a temperature 800 °C for 1-5 hours. In thermal decompose (TGA) with nitrogen gas; the chitosan was high weight loss 2 step. At 316 °C and 700 °C of the carbonization temperature could decompose 48% and 60% weight loss of feed because oxygen functional groups were volatilized. The hydrothermal treatment at the temperature of 200 °C for 24 hours was highest carbon content 59 %w/w. Then, the hydro-char was activated with $CaCO_3$ and K_2CO_3 at the temperature of 800 °C for 6 hours. The activated carbon was highest carbon content 85 %w/w. Impregnation $CaCO_3$ could improve specific surface area 1432 m^2/g while without $CaCO_3$ showed specific surface area 1023 m^2/g [28].

2.6.3 Conducting arc discharge

Sano et al. (2002) reported producing carbon onions by conducting arc discharge in water. 99.9% of pure graphite was used as anode and cathode material. It was found that a resultant product showed carbon onion structure with diameters 30-35 nm obtained from floating powder on the water. The density of onion particle is

higher than water but it is hydrophobic. For generating, carbon particle was summarized mechanism of onions in arc discharge in water as shown in **Fig** 2.7.

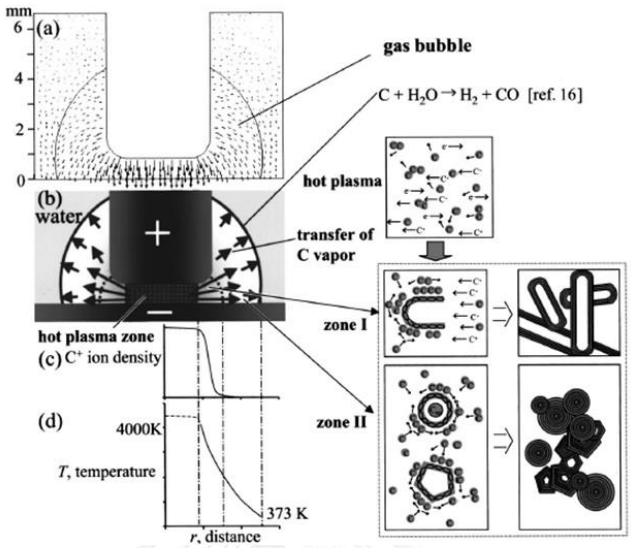


Fig. 2.7 Principle of arc mechanism in water condition [20]

Arc plasma temperature was estimated at temperature of 4000 K. Because of high-temperature in arc zone as water surrounding, carbon vapor and water was generated gas products such as CO and H_2 products as shown in equation 2.1

$$C+H_2O \rightarrow CO+H_2 \qquad (2.1)$$

Generating the carbon onions, graphite rod was vaporized. Then, the vaporized carbon converted to onion carbon particle. The interface of gas and water immediately condensed vaporized carbon [20].

Sano et al. (2004) reported producing Ni-hybridized carbon nano-horns. Ni–contained composite graphite was used as anode material in arc discharge. The cathode and anode were submerged in liquid nitrogen. The particle powder was collected on a flask. The carbon nano-horn showed a diameter of 50-80 nm. The resence of Ni-contained was found that Ni and C were vaporized. Then, both Ni and C particle were quenched by liquid nitrogen for producing Ni-hybridized carbon nanoparticle. It should be noted that surrounding liquid nitrogen stable than water [29].

Charinpanitkul et al. (2009) reported a single-step synthesis of copper and carbon nanoparticle. A copper wire inserted in graphite rods were utilized as an anode in arc discharge in liquid nitrogen. It was found that carbon power obtained from arc discharge by using graphite without copper composed of muti-walled carbon nanotube and some single-walled carbon nanohorn on the cathode and sedimentary. The cupper-graphite electrode, the sedimentary powder composed of MWCNT/Cu_2O. Cu2O was observed within MWCNTs structure. It should be noted that an increasing arc current 100 to 180A could observe multi-shelled polyhedral carbon nanocapsules (MSCNCs) because the increasing evaporation rate affected to generate large carbon structure [30].

Poonjarernsilp et al. (2011) reported a single-walled carbon nanohorns hybridized with Pd nanoparticle by single-step gas-injected arc in water method (GI-AIW). Pd wire inserted graphite as an anode electrode. In arc zone, carbon and Pd were simultaneously vaporized. Then, vaporized carbon and Pd formed to hybridized material. It should be noted that arc discharge in liquid hindered for large scale production. Based on TEM and CO chemisorptions analyzer, the Pd embedded in SWCNH. The different Pd wire diameter in graphite rods affect Pd vapor. The small wire, the Pd concentration is low therefore Pd nanoparticle could generate with low diameter and uniform. On the other hand, large diameter could increase growth rate Pd nanoparticle. It should be noted that the single-wall carbon nanohorn carbon aggregated a bud-like structure [21].

Poonjarernsilp et al. (2014) reported production of Fe-loading nanoparticles with SWCNHs. In arc zone, the plasma temperature showed approximately at 5,000 K. The carbon and Fe were vaporized from anode material. Then, they were quenched by cold water. SWCNH and Fe nanoparticles formed by self-assembly Fe and carbon vapor. Based on XRD, It was found that Fe nanoparticles showed non-oxidized Fe. In addition, Fe-hybridized SWCNH was high effectively utilized as a catalyst for esterification reaction [31].

CHAPTER III

EXPERIMENTAL

This research was divided into 4 aspects which are 1) hydrothermal treatment 2) making hydro-char rods 3) carbonizing hydro-char rods 4) conducting arc discharge in water as shown in **Fig.** 3.1. Water hyacinth has become an invasive plant species. For decreasing water pollution, water hyacinth could be utilized to convert carbonaceous product. This research used hydrothermal treatment for improving to value-added in a carbonaceous material because hydrothermal treatment is easy technology. Lignocellulose of water hyacinth was treated to produce the carbonaceous product. The carbonaceous product consists of oxygen-containing groups. Normally, resultant solid products of hydrothermal carbonization were called hydro-char. The making hydro-char a rod was prepared electrode for conducting arc discharge in water. The hydro-char was compressed under pressure. It should not that radicals on the particle of the carbonaceous particle could combine particle for making the rod. The carbonization process was used for removing radicals such as nitrogen, oxygen and hydrogen. Finally, carbonized hydro-char rods were utilized as anode material to be employed in arc discharge in water for exhibiting the possibility to carbonaceous nanoparticles.

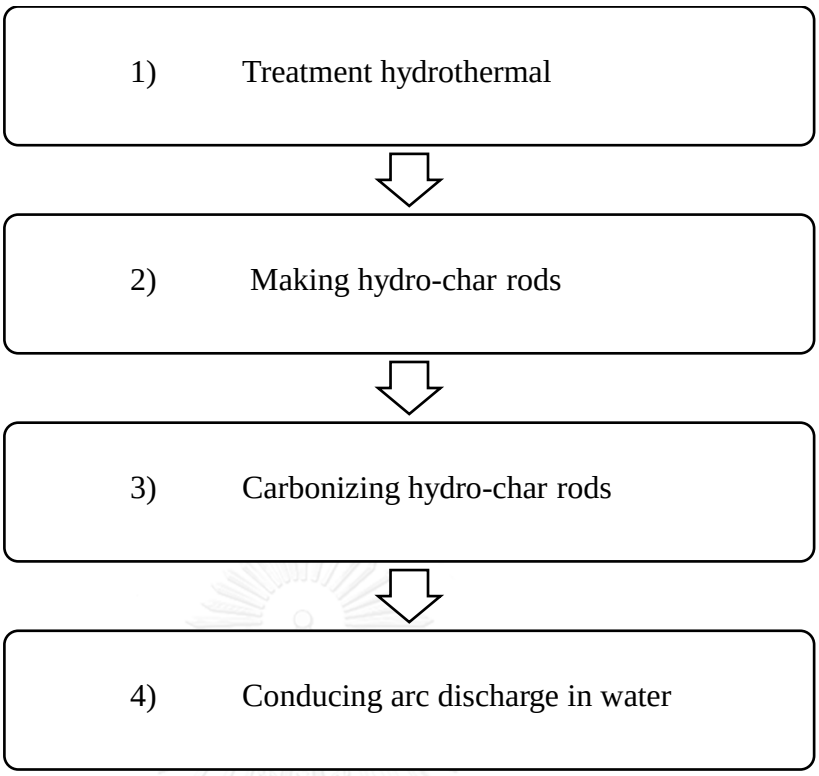


Fig. 3.1 Methodology research

3.1 Raw materials and Chemical

Raw material and chemical were used this research. They were summarized as follows,

3.1.1. Water hyacinth was collected from a Khlong nueng pond in Thammasat University Rangsit, Bangkok, Thailand.

3.1.2. De-ionized water was used hydrothermal treatment and filtrated to separate solid product and organic liquids.

3.1.3. 99.999% of Nitrogen (N_2) TIG/purity was used for carbonizing hydro-char and conducting arc discharge in water.

3.1.4. Ferric Nitrate, $Fe(NO_3)_3 \cdot 9H_2O$ was impregnated onto water hyacinth for producing Fe-hybridized carbonaceous particle.

3.2.5. 99.9995% of a commercial graphite purity rod was used as anode for conducting arc discharge experiment which was compared with there of using

carbonized hydro-char rods which were used as anode material by arc discharge in water.

3.2 Equipment and reactors

3.2.1 Disk mill machines

Dried water hyacinth was cut into small piece by using a disk mill (FCC15, Kaishan) as shown in **Fig.** 3.2. Voltage was shown 220 volt, Power showed 20-70 kilogram/hours

Fig. 3.2 Machine for cutting water hyacinth into small pieces

3.2.2 Stainless steels autoclave reactor

500 ml of a glass liner and stainless steels autoclave reactor were used for treating hydrothermal as shown in **Fig.** 3.3. The stainless steels autoclave reactor is a diameter 8.5 cm and height 14 cm.

Fig. 3.3 Stainless steels autoclave reactor

3.2.3 Horizontal furnace reactor

Horizontal furnace reactor (RHTH120-600/18, Nabertherm) was used for carbonizing hydro-char rods under nitrogen gas atmosphere as shown in **Fig.** 3.4. Horizontal furnace reactor can heat maximum 3000 °C. A quartz tube is a diameter 40 cm and length 180 cm.

Fig. 3.4 Horizontal furnace reactor

3.2.4 Hot air oven

Water hyacinth and resultant products were dried in a hot air oven (ED400, binder) as shown in **Fig.** 3.5 at 105°C for removing moisture content. And a temperature treatment was set for hydrothermal treatment in a temperature range of 160-220 °C for 4-12 hours in the hot air oven. The hot air oven is 48.6 cm of width, 30.1 cm of depth and 40.2 cm of height.

Fig. 3.5 Hot air oven for drying of raw material and solid products

3.4.6 Hydraulic press

Hydro-char was compressed using a hydraulic press (LF-20-8, Labtech engineering). For make rigid rods, Hydro-char rods were carbonized at temperature 900 °C under nitrogen gas. The resultant sample as electrode material was employed in arc discharge in water.

3.4.7 Arc discharge in water equipment

Carbonized hydro-char rod was utilized as an electrode in the arc discharge in water experiment as showed in **Fig** 3.6 Graphite Rod is a diameter 20 mm as the cathode. Operating condition of arc-in-water technique was set the N_2 flow rate 10 L/min, the discharge current 80 A and velocity of lower electrode 1.5 mm/s.

Fig 3.6 Arc discharge in water

3.3 Experimental procedures

3.3.1 Hydrothermal treatment of water hyacinth

3.3.1.1 Hydrothermal treatment of water hyacinth without ferric nitrate

20 g of dried water hyacinth powder and 40 ml of de-ionized water were added into an autoclave reactor. Hot air oven was set at a temperature of 160, 180, 200 and 220°C for 4, 8 and 12 hours. Then, the autoclave reactor was put into the oven. After achieving a set temperature and holding time, the autoclave reactor was immediately quenched by cold water to stop the reaction. Hydro-char products were washed with de-ionized water until pH of washing water achieved 5. Finally, the hydro-char sample was dried again at temperature 105 °C for 24 hours.

3.3.1.2 Hydrothermal treatment of water hyacinth with ferric nitrate

4, 8 and 12 g of ferric nitrate were dissolved in de-ionized water by stirring at room temperature for 30 minutes until the solution is homogeneous. 20 g of dried water hyacinth was added in an autoclave with ferric nitrate solution. The autoclave reactor was put into an oven at a temperature of 180 °C for 8 hours (The water hyacinth was hydrothermally treated at the temperature of 180 °C for 8 hours and carbonized hydro-char at 900 °C because this condition was highest specific surface area). The resultant products were washed with de-ionized water until pH of washing water achieved 5. Then, the hydro-char samples impregnated with Fe were dried at 105 °C for 24 hours.

3.3.2 Making hydro-char rods

Hydro-char powder was compressed for making rod under pressure by a hydraulic press at a temperature of 90 °C for 200 bars. A hydro-char rod is a diameter 0.5 cm and height 4 cm. Then, the hydro-char rod was put into a furnace for carbonizing hydro-char under inert gas.

3.3.4 Carbonizing hydro-char rods

Hydro-char rods were carbonized in a horizontal tube furnace reactor under nitrogen (N_2) atmosphere. In brief, 3.0 g of the hydro- char rods were put in a boat. The boat was put in the horizontal tube furnace reactor. Operating condition of N_2 flow rate, target temperature, heating rate of the furnace were used 100 cc/min, 500 ºC, 700 ºC, 900 ºC, 5ºC/min, 2 hours, respectively. Carbonized hydro-char rods were collected and weighted for characterization.

3.3.5 Conducting arc discharge in water

Carbonized hydro-char rods were used as anode material for using a gas-inject arc-in-water technique. Operating condition of arc-in-water technique was set a N_2 flow rate 10 L/min, discharge current 80 A. A resultant product was collected and dried in a hot air oven at a temperature of 105 °C overnight.

3.4 Product characterizations

Dried water hyacinth powder and resultant products were characterized by SEM analyzer for observing their structure and morphology, EDS analyzer for observing their dispersion iron/carbonaceous particle, FT-IR analyzer for observing their functional groups on surface material, CHNS/O analyzer for observing their determined composition compound , BET analyzer for observing their surface area, pore volume and pore diameter, XRD analyzer for observing their crystalline and atmospheres structure, AAS analyzer for observing their iron quality composition , current meter for observing their conductivity, TEM analyzer for observing their morphology and iron/carbonaceous particle dispersion and Raman specter analyzer for observing their graphitic carbonaceous products.

3.4.1 SEM and EDS analyzer

Water hyacinth and resultant products were coated with Au by a sputter coating (E-1010, Hitachi) for ensuring the consistent conductivity of particle. A morphologies and shapes solid product were characterized by a Scanning Electron Microscope (s3400N, Hitachi) as shown in **Fig** 3.7

Qualitative and quantitative carbon and iron particle of carbonized Fe-hybridized were characterized by an Energy Dispersive X-ray Spectrometer (6610LV, JEOL)

Fig 3.7 Scanning Electron Microscope (SEM) analyzer

3.4.2 FT-IR analyzer

Functional groups on a surface of solid products were analyzed by FT-IR or Fourier transform-infrared spectroscopy on ATR mode (Nicolet 6700, Thermo Scientific) as shown in **Fig** 3.8. The resultant products were measured absorption identifies chemical bonds in a molecule by producing an infrared absorption spectrum. A range wave number is identified chemical bonds in a molecule. This research, the resultant products were scanned in wave numbers range 400 to 4000 cm^{-1}.

Fig 3.8 Fourier transform-infrared spectroscopy (FT-TR) analyzer

3.4.3 Elemental analyzer

Elemental composition products were analyzed by CHN/S analyzer (CHN628, LECO) as shown in **Fig** 3.9

Fig 3.9 Elemental composition (CHN) analyzer

Result products were combusted under high-purity oxygen gas atmosphere temperature at 1050 °C. Gas products such as CO_2, H_2O and NO were calculated carbon, hydrogen and nitrogen content. In similarly, sulfur content was measured SO_2 gas by combustion under oxygen gas atmosphere at temperature 1200 °C. However, ash content samples were combusted sample under operating rate NREL condition by muffle furnace as shown in **Fig** 3.10 (LVT 15/11/P330, Nabertherm).

1) Temperature was set point temperature at 105 °C for 12 minutes

2) 250 °C of temperature inside furnace achieved set point temperature for 25 minutes

3) Temperature was set point temperature at 250 °C for 30 minutes

4) 575 °C of temperature was achieved set point temperature for 16 minutes

5) Temperature was set point temperature at 575 °C for 180 minutes

6) Temperature was cool down at temperature 105 °C

Fig 3.10 Muffle furnace

3.4.4 Surface area

The carbonized hydro-char porous structure was characterized by liquid nitrogen adsorption and desorption at –196 ºC (Belsorp-Mini, Bel Japan) as shown in **Fig** 3.11. In brief, 0.05 g of the sample was pretreated at 150 ºC under vacuum overnight for removing moisture content and gaseous residual.

Fig 3.11 Brunauer-Emmett-Teller (BET) analyzer

3.4.5 X-ray powder diffraction analyzer

Water hyacinth and resultant product were analyzed crystalline structure by X-ray diffraction analyzer (AXS, d8 advance, Bruler) as shown in **Fig** 3.12. The X-ray powder diffraction peak width is inversely related crystalline phase. The X-ray powder diffraction was scanned at range $10 \leq 2\Theta \leq 90$.

Fig 3.12 X-ray powder diffraction (XRD) analyzer

3.4.6 Atomic absorption spectroscopy

Atomic absorption spectroscopy was analyzed metal particle sample as shown in **Fig** 3.13. The Fe-hybridized carbonaceous was mixed with nitric acid for separation Fe and carbonaceous particle. Excited atoms and emit ions was measured for detecting metal. Metal atom was absorbed in wavelengths characteristic of a particular element (AA280FS, VARIAN) which elemental composition of metal presented metal oxide.

Fig 3.13 Atomic Absorption spectroscopy (AAS) analyzer

3.4.7 Four point probe tester

The carbonized hydro-char rods resistivity was analyzed by current meter (SRM101, SET) as shown in **Fig** 3.14. The amount of current was through electrode material. The voltage between the two probes was measured by a voltmeter. The current would be measured by using the two probes. The voltage and current were

shown resistance between the surface patterns from Ohms law equation and the volume resistivity.

Fig 3.14 Four point probe tester

3.4.8 Transmission electron microscope

Transmission electron microscope (TEM-2100F, JEOL) was analyzed morphology nanoparticle sample as shown in **Fig** 3.15

Fig. 3.15 Transmission Electron Microscope (TEM) analyzer

3.4.9 Raman spectroscopy

Raman spectroscopy was absorbed infrared for characterzing atoms and bond functional groups (NT-MDT, NTEGRA Spectra) as shown in **Fig**. 3.16. The resultant products were analyzed graphitic and disorder carbon structure.

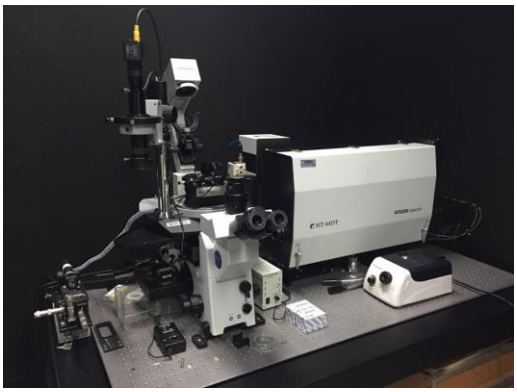


Fig. 3.16 Raman spectroscopy

CHAPTER VI

Results and discussion

4.1 Effect of hydrothermal treatment temperature and time on resultant hydro-char powder

Effect of treatment temperature in a range 160-220 °C and time in a range of 4-12 hours on characteristics of hydro-char powder was explained and discussed. Based on all experimental results of hydrothermal treatment of water hyacinth powers, hydro-chars obtained from the condition of carbonizing temperature at 900 °C was employed as an electrode material for fabricating rods which would be used in arc-discharge in water.

4.1.1 Temperature change within autoclave reactor

Dried water hyacinth and de-ion water were mixed in an autoclave reactor. A thermocouple was put into the autoclave reactor as shown in **Fig**.4.1. Dried water hyacinth powers were converted with hydro-char by hydrothermal treatment in a temperature range of 160-220 °C.

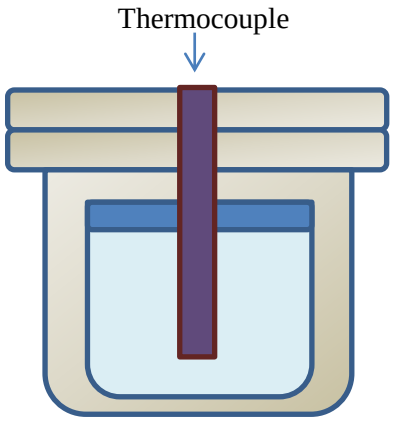


Fig 4.1 A schematic autoclave reactor

A temperature of a hot air oven was set in temperature range 160-220 °C. Then, the autoclave reactor was put into the hot air oven. Treatment time was employed which the residence was set in the hot air oven. The autoclave reactor could be considered as a close system. At a designated temperature of the oven, treatment in autoclave changed with respect to treatment time as shown in **Fig** 4.2.

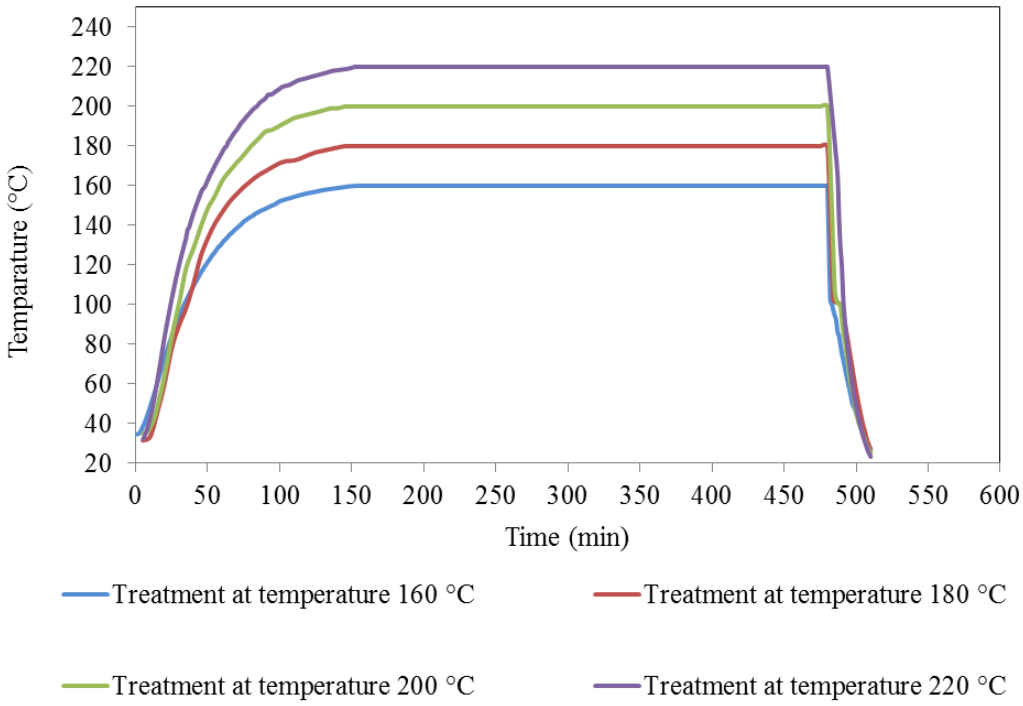


Fig 4.2 Sample temperature change with water hyacinth treated in autoclave reactor

Heat transfer from the oven to the achieve reactor resulted in a graded in an oven in the temperature inside the autoclave. Within a contain time period of 150 min, the temperature inside the autoclave reactor achieved a constant value which was the set-point temperature of the oven. It should be noted that under the atmosphere pressure, the treating temperature of powder water in at 100 °C which hemi-cellulose will be decomposed at 160 °C [7]. Base on a stream table of water, a pressure inside the autoclave was estimated from data of temperature and amount of water in the autoclave reactor as shown in **Table** 4.1.

Table 4.1 Pressure inside the autoclave

Sample	Pressure (bar)
HT 160 °C	6.2
HT 180 °C	10.0
HT 200 °C	15.6
HT 220 °C	23.2

After temperature achieves the set point temperature, the temperature inside the autoclave reactor held constant value at a set temperature until 8 hours. It should be noted that the water on hydrothermal treatment was explained by sup-critical water. Base on hydrothermal treatment, the water and reactant could react with a molecule for producing products in temperature range 160-260 °C for producing carbonaceous particle [14]. Finally, the temperature treatment was cooled under cool water for 30 minutes for stop reaction. The carbonaceous products were washed and collected particle for carbonizing and characterizing by SEM, CHNO/S, XRD and FT-IR.

Generally, biomass treated hydrothermally which showed 3 phases (gas, liquid and solid products). The solid products were called hydro-char. Conversion of hydro-char following in equation 4.1

$$\text{Hydro-char (\%)} = \frac{y_{\text{hydro-char}}}{y_{\text{dried water hyacinth}}} \quad (4.1)$$

where y, water hyacinth = Weight of dried water hyacinth

y, hydro-char = Weight of water hyacinth treated hydrothermally

This research focused on hydro-char product. Water hyacinth was hydrothermally treated in temperature range 160-220 °C for 4-12 hours. It found that the hydro-char product decreased with an increasing a constant value temperature and time of oven as shown in **Fig** 4.3.

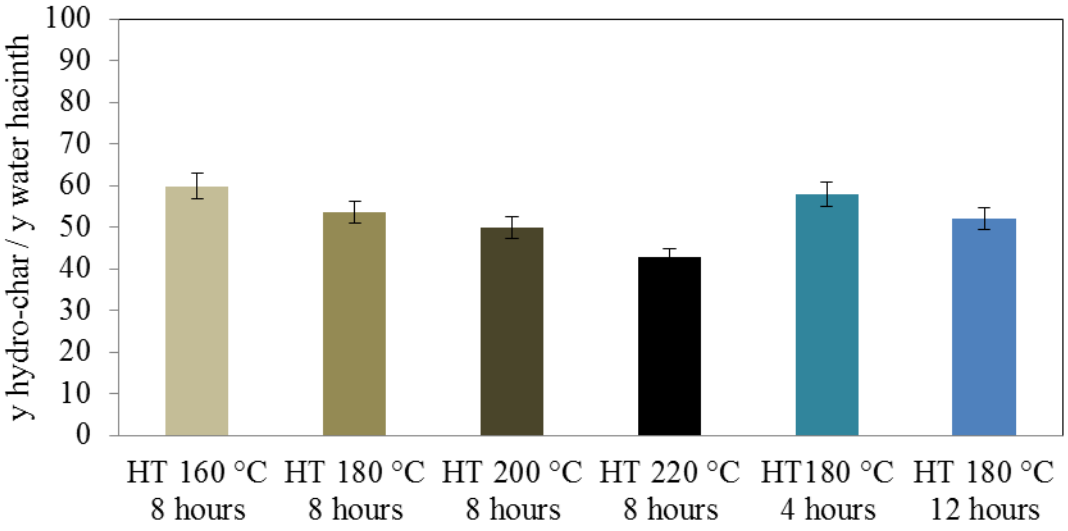


Fig 4.3 Hydro-char samples obtained from hydrothermal treatment of water hyacinth at different temperature and time

An increasing treatment temperature and time have significantly decreased hydro-char yield because a lignocellulosic material was decomposed and changed phase. H^+ and OH^- ion obtained from water reacted with water hyacinth for producing products. The lignocellulosic material could decompose by hydrolysis reaction [32]. The treatment temperature will be increased internal energy which reacts for producing products. The resultant carbonaceous particle on hydrothermal treatment showed high carbon content particle [22]. Hydrothermal treatment can remove volatile compound of water hyacinth which affected producing carbonaceous particle. Hydrothermal treatment was considered in close system. A decreasing solid product would cause an increasing gas and liquid products [14].

The Arrhenius equation following in equation 4.2 could describe activated energy for producing carbonaceous particle [33].

$$k = Ae^{\frac{-Ea}{RT}} \quad (4.2)$$

where k = rate constant

A = frequency factor (min^{-1})

Ea = activate energy (kJ/mol)

R = gas constant (8.31×10^{-3} J/mol-K)

T = Temperature (K)

Temperature treatment has affect hydro-char product which was explained by first order reaction [34]. The reaction equation could explain by following equation 4.3 Because of the temperature treatment, hydro-char products are significant explained activated energy in an autoclave reactor for producing carbonaceous particle

$$\ln[A] = \ln[A_o] - kt \quad (4.3)$$

A_o = Weight of dried water hyacinth

A = Weight of water hyacinth treated hydrothermally

k = Rate constant

t = Treatment time

Arrhenius equation can explain temperature treatment. 14.4 KJ/mol of E_a (activated energy) value was used for synthesizing a hydro-char product. It should be noted that this work shows low the activated energy which was compared bamboo treated hydrothermally in temperature range 180-260 °C. It was found that hydro-char obtained from bamboo showed activated energy 46.6-74.3 KJ/mol [33]. The activated energy explains to potential reacts for synthesizing hydro-char product.

4.1.2 SEM analysis of synthesized carbonaceous powder

4.1.2.1 Effect of treatment temperature

Dried water hyacinth powder and dried water hyacinth treated hydrothermally at temperature of 160, 180, 200 and 220 °C for 8 hours were characterized by SEM analyzer as shown in **Fig.** 4.4-4.5. Base on National Renewable Energy Laboratory (NREL) method, the water hyacinth composed of a cellulose 38.7%, hemi- cellulose 10.3% and lignin 18.7% which showed a fibrous structure as shown in **Fig** 4.4. Normally, the fibrous structure of biomass, core fibrous consists of the cellulose which composed compound of glucose linked units. Small fibrous mainly presents the hemi-cellulose and lignin [7]. The water hyacinth of this research used only leave and trunk because the root of water hyacinth has high ash and lignin content which affected on the carbonaceous particle [35].

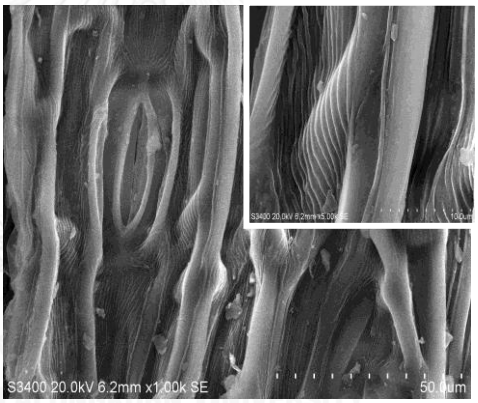


Fig 4.4 SEM micrograph of dried water hyacinth powder

A hydro-char sample obtained from hydrothermal treatment of a water hyacinth at a different temperature as shown in **Fig** 4.5. The water hyacinth treated hydrothermally at the temperature of 160 °C was destroyed a fibrous structure. Lignocellulosic compound was removed by thermal decomposition. The organic compounds were decomposed to produce small molecule products [7]. It should be noted that Lignocellulosic material could be converted to gas, liquid and soil product by using the hydrothermal treatment. Gas products mainly consisted of hydrogen, carbon dioxide, and methane. Liquid products presented organic compound and acid solution such as glucose, xylose, and acetic acid. Solid product showed high carbon

content because hydrogen, nitrogen, oxygen, and other compounds were eliminated by thermal treatment for producing carbonaceous structure [23]. It was found that treatment temperature at 160 °C could decompose hemi-cellulose to xylose led to rough on surface raw material [36]. The water hyacinth treated hydrothermally at the temperature of 160 °C lower destroyed fibrous structures than the water hyacinth treated hydrothermally at 180 °C. It was found that at 180 °C of treatment temperature could decompose some cellulose chain molecule [3]. The hydrothermal treatment significantly occurred hydrolysis reaction [11]. The acid solution could generate hydronium atom let to the hydrolysis reaction. It should be noted that a type of biomass has the significant to effect on treatment hydrothermal. Karagon et al. found that the biomass (Sawdust, Rice husk, Cellulose and Lignin) hydrothermally treated at different temperature but acetic acid was not observed in sawdust [35]. The water hyacinth treated hydrothermally at the temperature of 200 °C was found that cellulose could decompose to glucose structure at this temperature. The hydrolyzing cellulose could produce D-glucose, 5-HMF and acid respectively [22]. The water hyacinth treated hydrothermally at the temperature of 220 °C completely decomposed hemicellulose and cellulose compound [23]. Because of high temperature, a water molecule would high energy to react with the reactant. The dried water hyacinth changed the morphology and characteristic. Geo et al. found that hydrothermal carbonization of water hyacinth can generate microsphere shape [24]. This work was not found microsphere shape obtained from hydrothermal treatment of feed because water hyacinth presented high lignin content which hindered chemical reaction [9]. Rate constant importantly changed concentration. It should note that rate constant of treatment temperate at 220 ºC is higher rate constant of treatment temperate at 220 ºC by fist order reaction. However, water hyacinth treated hydrothermally appearance many functional groups on the surface. Hydro-chars showed oxygen compounds. Removing functional groups, the hydro-chars were carbonized under a nitrogen atmosphere. Carbonization could improve surface area and remove radical such as hydrogen, nitrogen and oxygen by thermal decomposition as shown as in **Fig** 4.6.

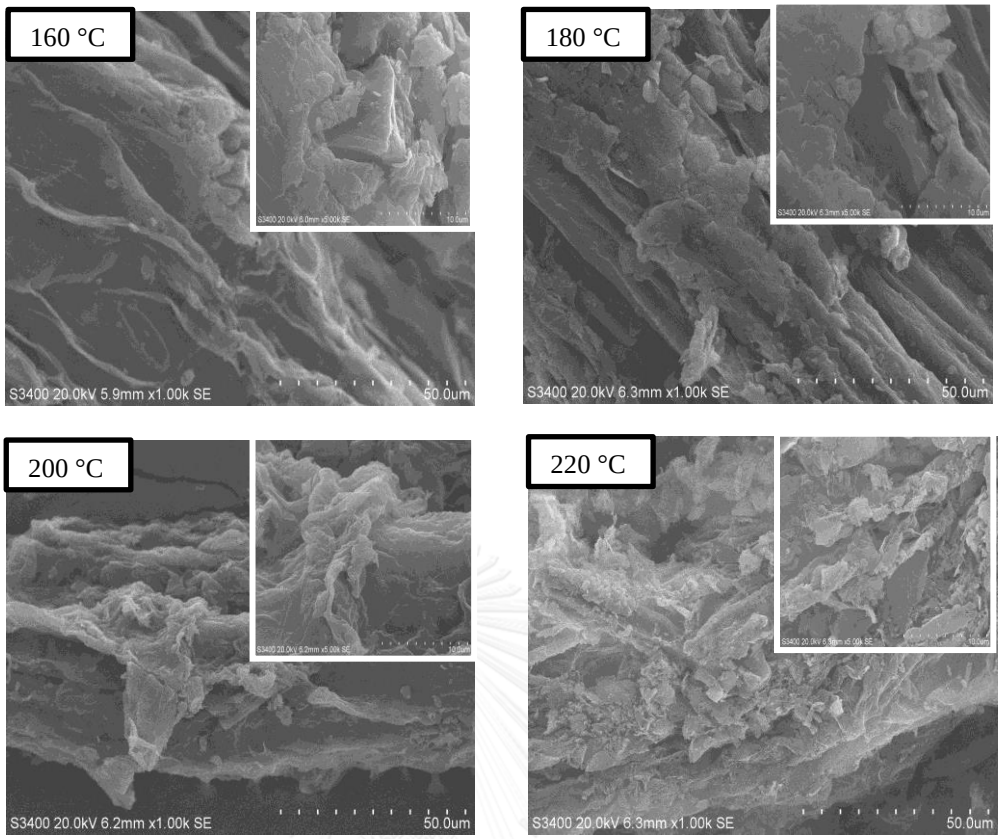


Fig. 4.5 SEM micrograph of hydro-char samples obtain form hydrothermal treatment of water hyacinth at different temperature

Carbonized hydro-char at 900 °C of water hyacinth treated hydrothermally at temperature of 160, 180, 200 and 220 °C for 8 hours (Carbonized hydro-char) were analyzed by SEM analyzer as shown in **Fig** 4.6 Carbonization process burned volatile compound at high temperature under inert gas for removing oxygen, hydrogen and evaporating radicals to gas products. The resultant product mainly consisted of high carbon content and surface area. This work found that hydrothermal treatment temperature affected to morphology water hyacinth treated hydrothermally. Both oxygen compound and lignin compound are destroyed functional groups on hydro-char. It should note that be found that the resultant products of carbonized hydro-char showed hexagonal ring or benzene ring carbon structure which was liked van der Waals bond [23].

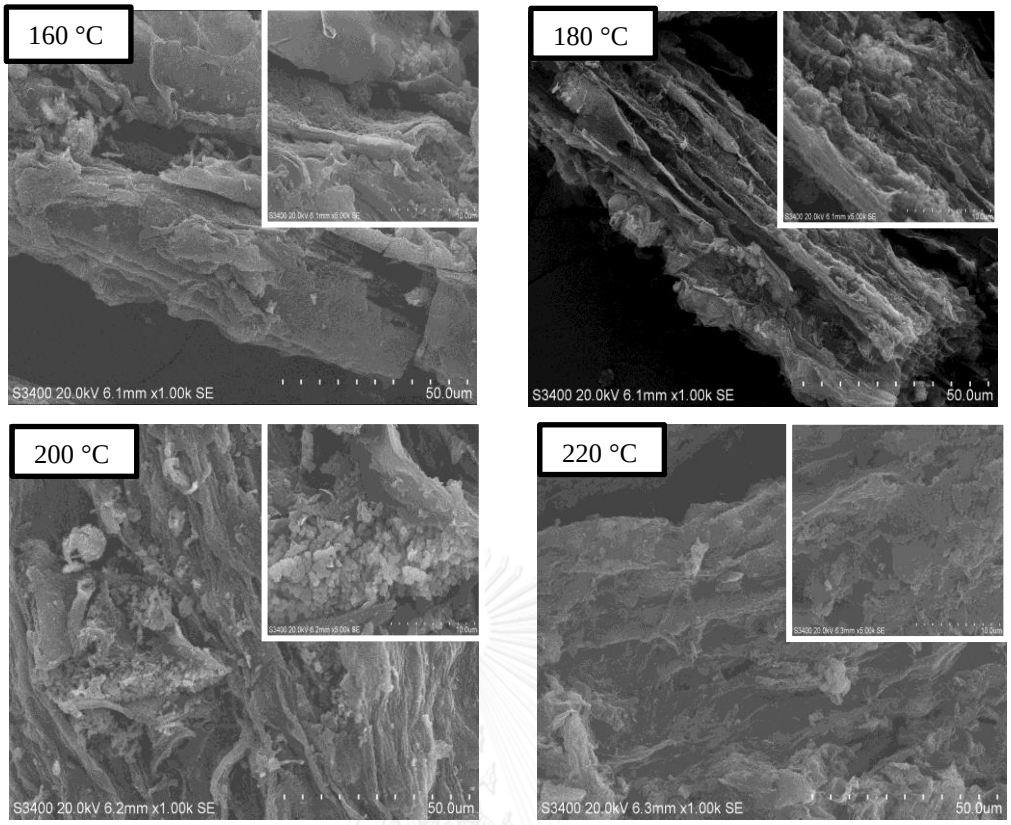


Fig. 4.6 SEM micrograph of products obtained from carbonized of hydro-char at different temperature

Carbonized hydro-chars were collected. The conversion of carbonized hydro-char was calculated from equation 4.2.

$$\text{Carbonized hydro-char (\%)} = \frac{y_{\text{carbonized hydro-char}}}{y_{\text{hydro-char}}} \qquad (4.2)$$

where

y, hydro-char = Weight of water hyacinth treated hydrothermally

y, carbonized hydro-char = Weight of carbonized hydro-char

The result conversion of carbonized hydro-char was shown in **Fig** 4.7. Carbonized hydro-char increased with an increasing hydrothermal treatment temperature. The treatment temperature corresponded with atom carbon chain. Hydrothermal treatment destroyed some hydrocarbon structure but high compound

and complex structure cannot be decomposed by hydrothermal treatment. The resultant products obtained from water hyacinth treated hydrothermally were remained lignin compound [7].

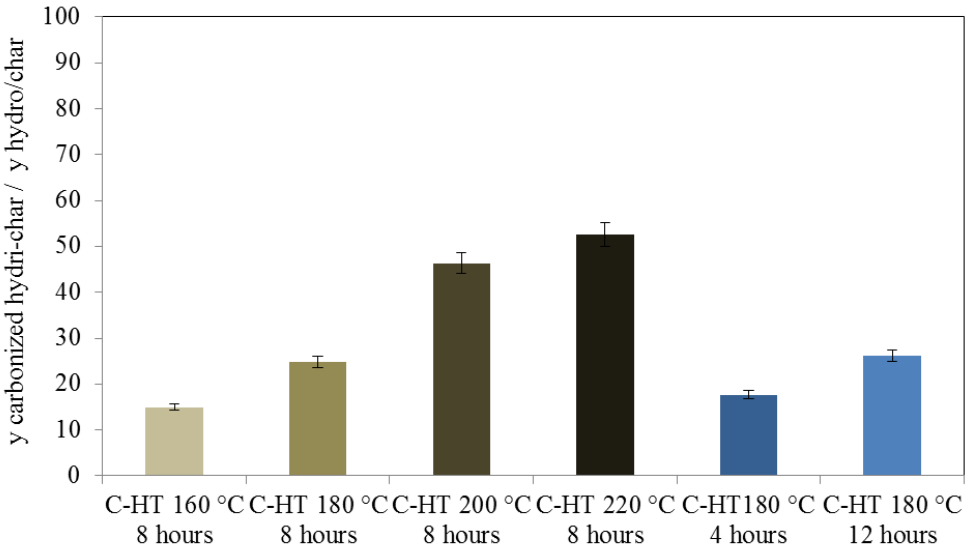


Fig 4.7 Carbonized hydro-char samples obtained from hydrothermal treatment of water hyacinth at different temperature

4.1.2.2 Effect of treatment time

Water hyacinth was treated at different treatment time as shown in **Fig** 4.8. Water hyacinth treated hydrothermally at a temperature of 180 °C for 4 hours was found that the water hyacinth still presented fibrous structure. Some surface structure decomposed because water molecule reacted with dried water hyacinth. The resultant products showed rough on the surface. 12 hours of the hydrothermal treatment time was compared with 4 hours of hydrothermal treatment time. It was found that long treatment time presented highest effect with surface area. The water hyacinth treated hydrothermally at the temperature of 180 °C for 12 hours would high chance to react with the reactant. This research, an autoclave was put into an oven. Then, the treatment temperature inside the autoclave was treated by thermal decomposition which achieved a constant value at 150 min. 4 hours of treatment time does not enough liked carbon bond and affect lignocellulosic material [24]. 12 hours of

treatment time could link carbon bond for generating carbon structure. The long treatment time was highest decomposed dried water hyacinth because water change reacted with water hyacinth. Yang et al. found that water hyacinth was hydrothermally treated at the temperature of 240 ºC for 30 min-24 hours. It should be noted that 6 hours of treatment time occurred stable the major transformation and arrangement of hydro-char [37]. The hydrothermal treatment temperature and time broke organic compound to generated acid solution. Liang et al. found that the hydrothermal carbonization of starch was observed under different pH solution. The acid solution has improved the hydrolysis of hydrocarbon and formed microsphere [38]. Similarly, hydro-char was carbonized at the temperature of 900 °C for elimination radical compound by carbonization under nitrogen gas.

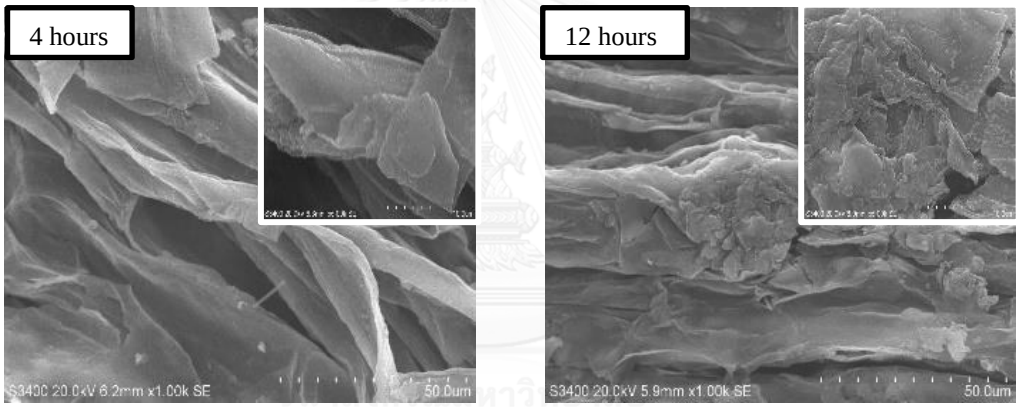


Fig. 4.8 SEM micrograph of hydro-char samples obtain form hydrothermal treatment of water hyacinth at different time

Carbonized hydro-char obtained from water hyacinth treated hydrothermally at a temperature of 180 °C for 4 and 12 hours were shown as **Fig**.4.9. Base on SEM image, it was found that treatment time effected to carbonized hydro-char particle. 4 hours of carbonized hydro-char showed fiber structure. For comparison, carbonized hydro-char obtained from 12 hours of hydrothermal treatment was found that SEM micrograph showed smaller particle size than 4 and 8 hours of hydrothermal treatment.

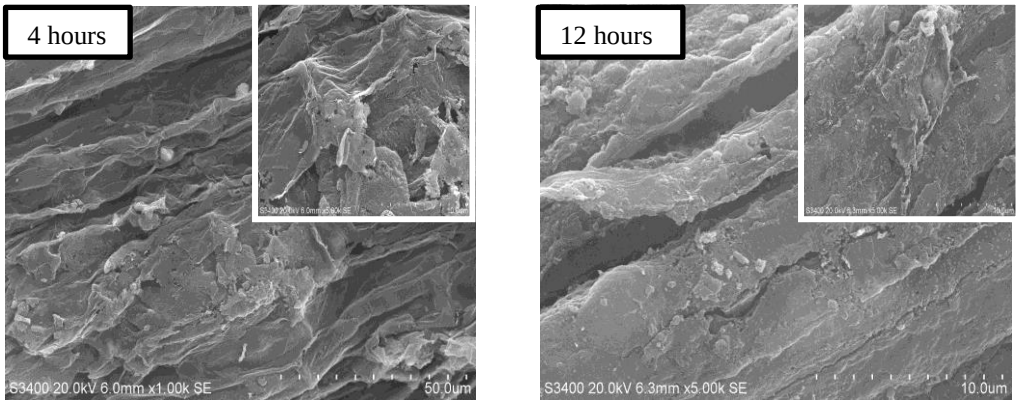


Fig. 4.9 SEM micrograph of products obtained from carbonized of hydro-char at different time

4.1.3 BET analysis of synthesized carbonaceous powder

Carbonized hydro-chars were analyzed by Brunauer-Emmett-Teller (BET) analyzer as shown **Table** 4.2. The table summarized specific surface, average pore diameter and total pore volume. Carbonized water hyacinth was not treated with hydrothermal treatment. It was found that specific surface is very low. The volatilized compounds of water hyacinth were decomposed by thermal temperature. Gas products obtained from carbonization which involved with burning compound. In another way, the water hyacinth was treated with hydrothermal treatment. The hydrothermal treatment can generate the carbonaceous structure. It should be noted that carbonized hydro-char at 180 ^{o}C was highest specific surface area and carbonized hydro-char at 220 ºC was the lowest specific surface area. They suggested that treating hydrothermally at 160 ^{o}C could be decomposed some impurity on surface area let to dried water hyacinth surface but treating hydrothermally at 180 ^{o}C could be composed both hemicellulose and cellulose [39]. Treatment temperature at 180 °C did not excessively hydro-char surface. Treatment temperature in temperature range 200-220 ^{o}C could be decomposed cellulose hemi-cellulose and some lignin. The high hydrothermal treatment can decompose compound including carbon atom. Because high temperature, treatment temperature affected increasing electron which was used decomposed reactant. The increasing electrons as H^{+} and OH^{-} promoted acid or base

the compound solution in water. It was suggested that acid and base solution could increase hydrolyzing lignocellulosic material [36]. It should be noted that hydrothermal treatment generated macro-pore diameter particle but carbonization process generated micro-pore diameter particle [22]. The increasing hydrothermal treatment improved small macro pore diameter as shown in Appendix A1-19. It should be noted that hydro-char obtained from hydrothermal treatment of lignin at 330 ºC presented 2.5536 m^2/g of specific area [25].

Table 4.2 BET of carbonized hydro-char at different temperature

Sample	Specific surface area (m^2/g)	Average pore diameter (nm)	Total pore volume (cm^3/g)
Carbonized dried water hyacinth	15.0	3.2	0.012
Carbonized hydro-char at 160 ºC	564.5	3.4	0.481
Carbonized hydro-char at 180 ºC	635.8	2.7	0.437
Carbonized hydro-char at 200 ºC	470.4	2.1	0.246
Carbonized hydro-char at 220 ºC	416.8	2.0	0.205

Comparison of hydrothermal treatment time was studied surface area as shown in **Table.** 4.3. 4 hours of carbonized hydro-char obtained hydrothermal treatment was showed lowest surface area. Hydro-char was not polymerized carbon chain because the temperature into hot air oven achieved into at 180 ºC of treatment temperature for 2 hours [24]. 12 hours of hydrothermal treatment could polymerize carbons atom and remove hydrogen, oxygen and nitrogen atom. The hydrothermal treatment time increased hydrolysis reaction. However, 8 hours of hydrothermal treatment time presented the highest surface area. They would suggest that water could be

decomposed reactant but 12 hours of hydrothermal treatment decomposed and polymerized carbon atom for producing large carbonaceous particle [24].

Table 4.3 BET of carbonized hydro-char at different treatment time

Sample	Specific surface area (m^2/g)	Average pore diameter (nm)	Total pore volume (cm^3/g)
Carbonized hydro-char at 180 ºC 4 hours	351.9	4.4	0.391
Carbonized hydro-char at 180 ºC 8 hours	635.8	2.7	0.437
Carbonized hydro-char at 180 ºC 12 hours	359.1	3.7	0.333

4.1.4 FT-IR analysis of synthesized carbonaceous powder

All characteristics of water hyacinth treated hydrothermally at 160, 180, 200 and 220 °C for 4, 8 and 12 hours were characterized by FT-IR analyzer as shown in **Fig** 4.10. It was found that all water hyacinth treated hydrothermally samples showed similarly the oxygen functional groups or free radicals on the surface. 3700-3000 cm^{-1} vibration significantly presented O-H stretching vibration in hydroxyl or carboxyl group. O-H vibration indicated carbon and alkyl bond which of alcohol group. Alcohol groups could be dehydrated for producing water and alkene carbon bond. It should be noted that acid treatment could improve dehydration reaction rate [23]. In O-H stretching was decreased with the increasing treatment temperature and reaction time. It found that decreasing O-H stretching vibration could describe dehydration reaction. Moreover, increasing temperature could generate hydronium ions from de-ion water let to the hydrolyzing lignocellulosic material. Comparison of transmittance of carbonaceous particles obtained from different treatment temperature which was significantly compared with dried water hyacinth. 2925 and 2850 cm^{-1} corresponded

C-H stretching vibration in polysaccharide of hemi-cellulose and cellulose. 1765-1700 cm^{-1} attributed to C=O vibrations in carbonyl, quinine, ester or carboxyl. 1650 cm-1 and 1550 cm^{-1} related to the aromatic -C=C- stretch of the aromatic rings of lignin. It should be noted that hydrothermal treatment of starch was decomposed. The resultant liquid product such as 5-HMF could produce carbonaceous particle [22] therefore aromatic -C=C- presented in hydro-char obtained from hydrothermal treatment of water hyacinth at temperature 220 ºC for 8 hours. 1200–900 cm^{-1} presented C-O stretching of hydroxyl, ester and ether. Water treated hydrothermally at 220 ºC, C-O stretching disappeared form hydro-char. Because of treatment temperature and reaction time, carbon content increased. Radical carbons polymerized into an aromatic ring for producing carbonaceous powder [33]. On the other hand, an increasing temperature could increase gas and liquid product. FT-IR peak could not clearly be descried decreasing of the radical atom. They are confirmed decreasing O-H stretching in CHNO/S as shown in **Fig** 4.12.

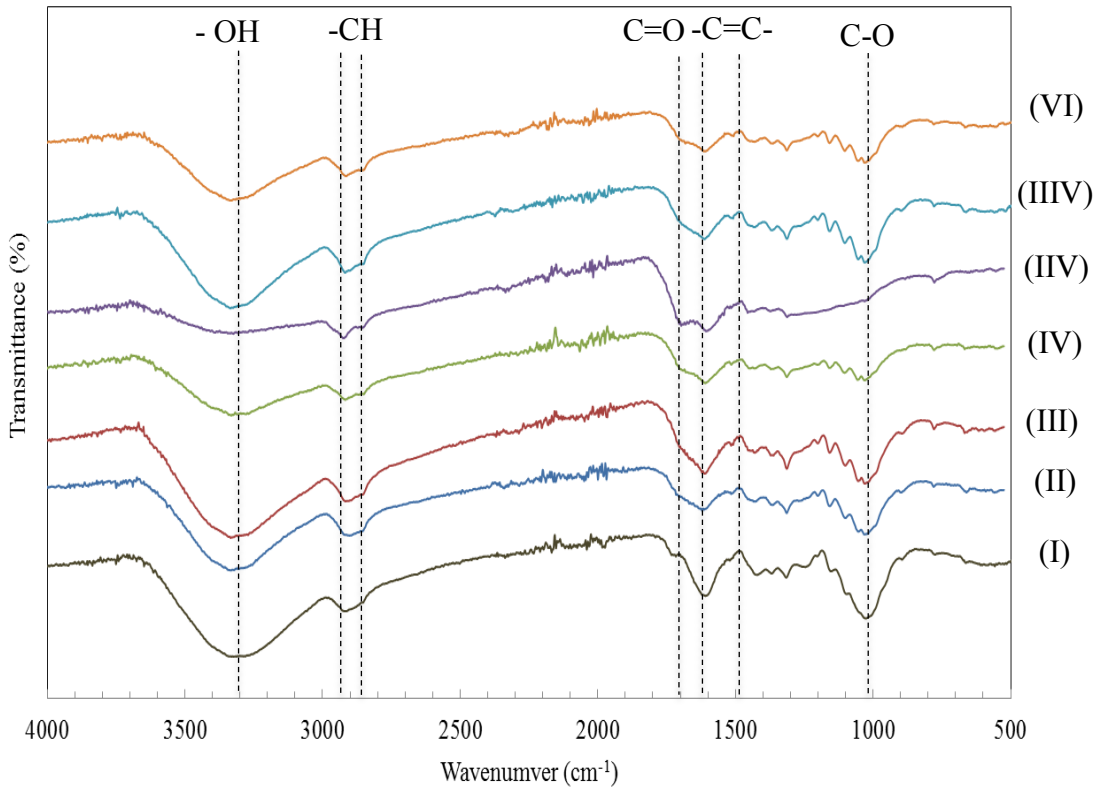


Fig. 4.10 FT-IR spectra of dried water hyacinth (I) and water hyacinth treated hydrothermally at different temperature 160 °C (II) 180 °C (III) 200 °C (IV) 220 °C for 8 hours and treatment time 4 hours (IIIV) 12 hours (VI) at 180 °C

Hydro-char was compressed for making a rod. They would suggest that radical on the surface of the hydro-char could involve with molecule char. After that, hydro-char was carbonized at a temperature of 900 °C for removing volatilized material. Carbonized hydro-chars were characterized by FT-IR analyzer. The functional groups could be eliminated and provided purity of carbonaceous particle as shown in **Fig**. 4.11. Carbon radical could be arranged carbon structure. There are showed crystalline structure. The crystalline structure is important conductivity carbonaceous particle [21]. The result of FI-IR graph was found that functional groups disappeared on carbonized hydro-char because volatile compounds are eliminated by thermal decomposition. It should be noted that Lignin decomposed at the temperature of 700 ºC [7]. Hydro-char rod was burned at high treatment temperature. In arc discharge process high purity carbon which related vaporization of carbon as anode material by arc discharge. However, all of carbonized hydro-char sample were similarly shown vibration with treatment at different temperature and time.

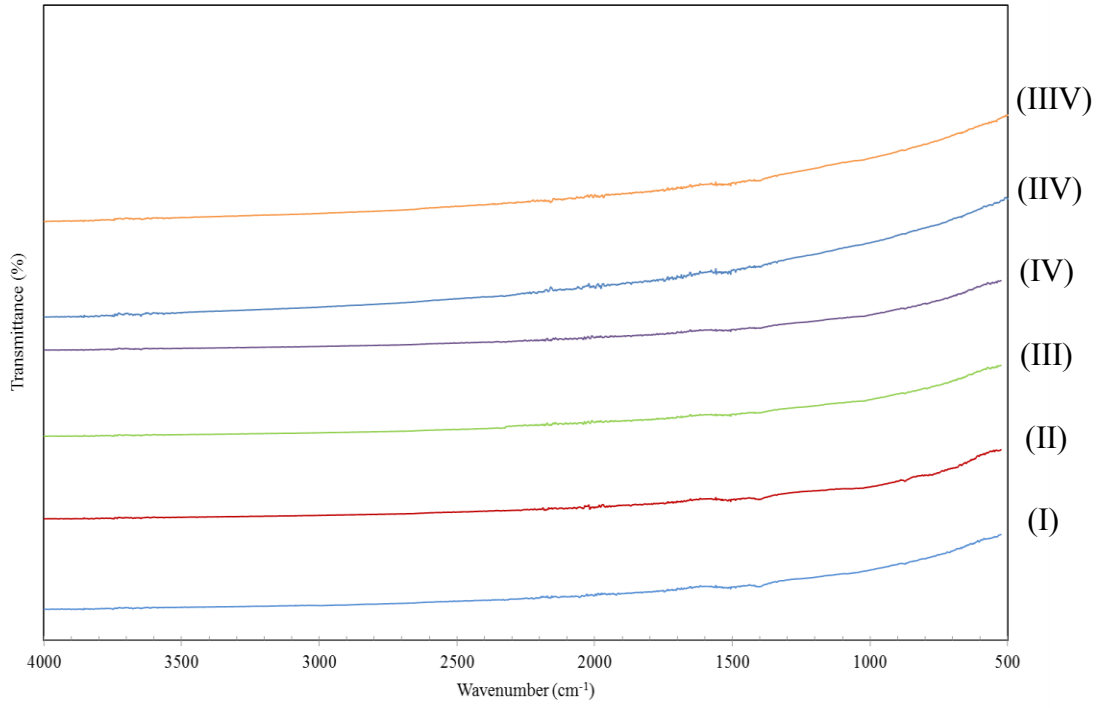
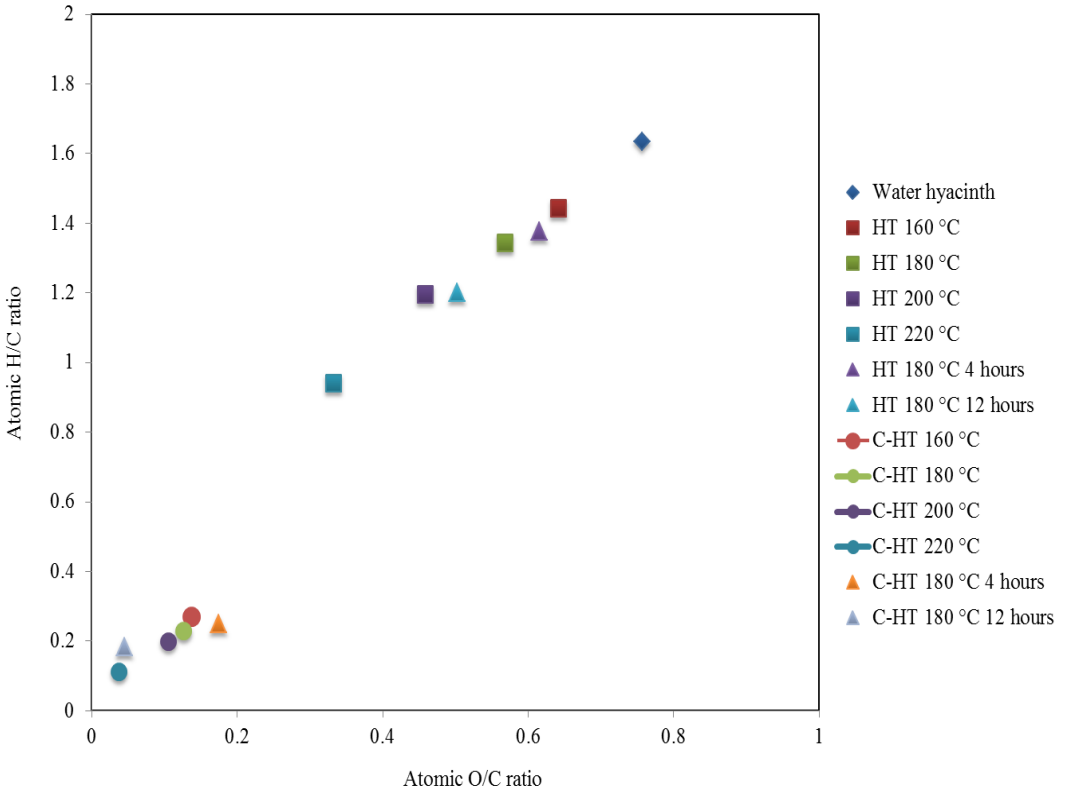


Fig.4.11 FT-IR spectra of carbonized hydro-char at 900 °C obtained from water hyacinth treated hydrothermally at (I) 160 °C (II) 180 °C (III) 200 °C (IV) 220 °C for 8 hours and treatment time 4 hours (IIIV) 12 hours (VI) at 180 °C

4.1.5 Composition of synthesized carbonaceous powder



HT = Water hyacinth treated hydrothermally (hydro-char)

C = Carbonized hydro-char at 900 °C

Fig 4.12 Composition of water hyacinth, water hyacinth treated hydrothermally and hydro-char obtained from water hyacinth treated hydrothermally

This study an alternative to increasing carbon content of hydro-char and carbonized hydro-char were recognized using hydrothermal treatment and carbonization process which used water hyacinth as raw material. The composition of water hyacinth, hydro-char and carbonized hydro-char were shown in **Fig** 4.12. Van Krevelen diagram described chemical reaction such as dehydration, decarboxylation and demethanation by among of H/C and O/C atomic ratio [22]. For example, 2 atomic ratio of H/C and 1 atomic ratio of O/C generated the dehydration reaction which has effects functional groups. The water hyacinth has presents low carbon and high oxygen content. The composition of treatment temperature and time obtained

from hydrothermal. It was found that H/C and O/C ratio were decreased. Water hyacinth was compared with water hyacinth treated hydrothermally at 160 °C. It could confirm that dehydration reaction examined by an increasing carbon content and decreased oxygen and hydrogen content. At 180 °C of treatment temperatures was compared with at 220 °C of treatment temperatures. It should be noted that an increasing temperature was treated hydrothermally let to carbon content. At the same time, oxygen and hydrogen content were decreased. The increasing carbon content was confirmed that treatment hydrothermal could improve value-add of water hyacinth for producing the carbonaceous material. Generally, the carbonaceous particle is a one of high conductivity material because free radical in carbon structure moved on carbon layer [21]. Therefore, the hydrothermal treatment is a one of technique which can provide carbonaceous materials. Generally, lignite plotted 0.8-1.3 H/C atom and 0.2-0.38 O/C atom ratio [40]. The carbonized hydro-char atomic ratio was considered higher than lignite material. The hydro-char atomic ratio was considered lower than lignite material. This research hydrothermal treatment was used for improving carbon purity properties on water hyacinth as feed. The resultant products of hydrothermal treatment remained oxygen, hydrogen and nitrogen. Carbonization was used for removing compound and improving a specific surface area. Carbonized hydro-char at 220 °C showed highest carbon content. This result confirmed that pre-treatment affected on carbon atom. It would be confirmed decomposition of lignocellulosic material and generating graphitic carbon which was shown in **Fig** 4.13

4.1.6 XRD of synthesized carbonaceous powder

(A) Carbon (B) Graphite (C) Cellulose (D) Lignin (E) $CaCO_3$

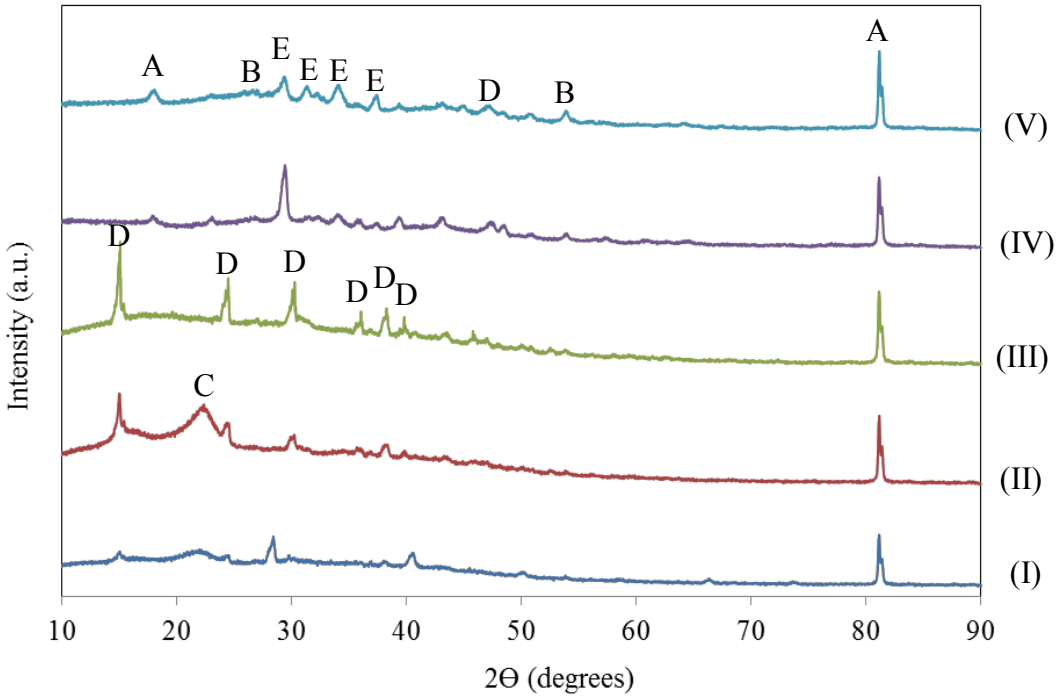


Fig 4.13 XRD patterns of water hyacinth (I), hydro-char at temperature 180 °C (II) and 220 °C (III) for 8 hours and carbonized hydro-char 900 °C obtained from hydro-char at 180 °C (IV) and 220 °C (V) for 8 hours

Crystallography of carbonaceous particle and water hyacinth was discussed by XRD graph which was shown in **Fig** 4.13. Water hyacinth involved with lignocellulosic materials. Cellulose showed amorphous in a range 16-22.7°. 26.5° and 53.5º peak vibrations described graphite carbon. In vibration range 14.9-20° and 82° showed carbon. Hemicellulose showed in vibration range 26-28° [41]. Lignin showed several of peak vibrations because lignin composed of complex carbon structure. It was found that water hyacinth treated hydrothermally at 180 °C for 8 hours was still present the cellulose peak. This resultant product confirmed that the himi-cellulose could be decomposed at < 180 °C by hydrothermal treatment. The cellulose peak disappeared at treatment temperature of 220 °C. The decomposition of hemi-cellulose and cellulose related by hydrolysis and hydration reaction[8]. The hydration reaction

corresponds addition water which resulted in an electrode for making a short molecule, alcohol group and acid or base via hydrothermal treatment.[22]. Base on XRD analyzer, carbonized hydro-char showed $CaCO_3$ structure Laginhas et al. found that hydro-char obtained from chitosan which was activated under nitrogen gas and impregnated $CaCO_3$. It should be noted that $CaCO_3$ could improve the specific surface area which 642 cm^3/g at temperature of 800 °C for 1 hour via carbonization process [28]. The graphitic carbon peak importantly utilized for conducting as electrode in arc discharge in water. Graphite has layered carbon structure which carbon atom of layer liked coverlet bond by van der Waals fore [20]. Comparison of the crystallography of carbonaceous material obtained from different sources which were the carbonized hydro-char and commercial graphite powders as shown in **Fig** 4.14.

(A) Carbon (B) Graphite

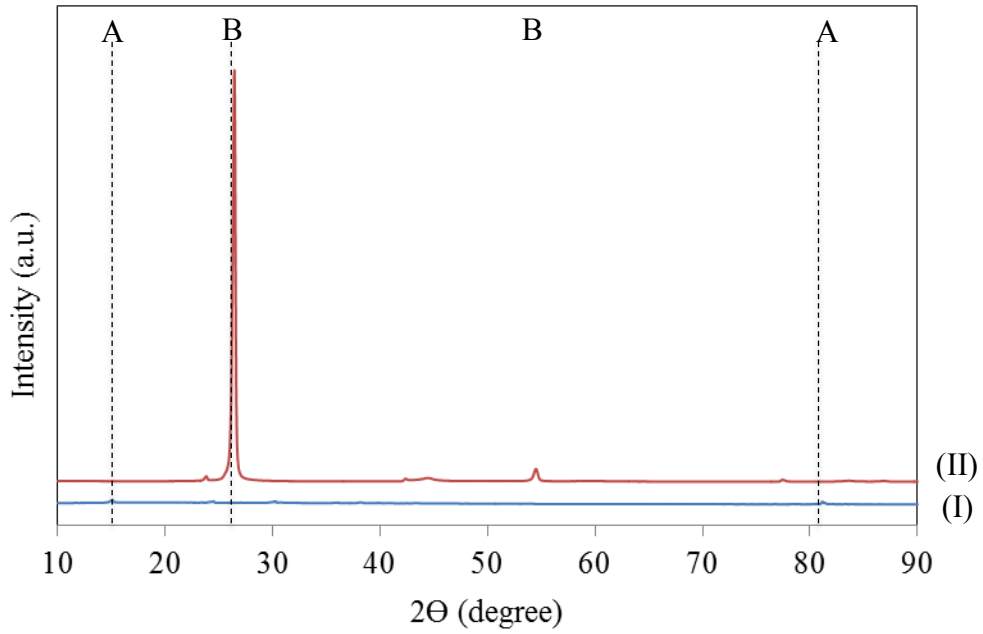


Fig 4.14 XRD patterns of commercial graphite (I) and carbonized hydro-char 900 °C obtained from water hyacinth treated hydrothermal at 220 ºC for 8 hours (II)

4.1.7 Effect of resistivity carbonized hydro-char

Electric conductivity is important for utilizing as electrode material via arc discharge in water. The resistivity of commercial graphite and carbonized hydro-char at different temperature was shown in **Table** 4.4. The result of experimental was found that carbon content of the sample significantly increased with different treatment temperature by hydrothermal treatment. The resistivity of carbonized hydro-chars was discussed. It was found that commercial graphite lowest electrical resistivity. This result confirmed that the commercial graphite easily flaked layer carbon which suitably utilized as electrode material by using arc discharge in water [20]. Electrical conductivity was not presented in water hyacinth treated hydrothermally. Functional groups of hydro-char blocked electrical conductivity. However, carbonized hydro-char showed high electrical conductivity. The resistivity increased with an increasing hydrothermal treatment temperature. It could be confirmed CHNO/S method that carbon content significantly tested electrical conductivity. At the same time, Kurniawan et al.were found that activate carbon microsphere obtained from water hyacinth by using carbonization and activating with KOH. It was found that they could be produced high specific area and electrochemical stability carbon [42].

Table 4.4 Resistivity of commercial graphite and carbonized hydro-char

Sample	Resistivity (mΩ-cm)
Commercial graphite	0.2±0.000
Carbonized hydro-char at 900 °C obtained water treated hydrothermally at 160 °C	13.9±0.07
Carbonized hydro-char at 900 °C obtained water treated hydrothermally at 180 °C	12.0±0.20
Carbonized hydro-char at 900 °C obtained water treated hydrothermally at 200 °C	10.2±0.10
Carbonized hydro-cha at 900 °C obtained water treated hydrothermally at 220 °C	7.9±0.05

4.2 Effect of carbonizing temperature

4.2.1 SEM analysis of synthesized carbonized hydro-char

Carbonizing temperature was investigated at a temperature of 500, 700 and 900 °C Carbonized hydro-char was utilized as electrode material by arc discharge. At 500 °C of treatment temperature was shown fibrous structure. Some lignocellulosic compound was not decomposed carbon structure. It was found that lignocellulosic material consists of cellulose, hemicellulose and lignin. Lignin was composed of complex hydrocarbon structure; therefore at 500 °C of carbonizing temperature cannot completely decompose lignin material [27]. Similarly, at 700 °C of carbonizing temperature was present some fibrous structure. However, SEM image could not confirm functional groups or radical on lignin. It was confirmed that lignin presented hydrocarbon bond on carbonized hydro-char by FT-IR analyzer as shown in **Fig** 4.15

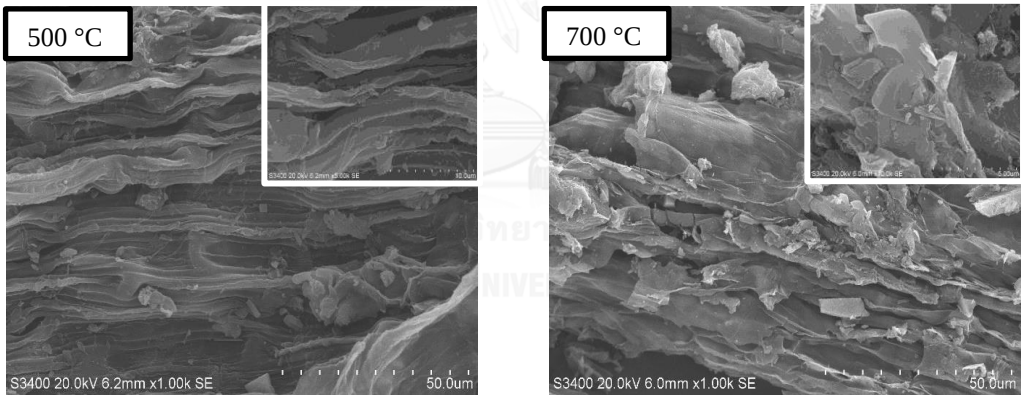


Fig. 4.15 SEM micrograph of carbonized hydro-char at 500 °C and 700 °C obtained from water hyacinth treated hydrothermally at 180 °C

4.2.1 FT-IR analysis of synthesized carbonized hydro-char

Carbonized hydro-char at different carbonization temperature was shown in **Fig** 4.16. The resultant products of 500 and 700 °C of carbonizing temperature showed functional groups on surface. It was found that 1350 cm^{-1} vibration showed aromatic -CH and carboxyl –carbonate in lignin of lignocellulosic materials. 867 cm^{-1}

vibration indicated C-C bond. This result confirmed that carbonization temperature importantly removed radical on hydro-char the surface. Functional groups on the surface affected the electrical resistance of the sample. Low conductance such as oxygen, hydrogen and nitrogen compound in biomass obstructed conducting carbon sample. 900 °C of carbonizing temperature could be removed all of the functional groups on the surface. It should be noted that carbonization of lignocellulosic material presented of oxygen groups lower than at temperature of 800 ºC [7]. The carbonizing temperature significantly synthesized carbonaceous particle. The carbonization temperature has affected decreasing liquid and gas on surface [27]. Carbon structure was arranged to depend on treating temperature. It should be noted that dehydration and decarboxylation reaction were observed of hydrogen and oxygen content [43]. Moreover, activation temperature indicated pour volume on the sample. However, Sevilla et al. found that microsphere obtained from hydrothermally treated organic material that carbonized at different temperature showed high specific surface area 1283-2370 cm^{-1} and developed super-microspores structure [22].

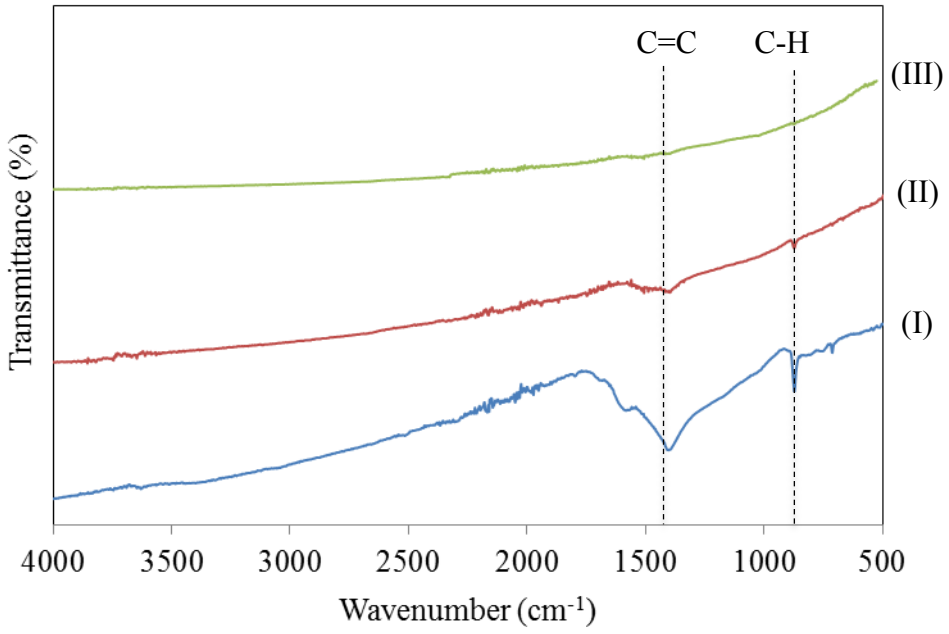


Fig. 4.16 FT-IR spectra of carbonized hydro-char at 500 °C (I), 700 °C (II) and 900 °C obtained from water hyacinth treated hydrothermally at 180 °C

4.3 Synthesis of hydro-char and carbonized hydro-char with ferric nitrate

4.3.1 SEM analysis of synthesized Fe-hybridized carbonaceous powder

Morphology of Fe-hybridized carbonaceous powder was studied by SEM as shown in **Fig** 4.17. $Fe(NO_3)_3$ and water hyacinth was added in an autoclave reactor at different contents. The addition of ferric nitrate solution has had an effect suspending iron particle solution with a carbonaceous particle. Then, the autoclave reactor was hydrothermally treated with water and water hyacinth. Normally, the addition of metal particle content could improve reaction rate, however type of metal could decrease activate energy reaction. Iron is a one of metal could increase chemical a reaction rate of hydrothermal treatment. Lee et al. found that metal oxide (Fe_3O_4, TiO_2 and Ni_2O_3) as Fe_3O_4 could promote fructose and 5-HMF which was intermediately used raw material for converting carbonaceous particle.[44] The intermediates such as furfural, 5-HMF and total organic carbon (TOC) were decreased which there are polymerized for producing char product. Glucose Hydrolyzed was faster than 5-HMF reaction [45]. However, there were increases to form other gaseous products (i.e. CO_2, CO, and CH_4) or liquid products (i.e. acetic acid, lactic, levulinic and formic acids) [46]. Because different of ferric nitrate content, iron particle size differently showed particle distribution. 4 g of presence ferric nitrate dispersed in Fe-hybridized carbonaceous particle with diameter of 0.6-1.8 μm. which was shown lowest distribution. Iron oxide particle showed sphere shape. Synthesizing iron oxide particle, temperature and reaction time affected particle size. Ozel et al. reported that iron oxide particle could be synthesized by treatment hydrothermal which could control growing of iron particle [47]. 8 g of presence ferric nitrate showed in the particle size with diameter of 0.4-1 μm. Fe-hybridized carbonaceous powder presented with 8 g of ferric nitrate presented a good dispersion of Fe_2O_3 particle. 12 g of presence ferric nitrate showed in particle size with diameter of 0.4-1 μm. However, the presence of iron particle was confirmed by EDS analyzer as shown in **Table** 4.17.

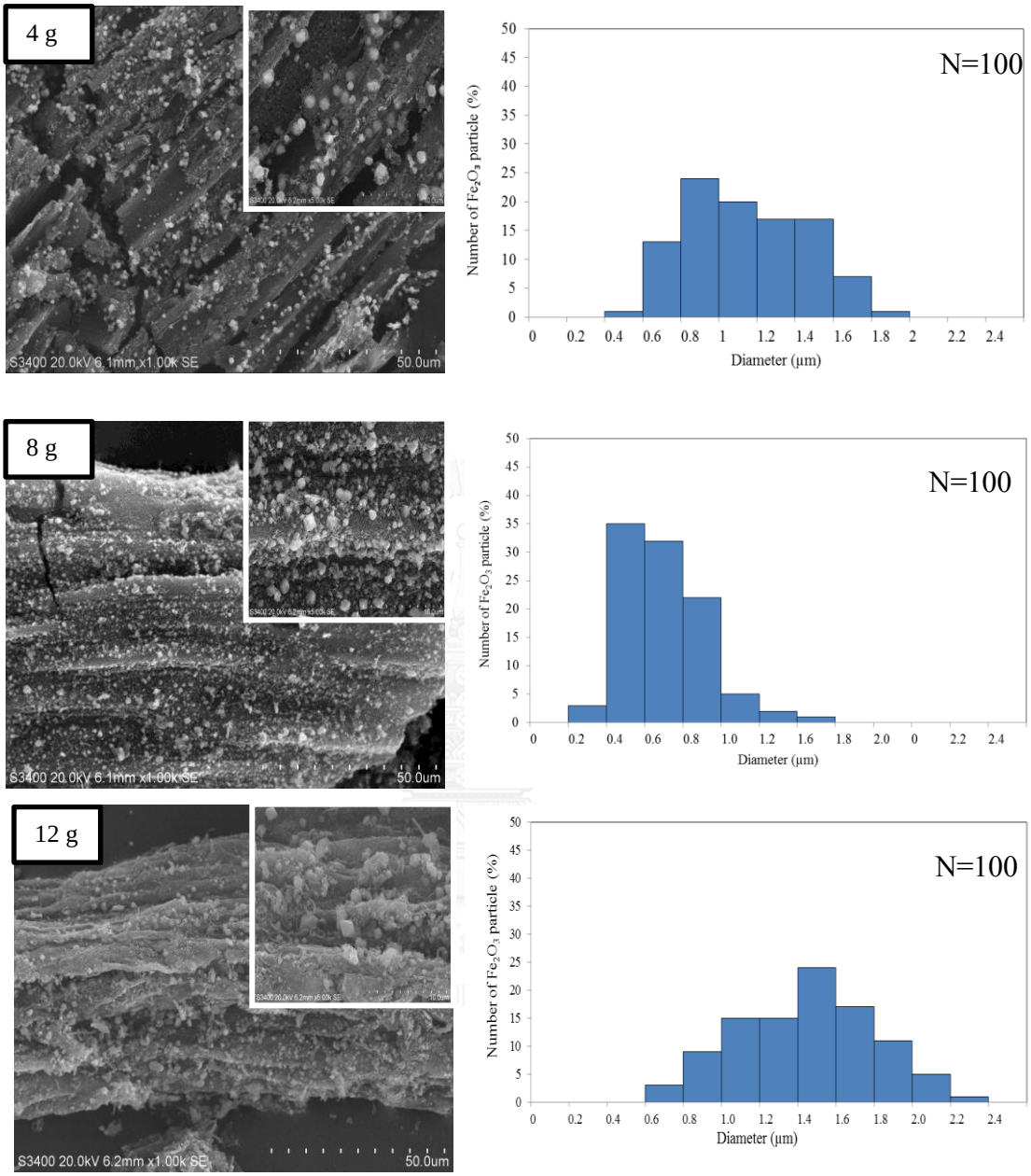


Fig. 4.17 SEM micrograph of products obtained from carbonized of hydro-char at different $Fe(NO_3)_3$ contents

4.3.2 EDS analysis of synthesized Fe-hybridized carbonaceous powder

4, 8 and 12 g of an addition of ferric nitrate were hydrothermally treated with water hyacinth. Then, resultant products were carbonized at temperature 900 °C. EDS analyzer could confirm that presence of ferric nitrate with water hyacinth by using hydrothermal treatment could synthesize Fe-hybridized carbonaceous particle as shown in **Table** 4.5. It was found that 4 g of presence ferric nitrate showed lowest iron particle content which presented 19% w/w of Fe/C particle. The resultant products by EDS analyzer described adding ferric nitrate ratio treated hydrothermally with water hyacinth. 8 and 12 of presence ferric nitrate similarly showed iron particle concentration. Therefore, 8 g of adding ferric nitrate enough treated with hydrothermal for synthesizing Fe-hybridized carbonaceous particle. The addition of ferric nitrate could improve liquid and gas reaction [48]. Therefore, they suggested that12 g of presence ferric nitrate could highest dope on carbonaceous particle and generate gas and liquid product.

Table 4.5 EDS result of carbonized hydro-char obtained from water hyacinth treated hydrothermally with the presence of 4-12 g of $Fe(NO_3)_3 \cdot 9H_2O$ at 180 °C for 8 hours

Sample	%Fe and C (%w/w)
Carbonaceous sample treated presence 4 g of $Fe(NO_3)_3 \bullet 9H_2O$	19.0
Carbonaceous sample treated presence 8 g of $Fe(NO_3)_3 \bullet 9H_2O$	29.0
Carbonaceous sample treated presence 12 g of $Fe(NO_3)_3 \bullet 9H_2O$	33.0

4.3.3 XRD analysis of synthesized Fe-hybridized carbonaceous powder

The crystalline structure of Fe-hybridized carbonaceous powder was analyzed by x-ray different spectrometer as shown in **Fig** 4.18. Detection of diffraction peaks was performed to identify the crystallographic structure of each sample. This work, the degree was scanned in range $10 \leq 2\Theta \leq 90$. The diffraction peaks in range 14.9-20° and 82° descried carbon. 26.5º and 53.5º observed graphite carbon. 30.20°, 35.5°, 43.2°,54° , 57.3° and 62.8° showed γ-Fe_2O_3 particle [31, 48]. The γ-Fe_2O_3 is a one of iron oxide which was high paramagnetic particle. Fe_2O_3 particle could be synthesized by treatment hydrothermal. The hydrothermal treatment could control particle size and dispersion particle by treating temperature and reaction time. Ferric solution ($Fe_2(NO_3)_3$,$FeCl_3$) was dehydrated by treatment hydrothermal. Chai et al. found that mixing of glucose and ferric nitrate solution could synthesize carbon-coated Fe_2O_3 nanocrystals. Glucose could be improved interconnection and self-assembled with iron particle [48]. However, this research the iron oxide particle was confirmed $Fe_2O_3$and sample ratio as show in **Table** 4.6.

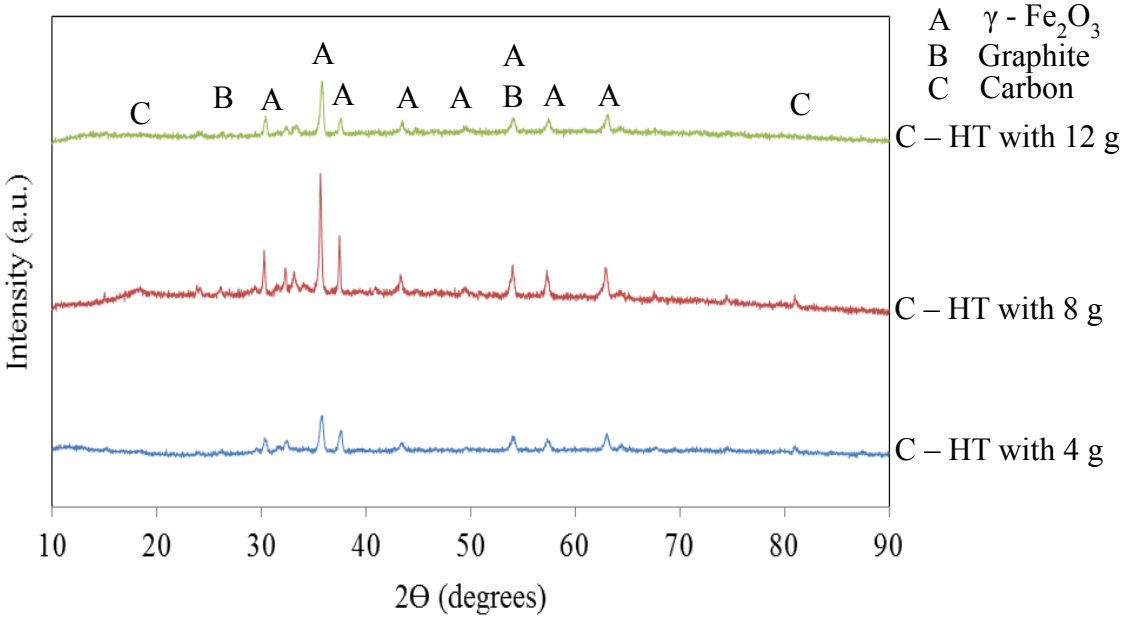


Fig 4.18 XRD patterns of carbonized hydro-char obtained from water hyacinth treated hydrothermally with the presence of 4, 8 and 12 g of $Fe(NO_3)_3 \cdot 9H_2O$ at 180 °C for 8 hours

4.3.4 AAS analysis of synthesized Fe-hybridized carbonaceous powder

Fe-hybridized carbonaceous particles were produced which used hydrothermal treatment and carbonization process. A quantity of Fe-hybridized carbonaceous particle was analyzed by AAS analyzer as shown in **Table** 4.6. It was found that 4 g of presence ferric nitrate could synthesize Fe_2O_3 -hybridized carbonaceous particle by 20.8 %w/w. The AAS result was found that 180 ºC of treatment temperature for 8 hours and 900 °C of carbonizing hydro-char temperature with presence 8g of ferric entreat could synthesize 28.2 % of Fe_2O_3 and carbonaceous ratio. This result confirmed that Fe_2O_3 particle on carbonaceous can check repeatability result of EDS analyzer. Base on EDS analyzer, 12 g of presence ferric nitrate was confirmed by AAS analyzer. They would suggest that iron particle was aggregated. Then, Iron particle was shown sedimentation particle on a reactor. However, the iron particle could increase organic compound to form gaseous products (i.e. CO_2, CO, and CH_4) or liquid products [46]. Therefore, 12 g of presence ferric nitrate showed highest Fe_2O_3-hybried sample by AAS analyzer. This research, 8 g of Fe-hybridized carbonaceous powder would be used as anode material for arc discharge in water.

Table 4.6 AAS result of carbonized hydro-char obtained from water hyacinth treated hydrothermally with the presence of 4-12 g of $Fe(NO_3)_3 \cdot 9H_2O$ at 180 °C for 8 hours

Sample	% Fe_2O_3: sample (%w/w)
Carbonaceous sample treated presence 4 g of $Fe(NO_3)_3 \bullet 9H_2O$	20.8
Carbonaceous sample treated presence 8 g of $Fe(NO_3)_3 \bullet 9H_2O$	28.2
Carbonaceous sample treated presence 12 g of $Fe(NO_3)_3 \bullet 9H_2O$	62.8

4.3.5 BET analysis of synthesized Fe-hybridized carbonaceous powder

A presence of iron oxide particle products was described by BET analyzer. Iron oxide placed on a carbonaceous particle. An increasing of ferric nitrate with hydrothermal treatment was investigated effect of decreasing surface area. It was found that adding of ferric nitrate affected a specific surface area. At without ferric nitrate, the specific surface area was showed 635.8 cm^{-1}/ g. This result was confirmed that iron particle connected with the carbonaceous particle as shown in **Table** 4.7. Base on AAS analyzer, it was found that the result of 12 g of Fe-hybridized carbonaceous powder confirmed aggregate iron oxide particle. It should be noted that iron oxide particle showed low surface area [47]. However, this work presented high Specific surface area when used 12 g of presence $Fe(NO_3)_3$• 9H2O, suggesting that iron oxide particle can provided specific surface area on the carbonaceous particle.

Table 4.7 BET result of carbonized hydro-char obtained from water hyacinth treated hydrothermally with the presence of 4-12 g of $Fe(NO_3)_3$· $9H_2O$ at 180 °C for 8 hours

Sample	Specific surface area (m^2/g)	Average pore diameter (nm)	Total pore volume (cm^3/g)
Carbonized hydro-char 180 °C 8 hours	635.8	2.7	0.437
Carbonaceous sample treated presence 4 g of $Fe(NO_3)_3$• $9H_2O$	374.6	3.3	0.309
Carbonaceous sample treated presence 8 g of $Fe(NO_3)_3$• $9H_2O$	217.1	3.8	0.205
Carbonaceous sample treated presence 12 g of $Fe(NO_3)_3$• 9H2O	259.4	3.4	0.219

4.4 Effect of using carbonized hydro-char and carbonized hydro-char as electrode in arc discharge method

4.4.1 TEM analysis of synthesized carbonaceous nanoparticle

Graphite features hexagonal structure which existed each of plan by covalent bonds. Each of graphite layers was linked by Van der Waals force. Because of low bonding, Graphite particle is one of high conductivity which depends on crystalline [20]. There are several methods to synthesize carbon particle. Those methods can be divided into a chemical and physical method. Arc discharge is one of cost-effective technique. It is compact and applicable in small-scale experiment. Generally, graphite rod was used as electrode carbon. Because of high conductance material, graphite carbon is easy decomposed. In arc discharge method, graphite was conducted cathode and anode carbon. However, anode was consumed for producing carbon nanoparticle. In arc discharge, electrode was employ producing carbon nano-horn material. The carbon nano-horn floated on water because carbonaceous particle showed hydrophobic [20]. Then, floating powder was collected and dried at 105 °C. Inert gas as such as CO_2, He, Kr, Ar and N_2 was used for conducting arc discharge. The inert gas affected yield and arrangement carbonaceous nanoparticle [49]. N_2 is a one of inert gas that low cost and high quantity. N_2 gas and water was utilized via arc discharge for producing carbonaceous nanoparticle [21].Graphite carbon was vaporized under inert gas, surrounding of carbon vapor was submerged water. The water could help to cooling carbon vapor for producing carbonaceous product [21]. Carbon nano-horn particle is a one of carbonaceous particle. It could be synthesized by arc discharge in water [20]. Conducting arc discharge is easy technology for producing carbon nanoparticle as shown in **Fig** 4.19.

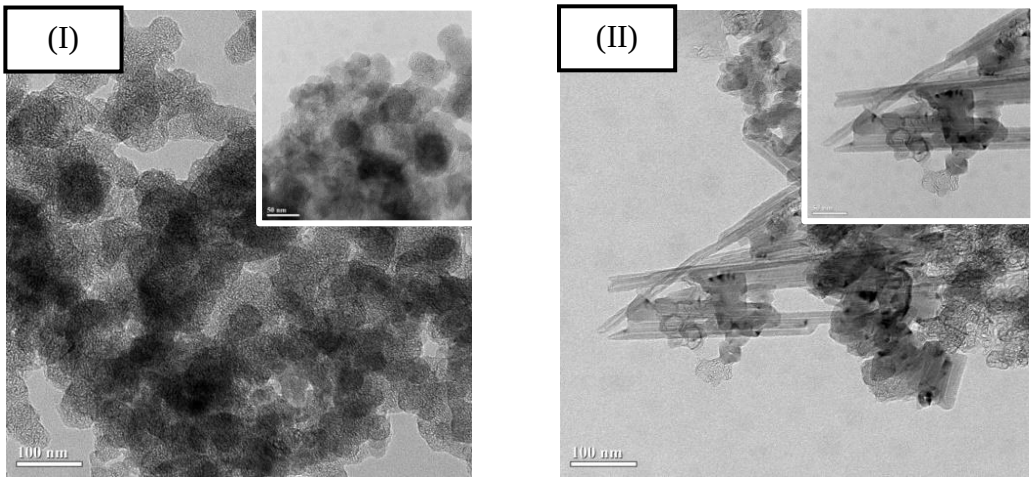


Fig. 4.19 TEM image of floating (I) and bottom (II) powder sample by using commercial graphite in arc discharge in water

However, commercial graphite rod is expensive. This research would utilize water hyacinth for producing carbonaceous rod. Carbonized hydro-char obtained water hyacinth treated hydrothermally and carbonizing hydro-char at temperature 900 °C was employed as anode material by arc discharge in water. Normally, char can be synthesized by biomass. It is present high quantity such as high carbon content, low cost and high HHV [50]. Carbonized hydro-char obtained from water hyacinth treated hydrothermally at temperature of 180 °C for 8 hours was used as electrode material by arc discharge in water. In arc discharge in water, carbonized hydro-char was vaporized carbon. Then, carbon vapors rearrange to carbonaceous nanoparticle. The carbonaceous nanoparticle was condensed by surrounding water. Finally, The carbonaceous nanoparticle fallen on the sedimentation. To collect sample, carbonaceous nanoparticle was dried at 105 °C in a hot air oven. It was found that carbonaceous particle obtained from carbonized hydro-char via arc in water showed carbon nanoparticle and some fiber carbon particle. Comparison of carbonized hydro-char obtained from water hyacinth treated hydrothermally at 180 °C for 8 hours and resultant product obtained from carbonized hydro-char conducted arc discharge in water was analyzed by TEM as shown in **Fig** 4.20. In generally, conducting arc discharge by using commercial graphite as anode material was found carbon nanotube on sedimentation and carbon nano-horn on floating [30]. However, carbonized hydro-char has an amount of $CaCO_3$. It should be noted that the temperature of arcing

temperature examined approximately in temperature range 4,000-5,000 ºK [20].They would suggest that $CaCO_3$ was vaporized to gas product. $CaCO_3$ vaporized at temperature at 800 ºC [28].Carbon content on carbonized hydro-char affected of synthesizing carbonaceous nanoparticle via arc discharge in water [21].

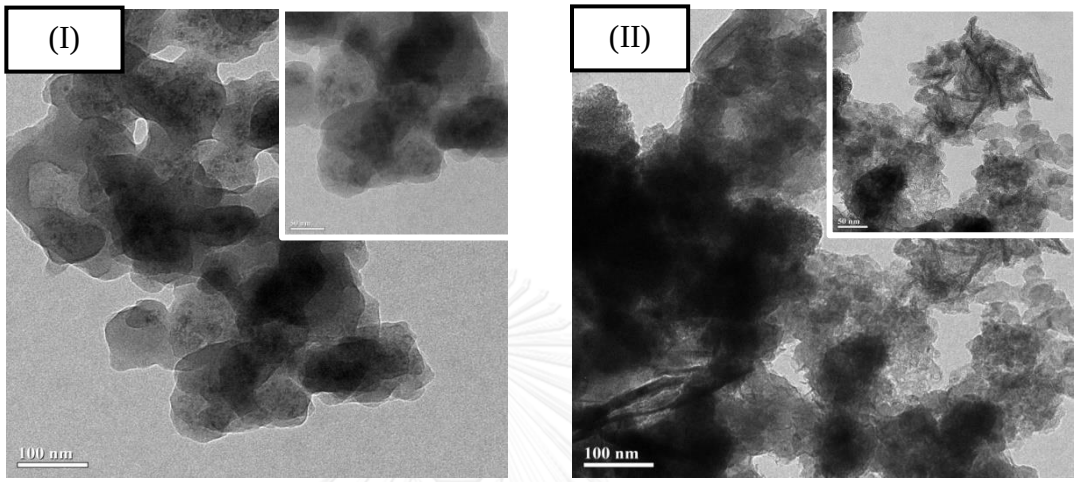


Fig. 4.20 TEM image of carbonized hydro-char obtained from water hyacinth treated hydrothermally at 180 °C for 8 hours and resultant product obtained from carbonized hydro-char conducted arc discharge in water (II)

Morphology of Carbonized hydro-char and resultant product obtained from carbonized hydro-char conducted arc discharge in water was examined by TEM analyzer as shown in **Fig** 4.21. Carbonized hydro-char obtained from hydrothermal treatment at 220 °C was highest carbon content and conductivity. It was found that carbonized hydro-char at 220 °C was compared with carbonized hydro-char at 180 °C for producing carbonaceous product. The carbon content and arc duration time importantly affected synthesizing carbonaceous nanoparticle [53].

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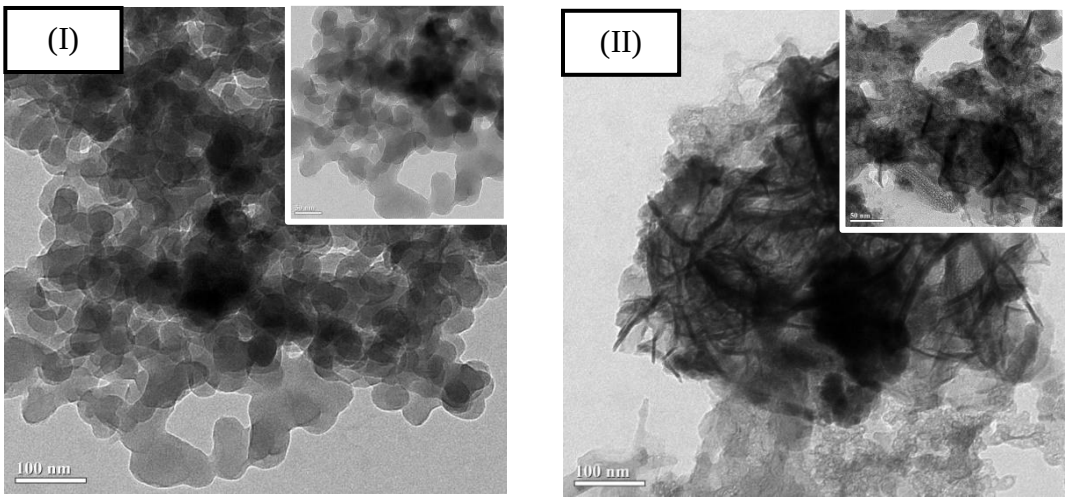


Fig. 4.21 TEM image**s** of carbonized hydro-char obtained from water hyacinth treated hydrothermally at 220 °C for 8 hours (I) and resultant product obtained from carbonized hydro-char conducted arc discharge in water (II)

Fe-hybridized carbonaceous was employed as an electrode material as shown in **Fig** 4.22. Poonjarernsilp et al. reported that Fe-SWCNH was synthesized by arc discharge in water. The arc plasma vaporized carbon and Fe from the anode and quenched by water [31]. This research, the Fe-hybridized carbonaceous was conducted as anode material by arc discharge in water. It was found that sedimentation particle was shown Fe-hybridized carbonaceous nanoparticle as shown in **Fig** 4.22. It should be noted that iron oxide particle on carbonaceous can improve carbon nanotube structure [30]. This work, carbon and Fe were vaporized. Then, carbon and Fe vapor was condensed in arc plasma zone by water. Agglomerated vapor was synthesized Fe-hybridized carbon nanoparticle.

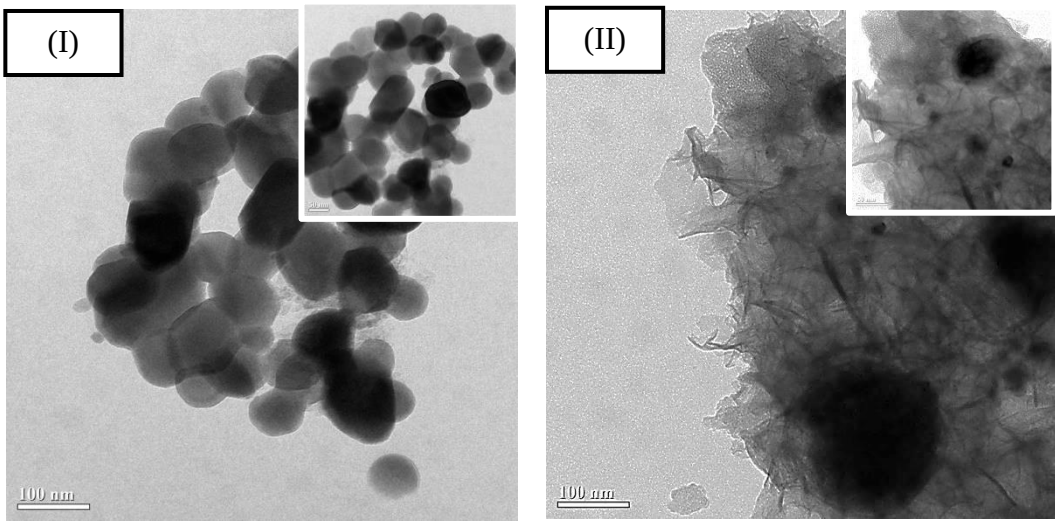
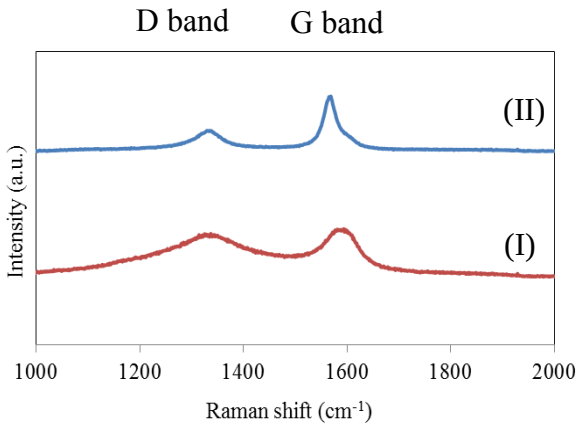


Fig. 4.22 TEM image**s** of carbonized hydro-char obtained from water hyacinth treated hydrothermally presence 8 g of nitrate at temperature at 180 °C for 8 hours (I) and resultant product obtained from carbonized hydro-char conducted arc discharge in water (II)

4.4.2 Raman analysis of synthesized carbonaceous nanoparticle

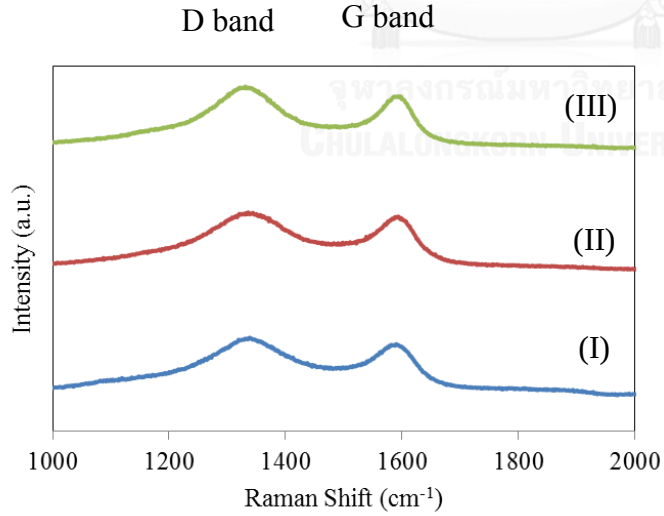
All of carbonaceous particle powers were analyzed by Raman analyzer as shown in **Fig** 4.23-25. Additional confirmation on the carbonaceous constituents in all synthesized samples was conducted by Raman spectroscopy with a 532 nm laser. Two distinctive peaks at Raman shift of 1,330 cm^{-1} and 1,580 cm^{-1}, which represents disorder carbon structure (D peak) and graphitic structure (G peak), respectively were detected in all samples [51, 52]. In general, ratio of intensity of both peaks (I_G/I_D) could be employed for determining the relative amount of graphitic carbon and disorder carbon existing in carbonaceous sample. As shown in **Fig** 4.23, it was found that the resultant products via arc discharge were shown graphitic structure higher than disorder carbon structure.



Sample	I_G/I_D
(I) Sedimentation particle	1.02
(II) Carbon nano-horn	1.16

Fig 4.23 Raman spectra of and result sample obtained from sedimentation sample (I) conducted arc discharge as using as commercial graphite and carbon nanohorn (II)

Characteristic of carbonized hydro-char was observed by Raman analyzer as shown in **Fig**.2.4. It was found that ratio of intensity of both peaks (I_G/I_D) low than 1. For this reason, the carbonized hydro-char presented both graphitic carbon and disorder carbon, suggesting that the synthesized carbonized hydro-char contained higher content of graphitic carbon structure which would refer carbon content.

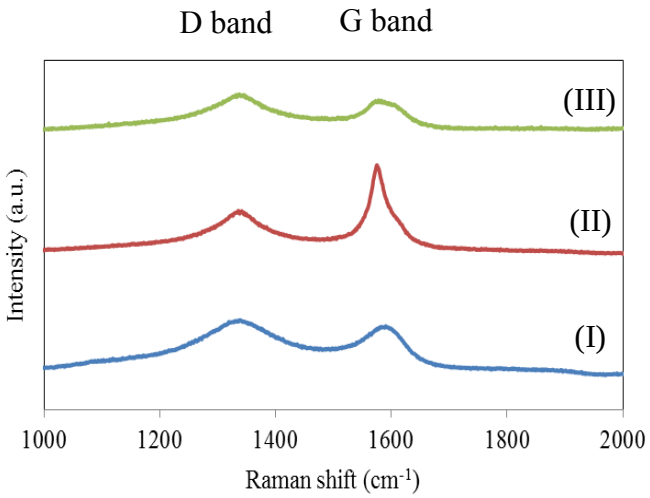


Sample	I_G/I_D
(I) C-HT at 180 °C	0.98
(II) C-HT at 220 °C	0.99
(III) C-HT at 180 °C with Fe_2O_3	0.97

Fig 4.24 Raman spectra of carbonized hydro-char at different temperature and Fe-hybridized carbonaceous particle

Conducting carbonized hydro-char as anode material via arc discharge in water was investigated by Raman analyzer. It was found that I_G/I_D increased with using carbonized hydro-char as electrode material. It confirmed that carbonaceous nanoparticle processed by conducting arc discharge in water. Carbonaceous particle rearrange to crystalline structure. However, it should be noted that SWCNH, SO_3H-SWCNH, SO_3H-AC and SO_3H-CB were compared graphitic and disordered structure. It was found that there did not significantly correspond with different material sources [53]. The disorder carbon structure and graphitic structure increased with carbonized hydro-char obtained from water hyacinth treated hydrothermally at 220 ° C. Carbon vapor was rearranged. The carbonaceous particle showed higher graphitic structure than carbonized hydro-char obtained from water hyacinth treated hydrothermal. It should be noted that the composition of carbon content at different hydrothermal treatment temperature which 220 ºC of hydrothermal treatment was higher than 180 ºC of hydrothermal treatment

With regard to all experimental data, it could be implied that the synthesized carbonaceous particle with presence iron oxide consists of carbonaceous co-existing with Fe nanoparticles. However, it was found that Fe-hybridized carbonaceous still showed higher disorder carbon structure than graphitic structure. The carbonaceous powder obtained from carbonized hydro-char as an anode was higher than carbonized hydro-char. It should be noted that Pd/SWCNH material was higher than Pd-free SWCNH [21].



Sample	I_G/I_D
(I) C-HT at 180 °C	0.98
(II) C-HT at 220 °C	1.14
(III) C-HT at 180 °C with Fe_2O_3	0.98

Fig 4.25 Raman spectra of resultant product obtained from carbonized hydro-char and Fe-hybridized carbonaceous rod conducted by arc discharge in water

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The carbonaceous particle was successfully synthesized form dried water hyacinth into high value-added material by 4 aspects hydrothermal treatment, making hydro-char rods, carbonizing hydro-chars rods and conducting arc discharge in water. This work aimed to investigate conversion of dried water hyacinth would have potential to be utilized as carbonaceous rod for fabricating electrode in arc discharge.

First, hydrothermal technique is an effective method for converting organic compounds. The hydrothermal treatment could be employed to convert dried water hyacinth to gas, liquid and solid products. The water hyacinth was hydrolyzed reaction let to breaking chemical bonds in lignocellulosic material. Base on SEM, water hyacinth treated hydrothermally would further result in change of physicochemical properties. CHNO/S confirmed microscopic properties. It should be noted that water hyacinth treated hydrothermally presented highest carbon content and lowest functional groups. However, hydro-char showed electrical conductivity.

Second, making hydro-char rods were conducted by hydraulic pressure. The water hyacinth is a one of binder for making rods. The radicals on surface could combine hydro-char for forming carbonaceous material.

Then, hydro-char rods were carbonized under nitrogen gas for increasing carbon and improving surface properties. Base on BET, it confirmed that water hyacinth treated hydrothermal was carbonized result in specific surface area. Carbonized hydro-char which was treated hydrothermally could exert the specific surface properties which would be appropriate for doping metal particle by hydrothermal treatment.

Finally, carbonized hydro-char was employed as carbonaceous material for conducting arc discharge in water. Carbonized hydro-char was utilized as electrode for producing carbonaceous nanoparticle. Moreover, carbonized hydro-char used as anode instead of commercial graphite. This research successfully converts water hyacinth to into high value-added carbonaceous materials.

5.2 Recommendations

1 .Improving physical property of carbonized hydro-char rods

2. Investigating chemical solution for improving carbonaceous particle properties

3. Investigating scale-up hydrothermal treatment for preparing hydro-char rods

4. Investigating the effect of carbonization on carbonaceous material

5. Investigating the porous carbonaceous particle. Carbonized hydro-char-have high surface area which can be utilized as catalyst materials

APPENDICES

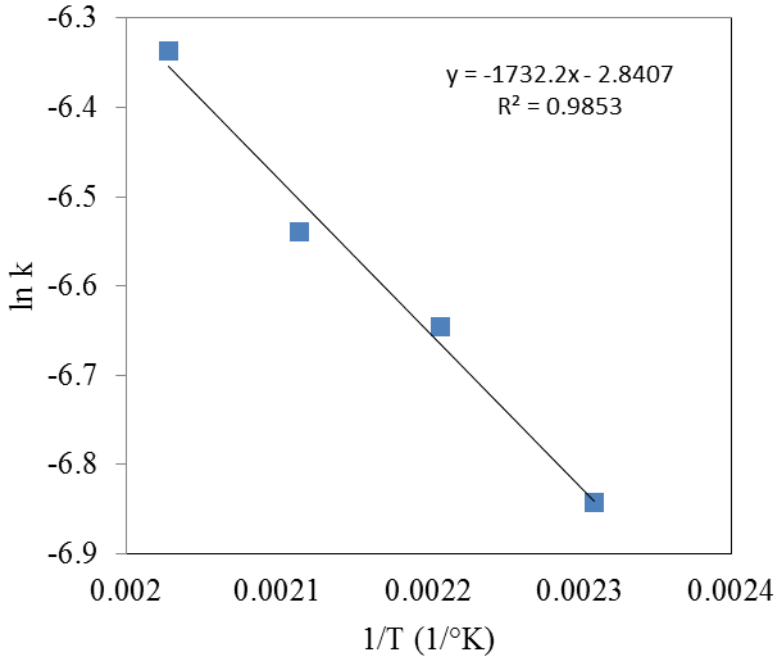


Fig A1 Calculation activated energy obtained treatment water hyacinth by first order model at different temperature

Table A1 composition of water hyacinth, Water hyacinth treated hydrothermally and carbonized hydro-char at different treatment and time

Sample	Elemental analysis (wt%)				
	C	H	N	S	O
Water hyacinth	39.31 ±0.02	5.36 ±0.36	0.66 ±0.66	0.23 ±0.03	39.67 ±0.98
Water hyacinth treated hydrothermally at 160 °C for 8 hours	48.00 ±0.20	5.77 ±0.04	1.52 ±0.067	0.24 ±0.03	40.93 ±0.91
Water hyacinth treated hydrothermally at 180 °C for 8 hours	49.06 ±0.98	5.29 ±0.32	1.90 ±0.06	0.37 ±0.0001	35.92 ±1.14
Water hyacinth treated hydrothermally at 200 °C for 8 hours	52.64 ±0.15	5.21 ±0.04	1.81 ±0.08	0.19 ±0.02	32.05 ±1.57
Water hyacinth treated hydrothermally at 220 °C for 8 hours	57.24 ±0.16	4.50 ±0.03	2.35 ±0.06	0.24 ±0.02	25.28 ±0.85
Water hyacinth treated hydrothermally at 180 °C for 4 hours	47.57 ±0.08	5.22 ±0.48	1.81 ±0.08	0.19 ±0.01	39.30 ±0.09
Water hyacinth treated hydrothermally at 180 °C for 12 hours	51.18 ±0.24	5.29 ±0.28	2.21 ±0.37	0.20 ±0.003	35.12 ±1.62

Sample	Elemental analysis (wt%)				
	C	H	N	S	O
Carbonized hydro-char at 900 °C obtained from water hyacinth treated hydrothermally at 160 °C for 8 hours	64.16 ±0.06	1.461 ±0.03	1.11 ±0.03	0.28 ±0.11	11.77 ±1.79
Carbonized hydro-char at 900 °C obtained from water hyacinth treated hydrothermally at 180 °C for 8 hours	65.51 ±0.57	1.24 ±0.008	1.02 ±0.07	0.43 ±0.45	10.75 ±2.57
Carbonized hydro-char at 900 °C obtained from water hyacinth treated hydrothermally at 200 °C for 8 hours	67.95 ±0.03	1.13 ±0.01	1.19 ±0.03	0.28 ±0.02	9.58 ±1.02
Carbonized hydro-char at 900 °C obtained from water hyacinth treated hydrothermally at 220 °C for 8 hours	73.10 ±0.18	0.73 ±0.0741	1.77 ±0.04	0.24 ±0.02	3.52 ±1.15
Carbonized hydro-char at 900 °C obtained from water hyacinth treated hydrothermally at 180 °C for 4 hours	63.89 ±0.20	1.50 ±0.35	1.72 ±0.11	0.42 ±0.11	14.57 ±1.53
Carbonized hydro-char at 900 °C obtained from water hyacinth treated hydrothermally at 180 °C for 12 hours	67.53 ±1.02	1.07 ±0.05	1.77 ±0.09	0.48 ±0.22	4.58 ±0.28

Sample	Elemental analysis (wt%)				
	C	H	N	S	O
Carbonized hydro-char at 700 °C obtained from water hyacinth treated hydrothermally at 180 °C for 8 hours	56.74± 0.72	2.44± 0.17	3.05± 0.12	0.14± 0.04	20.16± 0.74
Carbonized hydro-char at 700 °C obtained from water hyacinth treated hydrothermally at 180 °C for 8 hours	58.70± 0.06	2.03± 0.07	1.73± 0.30	0.17± 0.003	15.78± 0.35

Carbonized hydro-char was analyzed by BET analyzer as shown in **Fig** A1-A19

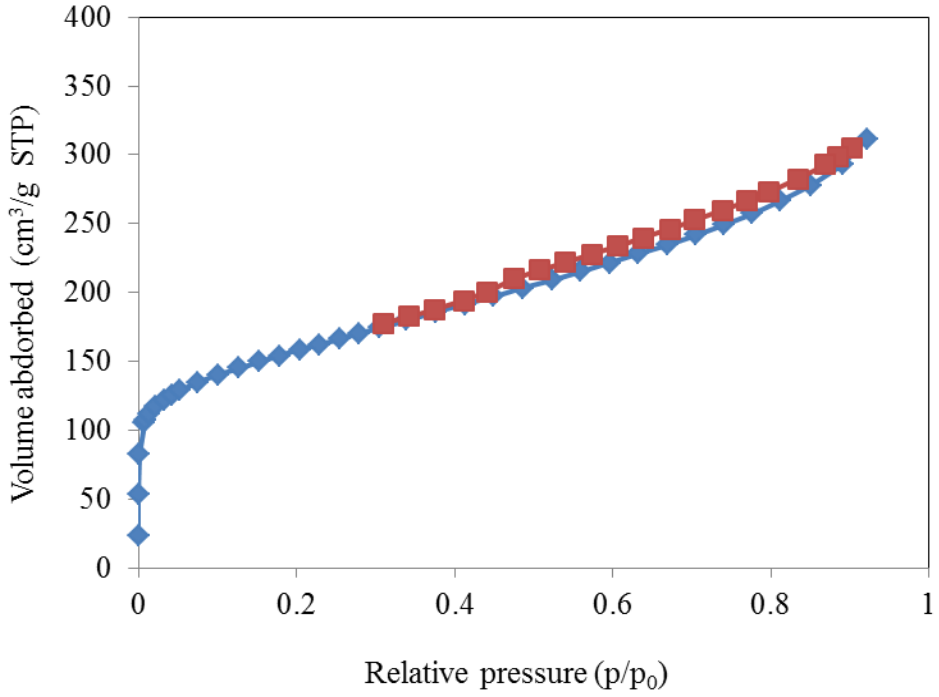


Fig A2 Adsorption and desorption of carbonized hydro-char at 900 °C obtained from water hyacinth treated hydrothermally at 160 °C for 8 hours

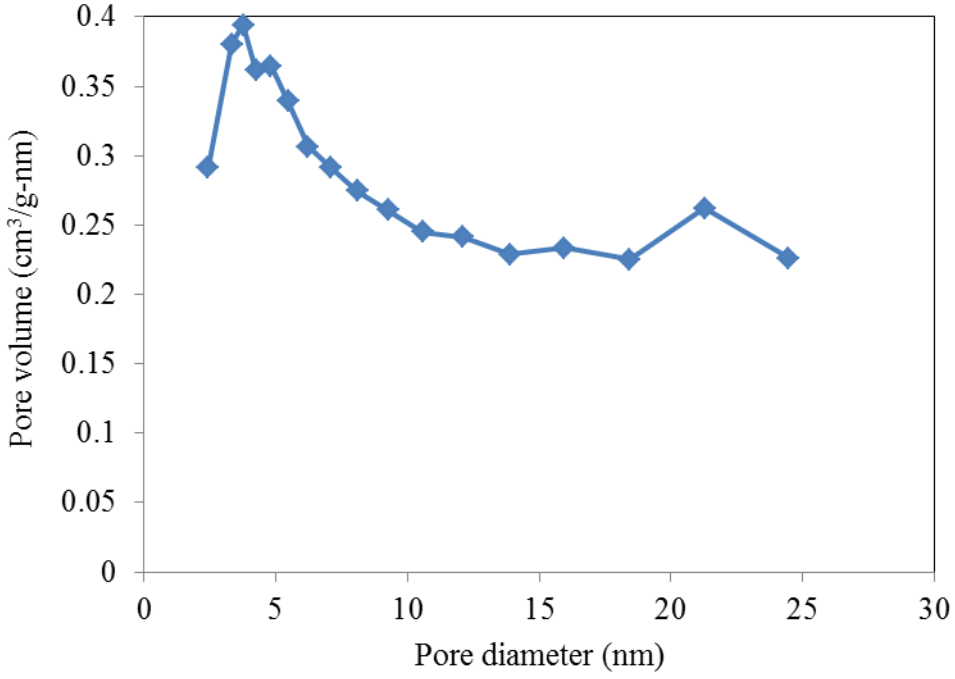


Fig A3 Pore diameter of carbonized hydro-char at 900 °C obtained from water hyacinth treated hydrothermally at 160 °C for 8 hours

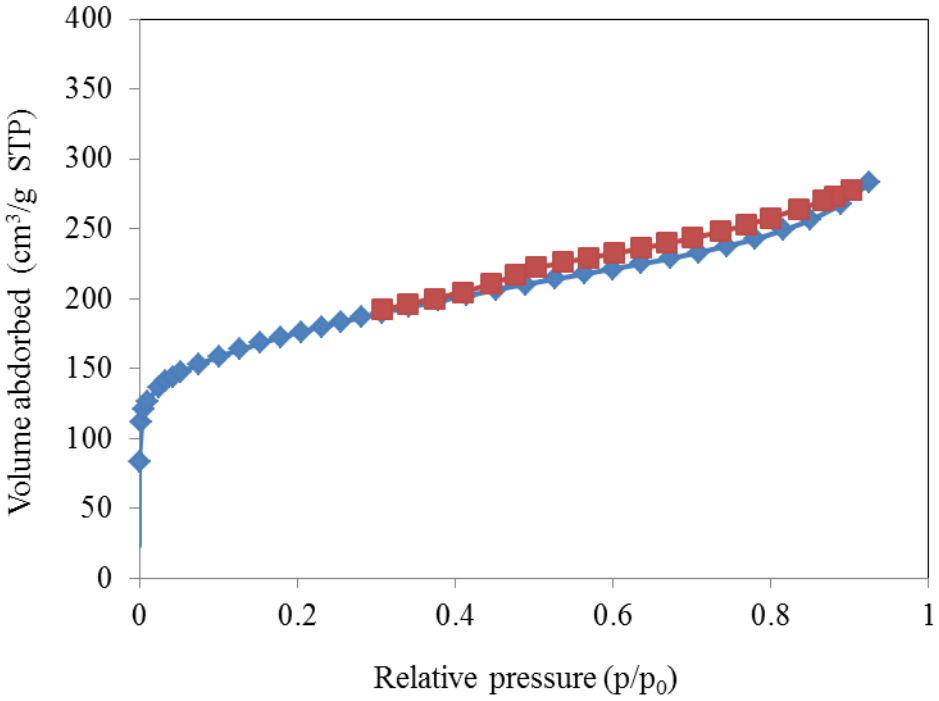


Fig A4 Adsorption and desorption of carbonized hydro-char at 900 °C obtained from water hyacinth treated hydrothermally at 180 °C for 8 hours

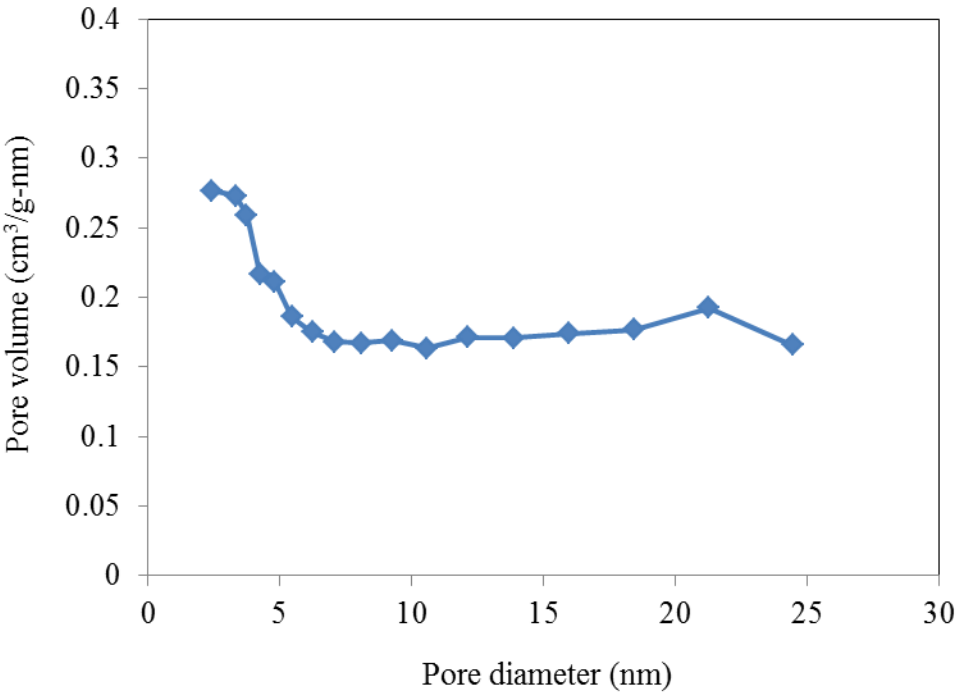


Fig A5 Pore diameter of carbonized hydro-char at 900 °C obtained from water hyacinth treated hydrothermally at 180 °C for 8 hours

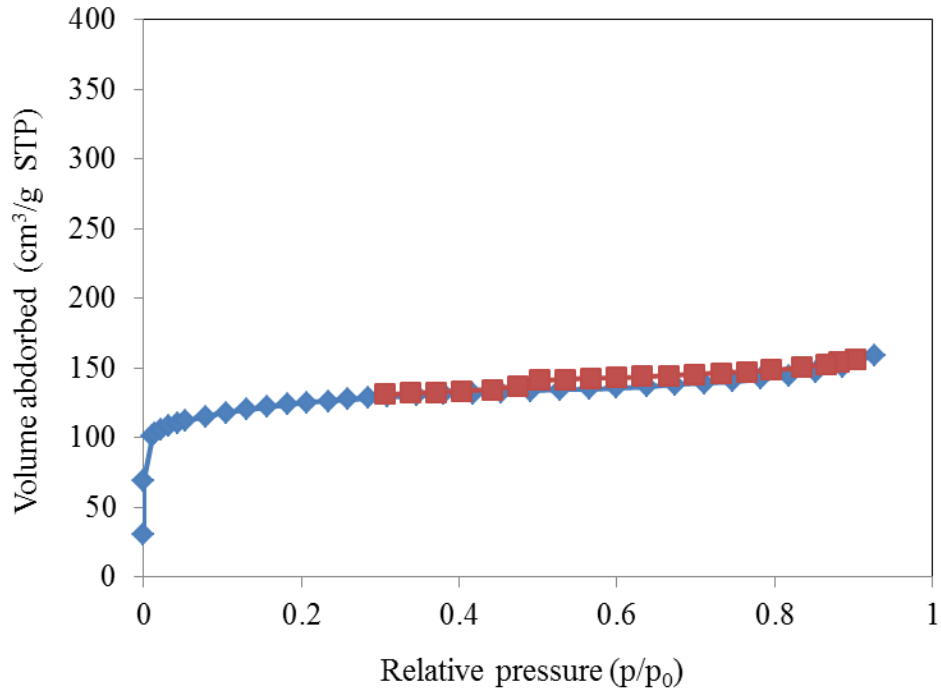


Fig A6 Adsorption and desorption of carbonized hydro-char at 900 °C obtained from water hyacinth treated hydrothermally at 200 °C for 8 hours

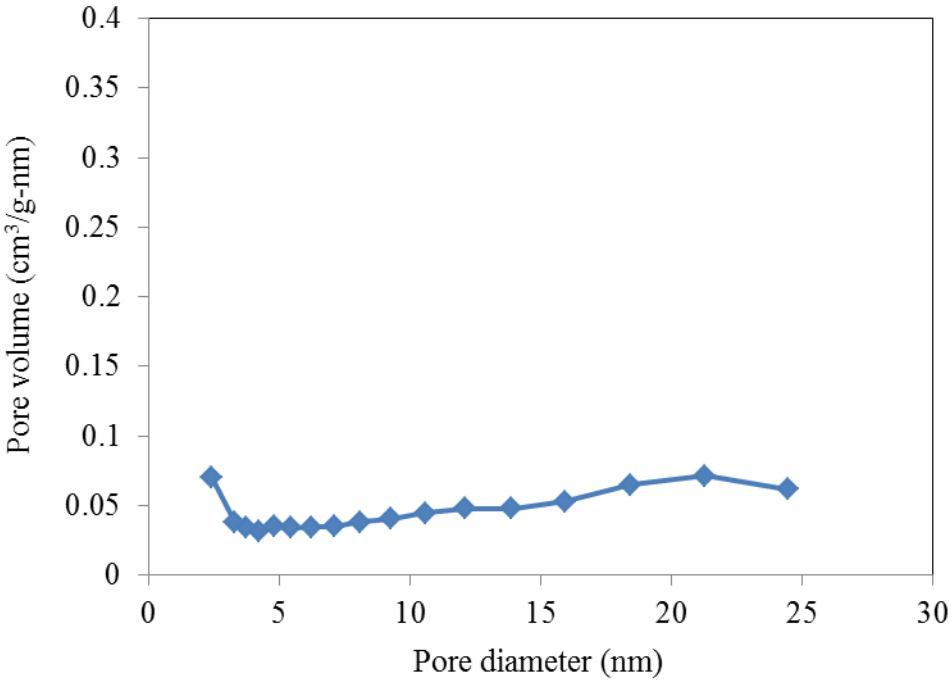


Fig A7 Pore diameter of carbonized hydro-char at 900 °C obtained from water hyacinth treated hydrothermally at 200 °C for 8 hours

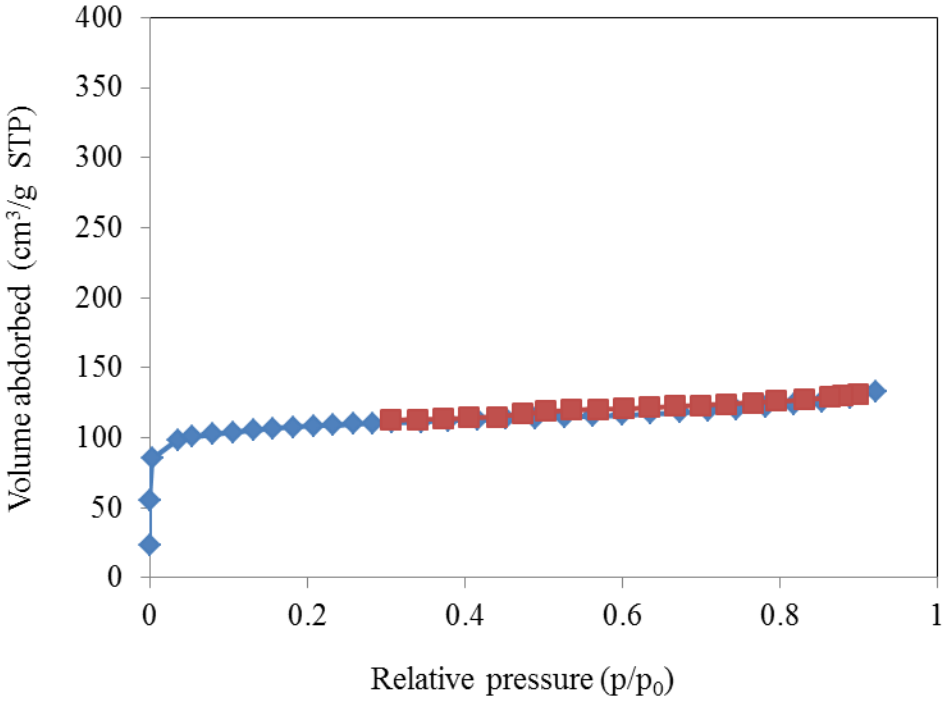


Fig A8 Adsorption and desorption of carbonized hydro-char at 900 °C obtained from water hyacinth treated hydrothermally at 220 °C for 8 hours

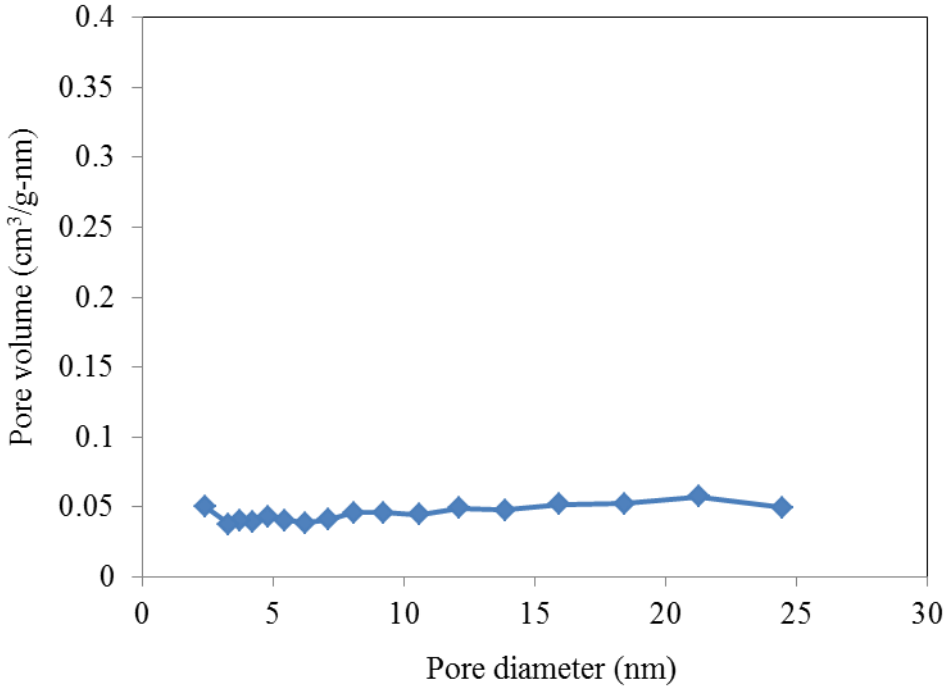


Fig A9 Pore diameter of carbonized hydro-char at 900 °C obtained from water hyacinth treated hydrothermally at 220 °C for 8 hours

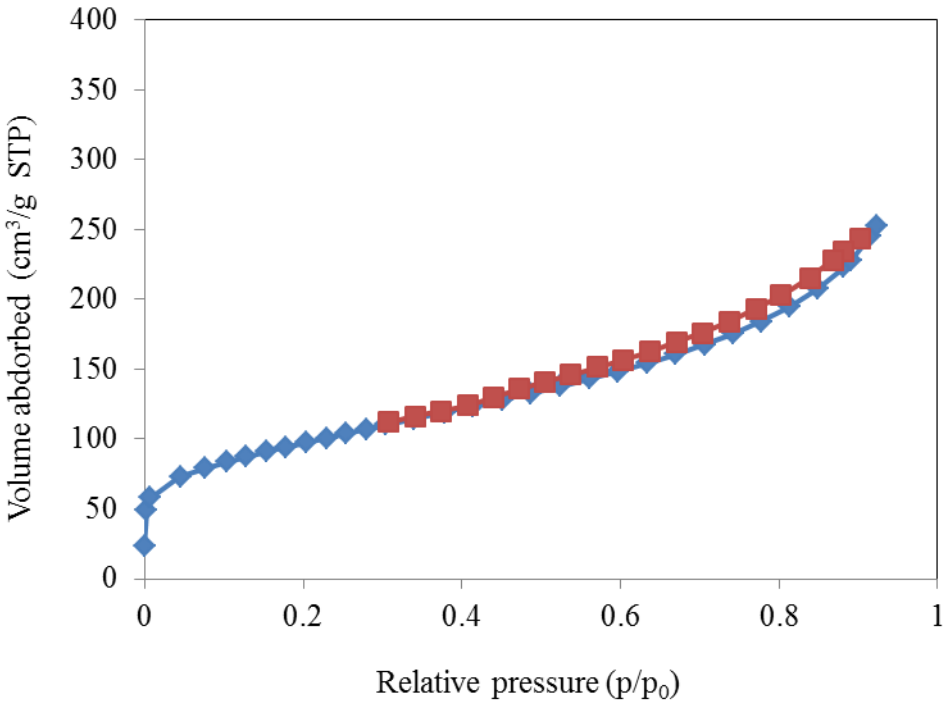


Fig A10 Adsorption and desorption of carbonized hydro-char at 900 °C obtained from water hyacinth treated hydrothermally at 180 °C for 4 hours

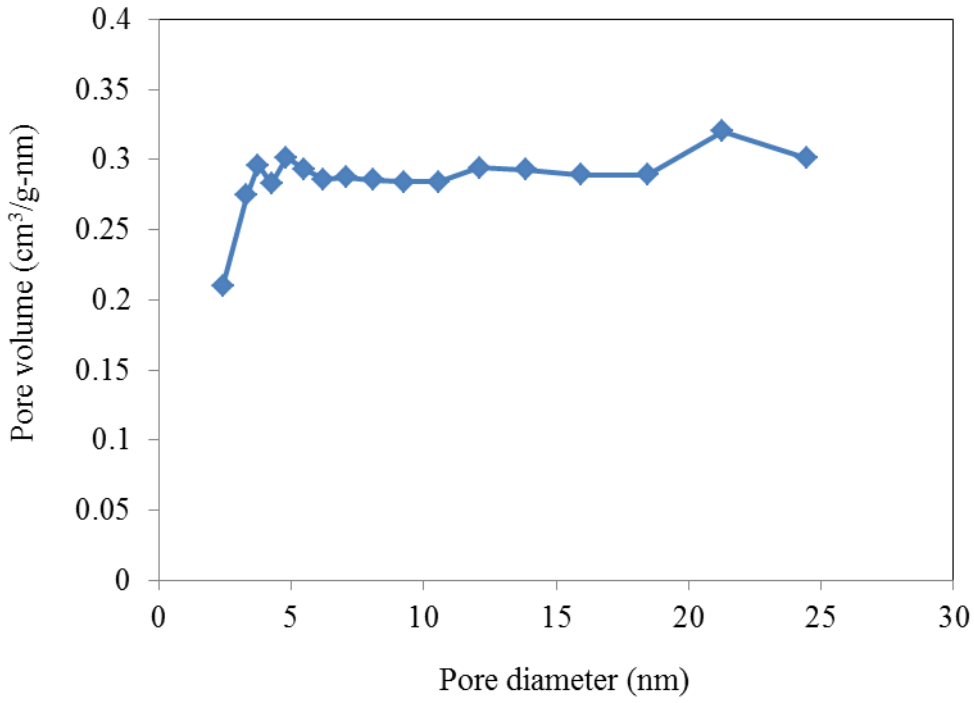


Fig A11 Pore diameter of carbonized hydro-char at 900 °C obtained from water hyacinth treated hydrothermally at 180 °C for 4 hours

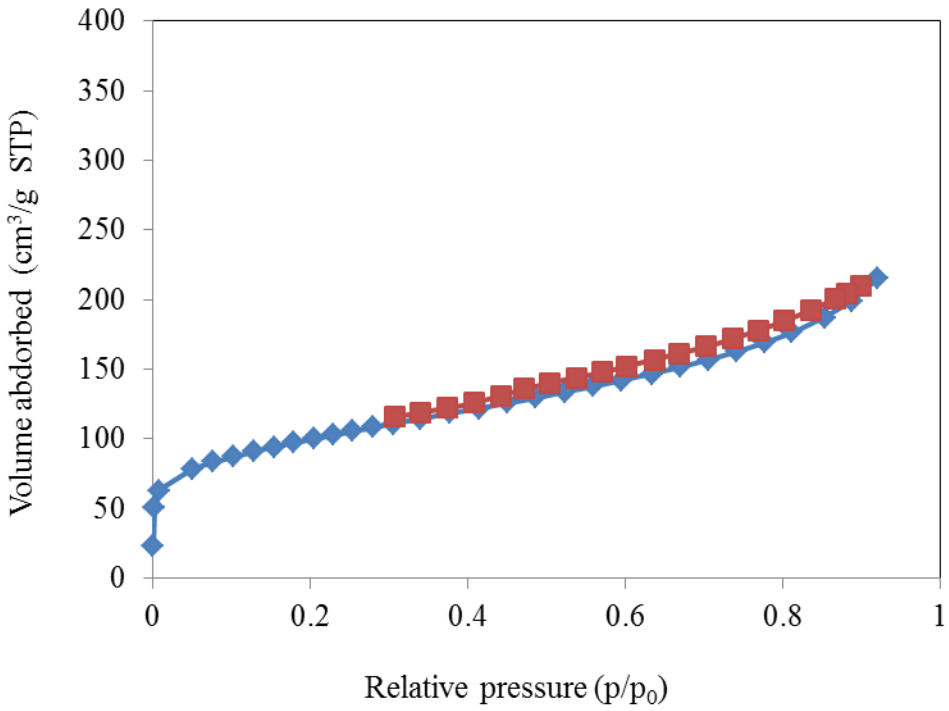


Fig A12 Adsorption and desorption of carbonized hydro-char at 900 °C obtained from water hyacinth treated hydrothermally at 180 °C for 12 hours

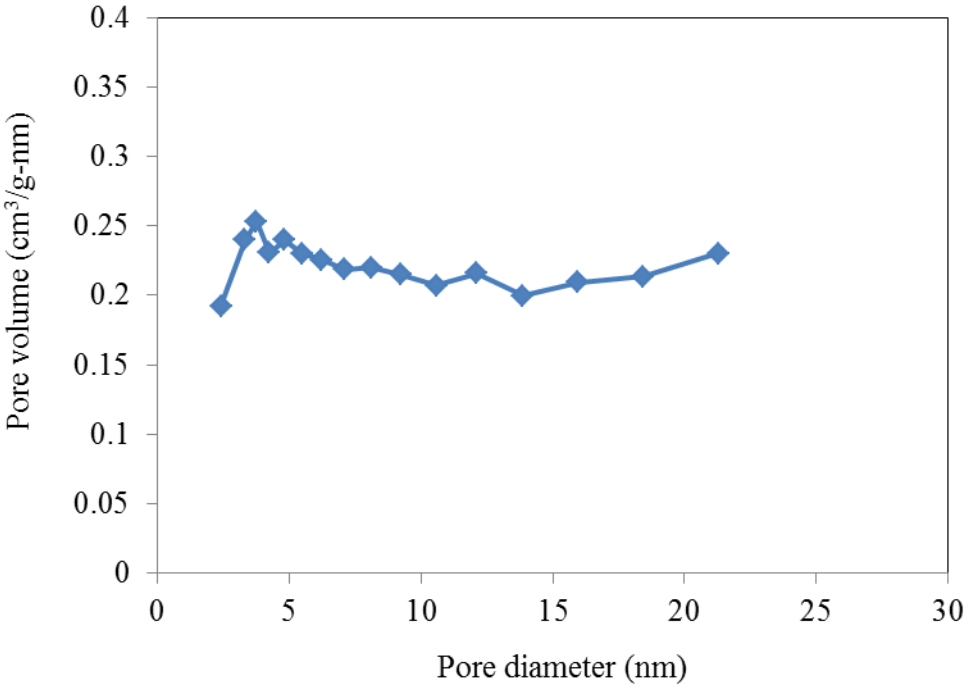


Fig A13 Pore diameter of carbonized hydro-char at 900 °C obtained from water hyacinth treated hydrothermally at 180 °C for 12 hours

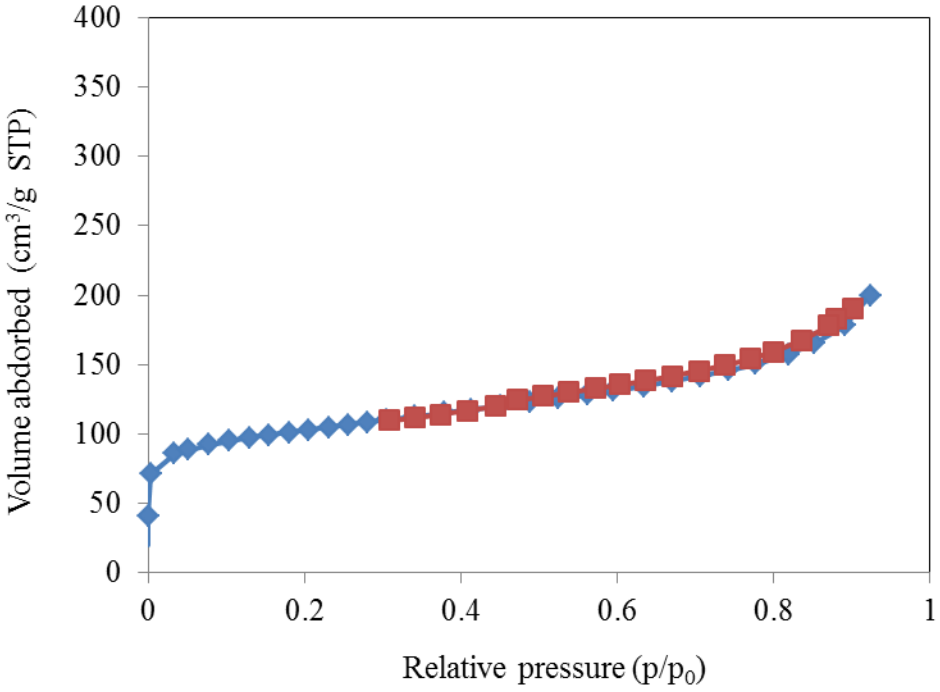


Fig A14 Adsorption and desorption of carbonized hydro-char obtained from water hyacinth treated hydrothermally with the presence of 4 g of $Fe(NO_3)_3 \cdot 9H_2O$ at 180 °C for 8 hours

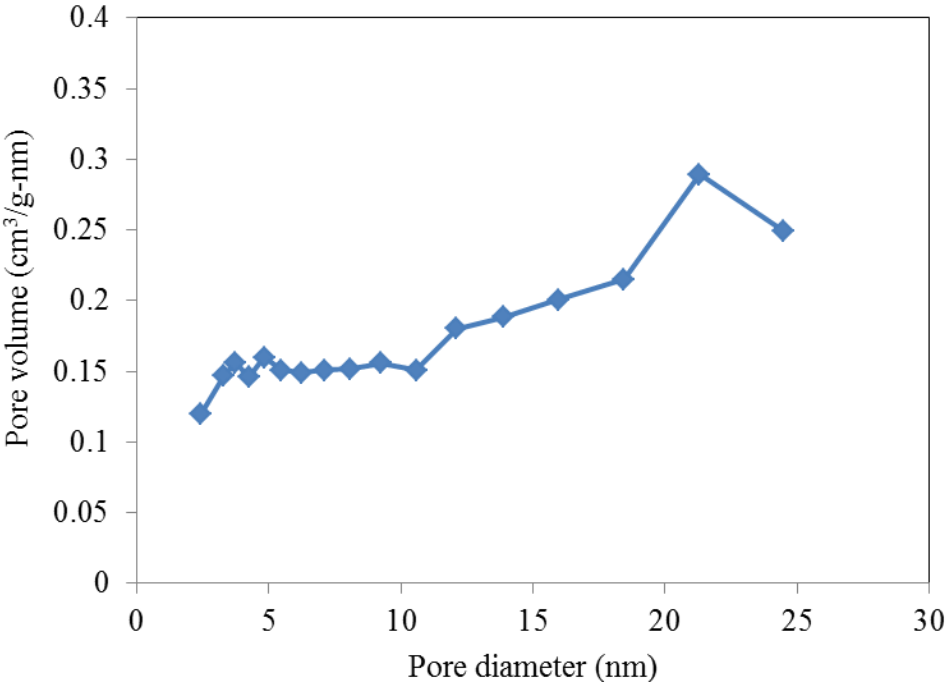


Fig A15 Pore diameter of carbonized hydro-char obtained from water hyacinth treated hydrothermally with the presence of 4 g of $Fe(NO_3)_3 \cdot 9H_2O$ at 180 °C for 8 hours

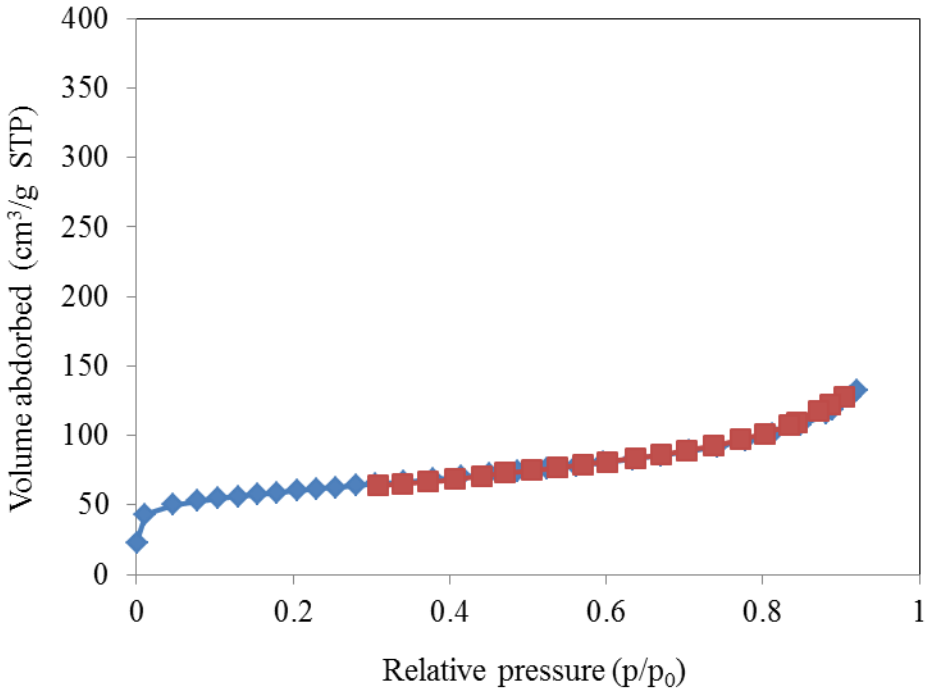


Fig A16 Adsorption and desorption of carbonized hydro-char obtained from water hyacinth treated hydrothermally with the presence of 8 g of $Fe(NO_3)_3 \cdot 9H_2O$ at 180 °C for 8 hours

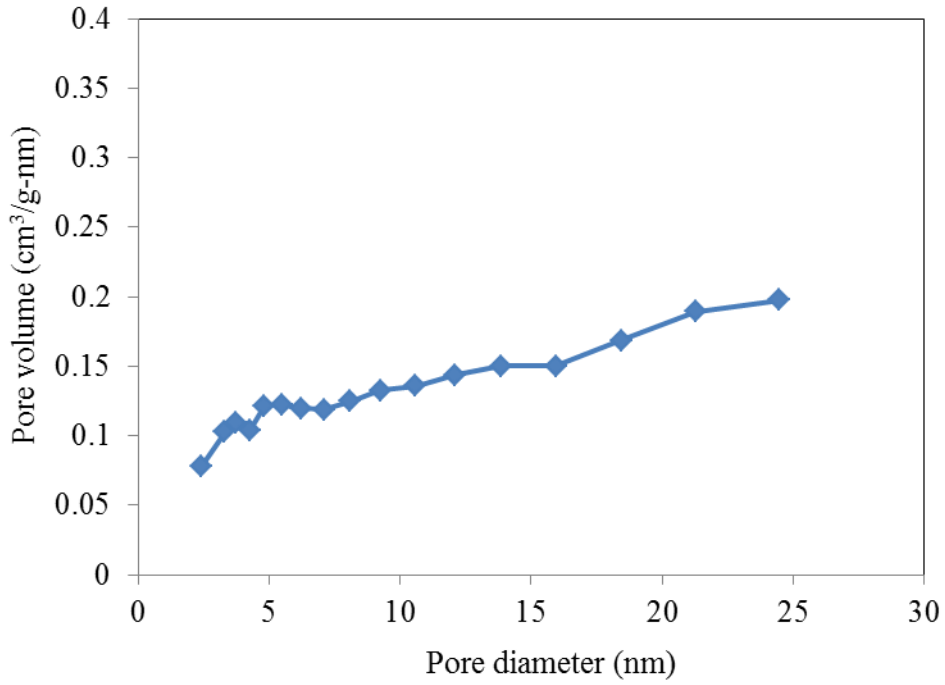


Fig A17 Pore diameter of carbonized hydro-char obtained from water hyacinth treated hydrothermally with the presence of 8 g of $Fe(NO_3)_3 \cdot 9H_2O$ at 180 °C for 8 hours

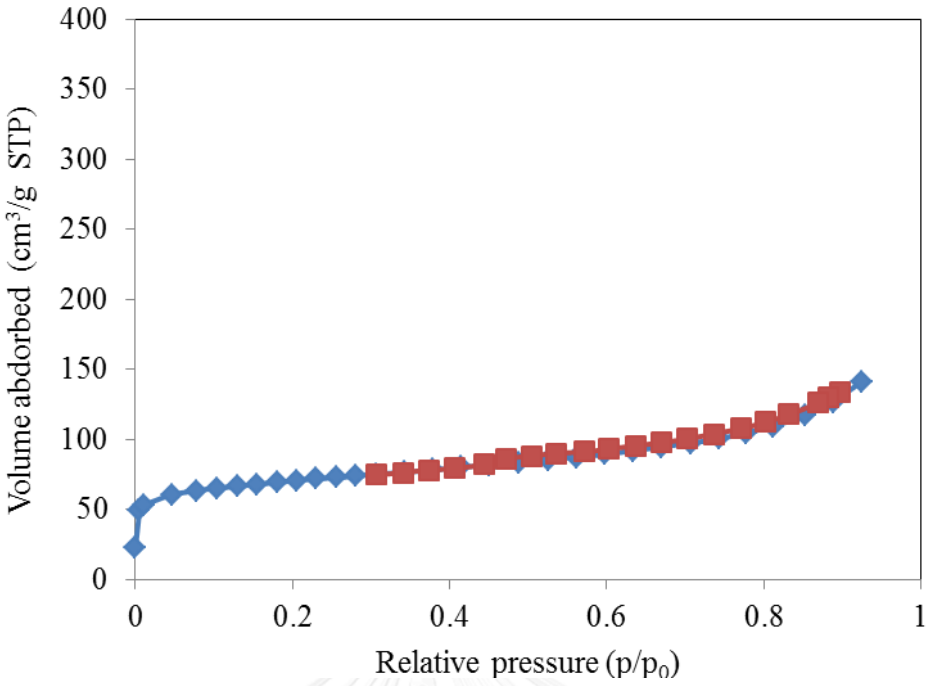


Fig A18 Adsorption and desorption of carbonized hydro-char obtained from water hyacinth treated hydrothermally with the presence of 12 g of $Fe(NO_3)_3 \cdot 9H_2O$ at 180 °C for 8 hours

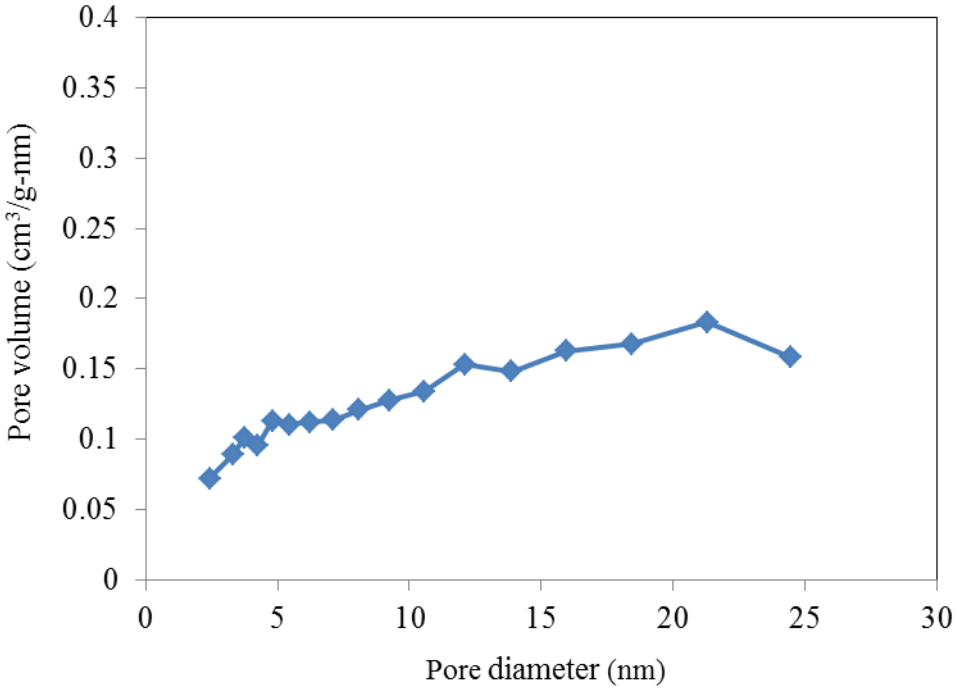


Fig A19 Pore diameter of carbonized hydro-char obtained from water hyacinth treated hydrothermally with the presence of 12 g of $Fe(NO_3)_3 \cdot 9H_2O$ at 180 °C for 8 hours

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