

EFFECT ACTIVATION OF CHEMICAL AND PHYSICAL TO STRUCTURE AND ACTIVATED CARBON QUALITY FROM CHARCOAL OBTAINED BY PYROLYSIS OF COCONUT SHELL

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Abstract

Activation of coconut shell charcoal has been done by a combination of chemical and physical activation to determine the effect of chemical activators and activation temperature to changes in the chemical structure and the quality of activated carbon. The study was conducted on charcoal coconut shell of pyrolysis results with variation of concentration and immersion time $ZnCl_2$ as an activator, respectively 0.5 to 2 M for 12 to 24 hours. Then proceed with the activation of physics in reactor the activation of the temperature variation of 500 to 800 °C with CO_2 gas flow rate 20 mL / min. Evaluation of the chemical structure and the quality of activated carbon performed FTIR, SEM, specific surface area, total pore volume, and average pore with Brunauer - Emmett - Teller (BET). The results showed the results of the analysis of SPSS through Coefficients test the concentration variables most affect to moisture content, ash content, and iodine absorption from temperature variable and time of activation. The best quality activated carbon produced at a concentration of $ZnCl_2$ of 1.5 M, 24 hours soaking time of 24 hours, temperature 800 °C and the activation time of 120 minutes. The results as moisture content of 8.47 %, volatile matter content of 18.55 %, ash content 1.44 %, bonded carbon content of 80.01 % and iodine absorption of 769.74 mg / g. The results of FTIR analysis showed the surface of activated carbon containing CO and CH bonds, and SEM analysis showed the number and diameter of pores increased with the higher calcination temperature. Surface area (BET) of 359.286 m² / g, pore volume of 1.984 x 10⁻¹ cm³ / g and pore mean of 11.46 Å.

Keywords : coconut shell, activated carbon, $ZnCl_2$, SPSS, FTIR, SEM, BET

Introduction

Fulfilling active carbon need in the world increase every year. For example in 2007 it reached 300,000 per year. In big countries such as United States, its demand per capita was about 0.4 kg per year and Japan it was about 0.2 kg per year. In Indonesia, active carbon demand was more than 200 ton a month or 2400 ton per year; most of them was still imported for pharmaceutical industry and other industries (Bansal and Goyal, 2005; Fitriani, 2008). The greater demand for domestic active carbon requires searching basic material source as alternative to make active carbon. One of the alternative sources is product of coconut tree in which coconut shell have not been used optimally yet. When the coconut shell is processed further, it will give higher economic value (Mandey, 2007). One of ways to process coconut shell is pyrolysis process. Pyrolysis process will produce coconut shell charcoal, liquid smoke, tar, and uncondensed gases. Charcoal is porous solid material resulted from material containing

carbon. Most of its pore is still covered with hydrocarbon, tar and other organic compound. Its component consists of fixed carbon, ash, water, nitrogen and sulphur. Coconut shell charcoal from pyrolysis process is potential to process as active carbon (Scok et al, 2005). Active carbon product from coconut shell charcoal has many micropore, high surface area and high adsorption capacity (Keneeth, 2002; Manocha, 2003).

Process of making active carbon consists of two steps: carbonization process and activation process. Main product resulted from carbonation process is charcoal with side product of tar, liquid smoke and carbon. However, resulted carbon has low surface area and usually less active due to very small adsorption rate. So, it is necessary followed with activation process functioning to develop porosity and adding surface area (Rodenas et al, 2005; Cuhadaroglu and Uygun, 2008).

Activation method commonly used in making active carbon is physical and chemical activation. Physical activation process is charcoal activation to develop pore from active carbon with aid of hot vapor and inert activating gas in high temperature of 800 to 1100^oC (Teng et al, 1998; Hong et al, 2000; Lee and Lee, 2001). Activation temperature is a variable that very influence characteristic of active carbon. In high temperature condition without air will resulted high quality active carbon where volatile components will loss so fixed carbon level is high. Chemical activation is a process of cutting carbon chain from organic compound using chemical material as activator (Derbyshier et al, 1995). Some activators commonly used in making active carbon are KOH, NaOH, ZnCl₂, KCl, H₃PO₄ HCl and so on (Sricharoenchaikul et al, 2008; Babel, 2004). However, in other side, making active carbon with only chemical activation has weakness of corrosion process, washing process and cannot regulate resulted active carbon pore (Balci et al 1994; Sricharoenchaikul, 2008; Timur et al, 2006).

This research studied activation process of coconut shell charcoal from pyrolysis process using chemical activation and physical activation using ZnCl₂ as activator with CO₂ activating gas. The combination method is expected to make active carbon at lower temperature, easier and at lower cost but with high commercial value. The combined method will result in high quality active carbon with greater surface area and high adsorption capacity. It will contribute to science and technology of making active carbon useful for industry in the future and it can develop optimally distribution of pore dimension according to industry desire.

Experimental

Material

Coconut shell resulted from pyrolysis from PT TNI, ZnCl₂, gas CO₂, KI, Na₂S₂O₃5H₂O, distilled water, KIO₃, I₂, HCl

Instruments:

A set of pyrolysis tool, a set of activating reactor, 100 mesh and 80 mesh sieve, electronic balance, oven, desiccator, electric furnace, magnet stirring, pH meter, laboratory glass tools.

Procedure

Preparation of coconut shell sample

Coconut shells were cleaned and their dimension were decreased to about 3 x3 cm, and weighted for 1500 gram and used as pyrolysis sample.

Carbon activation step

Coconut shell charcoal of pyrolysis process is grind and pound to make fine powder. Then it was filtered using 100 mesh sieve. Charcoal is activated by being flowed with CO₂. In this step, chemical activation was done by soaking and followed with heating with CO₂ flow.

1. Chemical activation step
In this step coconut shell charcoal from pyrolysis that has been sieved was soaked in $ZnCl_2$ solution with various concentration and soaking duration (0.5 – 2.0 M and 12 to 24 hours). Charcoal that have been soaked was sieved with vacuum filter and heated in oven at $120^{\circ}C$ for 2 hours to produce dry charcoal then put into desiccator.
2. Physical activation step
Charcoal resulted from chemical step was put into tube furnace activation reactor given with glasswool at lower and upper part, then activated at various temperature (500 to $800^{\circ}C$) and flowed with CO_2 20 ml/minute for two hours. Then, the charcoal was soaked in 1M HCl solution for 24 hours. Then the charcoal was washed with distilled water to make neutral filtrate (measurement with pH meter). It was sieved and dried in oven at $110^{\circ}C$ for two hours. Active carbon was ready to analyze
3. Active carbon analysis
Active carbon test including physical and chemical characteristic consist of macro and micro analysis. Macro analysis includes moisture content, volatile content, ash content, fixed carbon content, and adsorption capacity iodine. Result of macro analysis is tested with coefficient test using SPSS. Analysis of micro structure include function group with FTIR, surface structure with SEM, BET surface area, total pore volume and average pore diameter.

Fourier Transform Infra red (FTIR) analysis

Active carbon sample structure of activation result was analyzed using Fourier Transform Infrared (FTIR) Shimadzu model IR-prestige-21 and made pellet KBr. It was used to identify mineral function group.

Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) was used to analyze micro structure of surface of active carbon before and after activation.

BET surface area analysis

Pore structure analysis and surface area analysis was done using surface area analyzer Nova ver 2.2. Determination of surface area was done with BET method to calculate surface area of active carbon resulted from pyrolysis of coconut shell charcoal. In addition with BET equation, total pore volume and average pore radius may be determined.

RESULT AND DISCUSSION

This research was done to identify effect of chemical treatment using $ZnCl_2$ activator in making active carbon from coconut shell charcoal using chemical and physical activation methods.

Moisture matter of active carbon

Presence of water in carbon related to hygroscopic characteristic of the carbon, in which carbon has greater affinity than water. Data obtained indicated that moisture content of active carbon resulted from this research meet Indonesian Industrial Standard (SII no. 0258-79) maximally of 15%. Its graphical perspective is presented in figure 1.

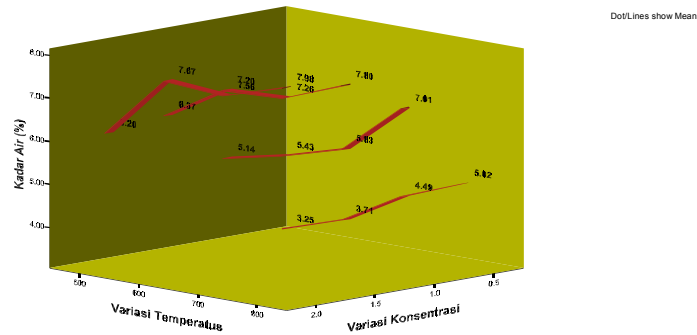


Figure 1. Effect of ZnCl₂ concentration and temperature on moisture content of active carbon

Figure 1 reveals that greater concentration of activator solution used in active carbon soaking will result in higher moisture content. Soaking process with activator was done to reduce tar content, so the more concentrated activator the less tar content in carbon. In result, pore in active carbon is increasingly great and much. Greater and more pore lead to increase in its hydroscopic characteristic. It causes adsorption of water from atmosphere by active carbon will increase, which lead to increase in moisture content in the active carbon.

Coefficient test indicates three independent variables on moisture content (%) is temperature (16.159), concentration (12.110) and soaking duration (4.822) (see t count in t column t in coefficient table). Result of multiple regression test using SPSS software indicate that the three variables affect water content.

Ash content

Process of testing ash content will indicate ash of metal oxide in charcoal consisting of mineral that can evaporate in incineration process. Effect of activator concentration on ash content in active carbon is presented in figure 2.

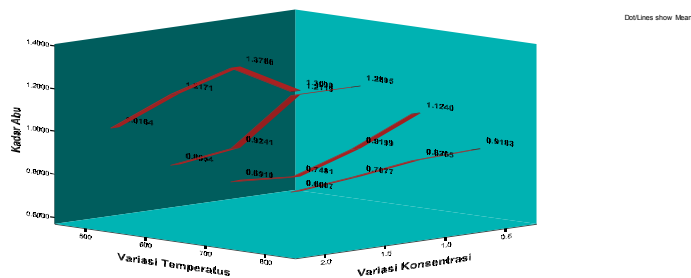


Figure 2. Effect of ZnCl₂ concentration and temperature on as content of active carbon

Figure 2 shows that ash content of all active carbon obtained in this research fulfill SII no 0258-79 (maximal 10%) because it was about 0.55-1.44. at activator concentration of 0.5-2.0 M, ash content increased. It relates to forming pores in active carbon. Ash content in active carbon also relates to raw material and its process. High activator concentration will add surface area of active carbon due to great and many pores. Active carbon consists of layers piling to each other making pore. During pore forming, there occur crystal field burning that resulting ash. The more pore made, the more ash produced.

Coefficient test indicated three independent variables affecting ash content are

temperature (7.296), concentration (-2.501) and soaking duration (1.096) (see t count in t column t in coefficient table).

Volatile matter content

Volatile substance in active carbon consists of water and tar residue that does not fully disappear in carbonization process. Obtained data indicated that volatile substance content in active carbon obtained in this research still comply with SII no 0259-79 (25%), as indicated in figure 3.

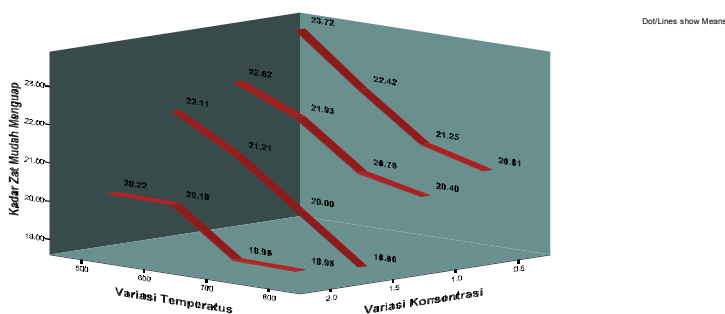


Figure 3. Effect of $ZnCl_2$ concentration and temperature on volatile matter content of active carbon

Figure 3 indicated that higher concentration of activator solution will decrease volatile substance. So, higher ash content indicated lower volatile substance content in active carbon. It is due to absorbed activator will cause erosion in carbon, which reduce efficiency of heating process in activation. In other words, temperature of activation process is low. When activation was done in low temperature, then volatile substance content will increase. Then, decomposition of non carbon compound such as CO , CH_4 and H_2 is expected not perfectly running. The graphic indicated that various concentrations can reduce volatile substance content but their decrease is not great so did not affect the volatile matter.

Based on coefficient test, the three independent variables most influencing volatile matter content are temperature (-4.021), concentration (-3.233) and soaking period (-2.126) (see t count in t column in coefficient table).

Fixed carbon content

Fixed carbon content is carbon obtained based on deduction of all sample weight (100%) on volatile matter and ash content. Fixed carbon content in active carbon was 50%-90%. Therefore, main composer of active carbon is carbon. The data indicated that highest fixed carbon content resulted from carbon activated with 1.5M $ZnCl_2$, with 24 hour soaking period and at $800^{\circ}C$. Fixed carbon content obtained with various concentration still comply with SII no 0258-79 (at least 65%). The data is presented in figure 4.

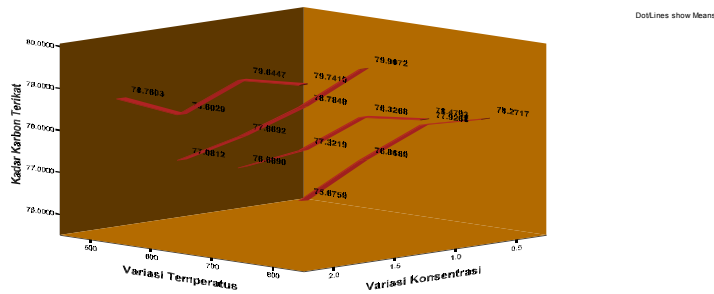


Figure 4. Effect of ZnCl₂ concentration and temperature on fixed carbon content of active carbon

Figure 4 indicated that increase in activator solution concentration will increase fixed carbon content. Factors influencing increase in carbon content are ash content and volatile matter content. Lower ash content and volatile matter content in active carbon indicated higher fixed carbon content. Therefore, purity of active carbon will be higher.

Based on coefficient test, the three independent variables most influencing fixed carbon content are temperature (3.418), concentration (3.400) and soaking period (2.023) (see t count in t column in coefficient table).

Iodium number

Adsorption of aqueous iodine is one of main characteristics of active carbon determining quality of active carbon. Test result indicated that active carbon having best adsorption number iodine is that in 1.5 M concentration (769.74 mg/g). The adsorption number on iodine resulted in this research comply with SII no.0258-79 (at least 200 mg/g).

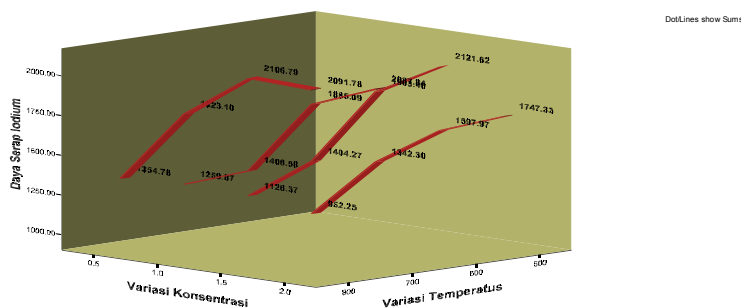


Figure 5. Effect of ZnCl₂ concentration and temperature on iodine adsorption number active carbon

Figure 5 reveal high activator solution will increase adsorption number over iodine. It is cause due to tar content in active carbon increasingly decrease with increasing activator concentration at soaking, where soaking process with activator was done to reduce tar content. Therefore, more concentrated activator solution used indicates decrease in tar content in active carbon. It causes greater pores in active carbon or increase in surface area of active carbon. The grater surface area of active carbon, the higher absorption number it has.

Based on coefficient test, the three independent variables most influencing adsorption

number iodine are temperature (12.668), concentration (9.417) and soaking period (3.964) (see t count in t column in coefficient table).

Analysis of function group using active carbon FTIR before and after activation with activator Zinc chloride ($ZnCl_2$) at concentration of 1.5 M, 24 hour soaking period and $800^\circ C$

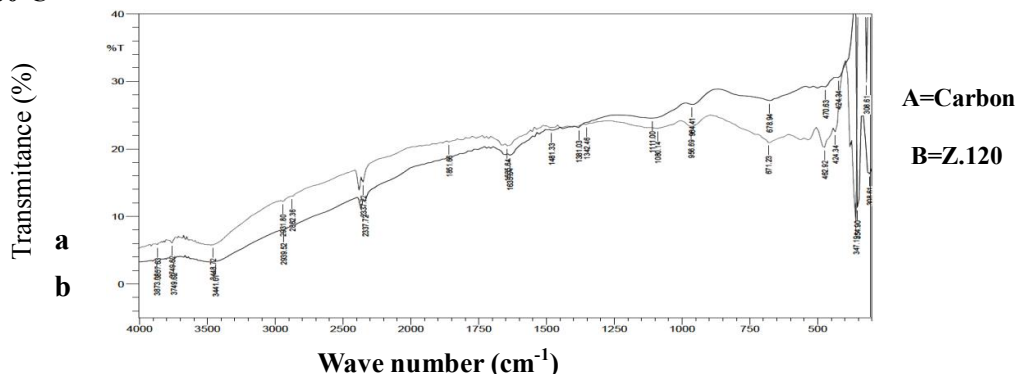


Figure 6. FTIR spectrum of carbon before and after activation with various activation periods

The FTIR spectrum of coconut shell charcoal of pyrolysis without activation informs presence of absorption band in wave number $3487.3-3417.86\text{ cm}^{-1}$ appearing stretching vibration of O-H group. This vibration is supported with absorption band in wave number $1381.03-1165$ that is stretching vibration of C-O and bending vibration of OH from alcohol and carboxylate acid. In addition, in wave number 2337.72 cm^{-1} is stretching vibration of carboxylate acid. Wave number $1581.63-1527.62\text{ cm}^{-1}$ is stretching vibration of C=C in aromatic ring. Absorption band $802.39-747.38\text{ cm}^{-1}$ indicated C-H out of plane bending in aromatic ring.

The spectra of the prepared activated carbon resulted from activation with $ZnCl_2$ is relatively similar to shell charcoal without activation. However, its absorption rate decrease or increase according to activation duration so there is shift in wave number. Absorption band in wave number 3448.72 cm^{-1} appear stretching vibration of O-H. The vibration is supported by absorption band in wave number $1342-1080.14\text{ cm}^{-1}$ that is stretching vibration of C-O and bending vibration of OH from alcohol and carboxylate acid. In addition, there is absorption in wave number 2337.72 cm^{-1} that is stretching vibration of carboxylate acid. While in wave number 1635.64 cm^{-1} is stretching vibration of C=C in aromatic ring. Absorption band in wave number 802 cm^{-1} indicate C-H out of plane bending in aromatic ring. Change in function group structure in active carbon may be due to effect of charcoal calcination temperature and duration of activation. Active carbon resulted in activation process has absorption pattern with bonding type -OH, C-H, C-O, and C=C. OH and C=O bonding indicated active carbon tend to be polar so active carbon can be used as adsorbent.

Active carbon analysis with scanning electron Microscope (SEM)

Carbon before and after activation process was analyzed using SEM. Result of imaging using SEM describing carbon surface is presented in figure 7 and 8.

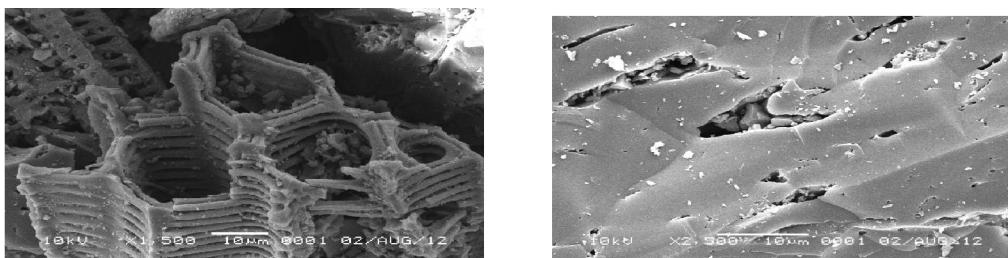


Figure 7. SEM photograph of coconut shell charcoal before activation with 1500 times and 2500 times magnification

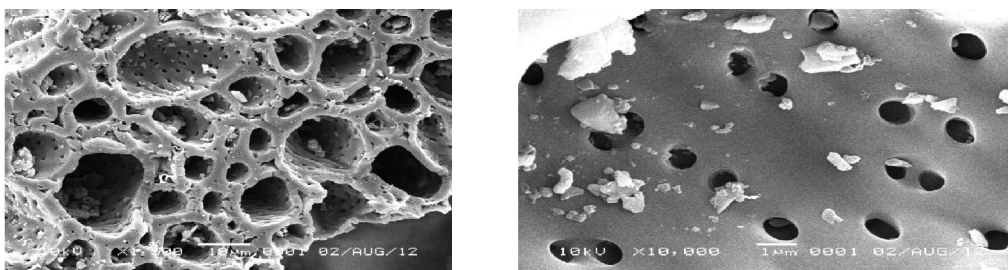


Figure 8. SEM photograph of coconut shell charcoal after activation at 1.5 M $ZnCl_2$ concentration, 24 hours soaking, at $800^{\circ}C$ and 120 minutes activation period with 1500 times and 10.000 times magnification

Figure 7 and 8 indicates shows active carbon before and after activation with activator $ZnCl_2$. Result of SEM before activation indicate much impurity covering pore surface of the carbon (figure 7) compared with after activation (figure 8) in which carbon pore surface more porous. It indicates that activation process can open and shape new pore in carbon. New pore shaping appear in pore diameter distribution

Characterization of active carbon from coconut shell charcoal with nitrogen adsorption-desorption

Adsorption-desorption isotherm for active carbon of coconut shell charcoal before and after activation is presented in figure 9. Based on classification of adsorption type, adsorption isotherm obtained is type IV. Hysteresis indicate mesoporous isotherm. Occurring hysteresis is loop but there is no presented in figure 9 because it occurred in relative small pressure. Coconut shell charcoal resulted from pyrolysis indicated broader hysteresis than active carbon resulted from chemical and physical activation with $ZnCl_2$. However, both samples have hysteresis in low pressure. It provides information about addition of complexity of active carbon pore after activation.

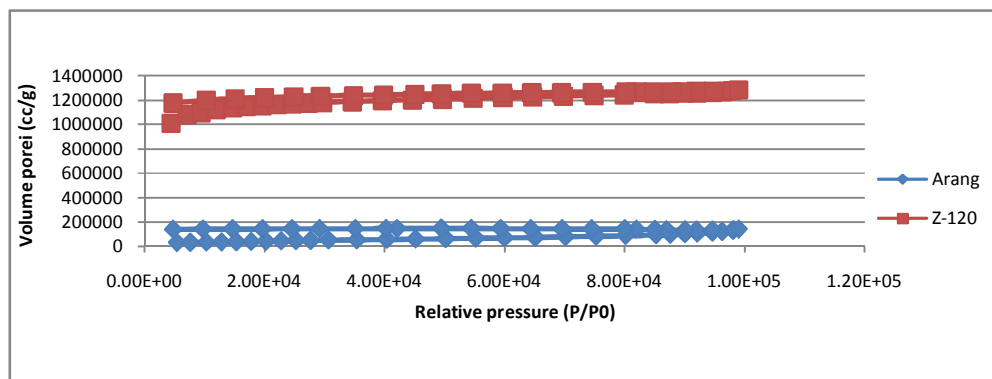


Figure 9. Isotherm of adsorption-desorption of active carbon resulted from activation

Activation of active carbon from coconut shell charcoal have changed its characteristic. It is due to effect of active carbon cavity blocking by cation after activation process. Distributions of active carbon pore dimension before and after activation increase significantly as revealed in figure 10. The figure shows that distribution of active carbon pore dimension after activation with $ZnCl_2$ has peak around pore radius 11.04 Å so dimension of the active carbon pore is mesopore.

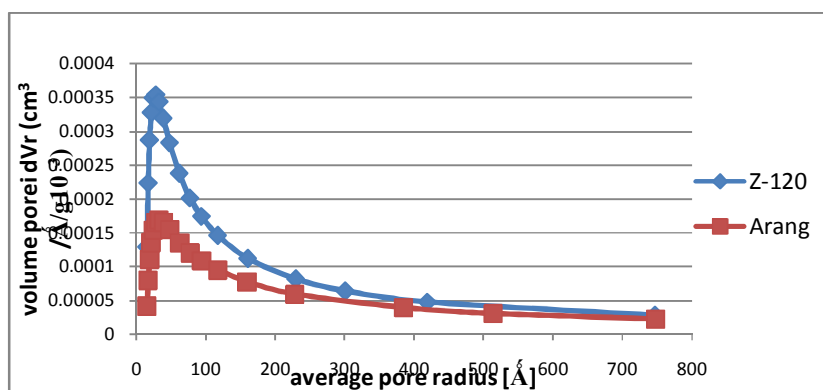


Figure 10. Distribution of active carbon pore dimension before and after activation

Surface area, pore size and pore volume is very important characteristic for material function as adsorbent because it determine measurement of internal surface available for active site. Parameter of active carbon pore structure before and after activation may be seen in table 6. The table indicates that active carbon before and after chemical activation with activator $ZnCl_2$ and physical activation at concentration of 1.5M soaking duration of 24 hour at $800^{\circ}C$ and 120 minutes activation period change pore structures of surface area, pore radius and pore volume.

Table 1. BET surface area, total pore volume, average pore radius of active carbon

| Sample | BET surface area (m^2/g) | Total pore volume ($\times 10^{-1} cm^3/g$) | Average pore radius (Å) |
|---------------|------------------------------|---|-------------------------|
| carbon | 15,451 | 0,217 | 26,478 |
| Z8-1.5-24-120 | 359,286 | 1,984 | 11,045 |

Table 1 indicates that active carbon surface area before and after activation increased from 15.4561 m²/gram to 317.1 m²/gram along with increase in ZnCl₂ activator concentration and activation temperature (1.5M and 800⁰C). It is due to at 800⁰C, volatile substances or non volatile substance will discharge from pore that will form new pore and increase surface area and pore volume and decrease average pore radius.

Conclusion

1. Result of SPSS analysis on coefficient test indicated temperature most influence moisture content, volatile matter, ash content, fixed carbon content, iodine number compared concentration and soaking duration variables.
2. Active carbon resulted from activation process has adsorption pattern with binding types of O-H, C-H, C-O, and C=C. O-H and C=O bonding indicates active carbon tending to be more polar that can be used as adsorbent. Effect of carbonization process and activation can increase aromatic compound as composing hexagonal structure of charcoal and active carbon.
3. Chemical and physical activation of coconut shell charcoal with ZnCl₂ activator affect characteristic of active carbon. It may be seen in morphology of surface structure that is more porous and greater surface area.
4. Best active carbon obtained in ZnCl₂ concentration of 1.5 M, 24 hour soaking duration, 800⁰C and 120 minutes activation duration. The condition resulted in 8.47% moisture content, 18.55% volatile matter, 1.44% ash content, 80.01% fixed carbon and 769.74 mg/g iodine number.
5. Active carbon from activation with various activation has similar pattern, smaller pore diameter and grater pore volume than that without activation. The active carbon has BET surface area of 359.286 m²/g, pore volume 1.984 x 10⁻¹cm³/g and average pore radius of 11.045 Å.

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