Synthesis activated carbon of Screw-pine leaves by HNO₃ and its properties

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Synthesis activated carbon of Screw-pine leaves by HNO3 and its properties

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Abstract. The leaves of Screw-pine (Pandanus odorifer) which contain natural cellulose were used as sources of carbon to prepare activated carbon. Contained 28-30% of water, the leaves were dried for 3-5 days by sunlight. The pyrolysis process of dry leaves yielded 25.7% of carbon that was then followed by grounding and sifting steps to 80 mesh of particle size. This uniform particles were mixed with 5% HNO3 activator in batch system for 24 hours. Physical activation conducted at 700°C and obtained 70.8% activated carbon. The characteristics of activated carbon were compared to the carbon base by using porosimeter, referencing to SNI 06-3730-1995 and finding the adsorption isotherm patterns. Activated carbon surface area was 337.9 m²/g that is classified as micro-pore substance. In accordance to SNI requirements, the activated carbon fulfilled water content, ash content and adsorption capacity of I2 while the study of efficiency adsorption is satisfy at 92.5436%, 97.5707%, 97.9811% and 96.2066% of Cd, Cu, Zn and Fe respectively.

1. Introduction

Screw-pine (Pandanus odorifer) is a species of pandanaceae family that commonly can be found along the coastal area. This species has not been used maximally as it used as basic ingredients of making handy-craft that sometimes leave a lot of wastes. Actually, the tree also has abundant potential to be used in modern industry due to cellulose content of the leaves. Naturally, its untreated-leaves have cellulose content of about 35% and can be maximized into 70% of cellulose extract by enrichment process with a chemical [1].

The natural cellulose content can be used as precursor of making activated carbon because the cost is very cheap and the amount of leaves are abundant in nature. Additionally, the based carbon to the activated process is low cost but effective in producing a material that are easy to regenerate and selective to adsorb heavy metals [2].

The natural cellulose can be converted into carbon via carbonation process. In order to increase adsorption capacity, the raw carbon must be activated in chemical and physical activations. The enlarger capacity aims to remove dissolved organic compounds, inhibits tar formation, and increases adsorption capacity of heavy metal contaminants due to the large carbon surface area [3-4].

Chemical activation of carbon involves the use of activators in the form of base or acidic compounds. Basically, the use of acid activators will produce activated carbon with a better quality compared to alkaline activators [5]. HNO3 solution is one of acid activators that can be used to treat the raw carbon because HNO3 is strong acid that can properly dissolve organic impurities and inhibit tar formation, so that the pores on the surface of the activated carbon become larger [6]. According to Tao and Xiaqin [7], the activation of carbon from peanut shell by HNO3 (20% (by mass)) produced adsorption efficiency
10.3 times greater than commercial activated carbon. All the acidic activation to the raw carbon were followed by physical activation by involving heating and carbon gasification at high temperatures to expand the carbon surface area to the maximum [8].

Escalating interest in activation with nitric acid from such leaves precursors has led to focus on the mechanism of the activated carbon synthesis with a good developed micro-porous structure and a high capacity adsorption. The activated carbon characterization will refer to SNI 06-3730-1995 because this ordinance regulates the use of activated carbon mainly for industrial/commercial purposes. Investigation of adsorption patterns in several metal solutions of Cu, Cd, Fe, Zn as the simulation of liquid waste will complete the physical properties measurements.

The paper presents the investigation results on character of Screw-pine leaves activated carbon which was activated by 5% HNO₃ and the adsorption properties in liquid waste systems. The concentration of HNO₃ chosen is purposed for finding the better character of activated carbon with lower concentration than Tao and Xiaqin [7] did, because the lower acidic is the better for environment.

2. Experimental Section

2.1 Materials and Instruments

Material for making raw carbon was Screw-pine leaves (P. odorifer) from the coastal area of Trisik, Kulonprogo. The chemicals were 5% HNO₃, 0.1M I₂, 0.1M Na₂S₂O₃, Cu(NO₃)₂, CdSO₄, Fe(NO₃)₃, Zn(NO₃)₂, amylum, distilled-water and completed with filter paper and pH paper. All the chemicals were provided from various commercial distributors with pure analysis (p.a.) grade and used without further purification. The characterization were done by Surface Area Analyzer (SAA) and Atomic Absorption Spectrophotometer (AAS), supported with blowing furnace, 80 mesh strainer, analytical scale, magnetic stirrer, oven and laboratory glass wares.

2.2. Synthesis of carbon

The Screw-pine leaves were washed and then cut into small pieces before dried under the sun until completely dry (got constant weighing). The leaves then being carbonated in 500°C for 6 hours using a furnace. The obtained carbon was smoothed to reduce the particle size and strained with 80 mesh sieve to make it more uniform.

2.3 Activation of Carbon

Five percent of HNO₃ was mixed with homogeneous raw carbon (in size) in a batch system for 24 hours at ambient temperature. Followed by filtering the liquid, the activated carbon product was being washed with distilled-water until neutral in pH in accordance with pH of distilled water. The next step was drying the neutral carbon with oven at 100°C for 3 hours or until the carbon weight has not changed when carbon underwent in further drying process. The yielded carbon then was heated at 700°C for 2 hours.

2.4 Characterization

The size of porous were identified by porosimeter for both raw and activated carbons. According to SNI 06-3730-1995, the activated carbon was tested in finding of the content of water, ash level, volatile degree, and the capacity adsorption of activated carbon to I₂. The properties of adsorption were investigated by interacting activated carbon with solutions of Cu, Cd, Fe and Zn in a ratio of 1:50 (g/mL) for 24 hours in medium pace respectively to find the capacity, the efficiency and the isotherm models.

3. Result and Discussion

Synthesis of activated carbon from natural cellulose has a lot of advantages due to its renewable source characteristic. It opens the possible commercialization of product because the activated carbon capable to achieve prominent adsorption level mainly in removing hazard substances. Higher degree of adsorption, larger benefit of using activated carbon will be gained. The quality of activated carbon depends on the making process and the choices of appropriate chemical to activate carbon.
The Screw-pine leaves were selected as source of carbon due to cellulose level of both lignocellulose and hemicellulose [9]. It can easily be found in the south coastal of Yogyakarta of Trisik, Kulonprogo. To start the activated carbon process, the selected leaves of Screw-pine were dried under the sunlight for 3-5 days depend on the weather until it really dried. A significant weighing reduction showed that the water content of the leaves is 28-30%.

The dried leaves were ready to place in the furnace at 500°C for 6 hours to get raw carbon. The yielded raw carbon presented in the ratio of 1:5 to the wet leaves. The raw carbon was treated in further steps of activation both chemically and physically. It aimed at getting high capacity of adsorption that will be meaningful if the activated carbon has a great surface area. According to Alfiany et al [6], the size of the carbon particles affect the surface area of carbon produced. The smaller size of the carbon particles, the greater the carbon surface area so that during activation process, the larger pores will be formed on each carbon particle.

Chemical activation process using 5% HNO₃ solution was done to the raw carbon of Screw-pine leaves in batch system for 24 hours by solid-liquid interaction in constant stirring. This acid solution can clean the pore surface of the impurity compound, limit the formation of tar, degrade organic molecules in subsequent heating processes, and rearrange interchangeable atoms. This 5% HNO₃ solution is then removed from activated carbon by washing it using distilled-water to neutral pH compared to pH of distilled-water. After that, the carbon were activated physically at temperature 700°C for 2 hours. Heating at high temperatures will influence the carbon structure to be more organized and evaporate water trapped in the pore of carbon. It aims to open the pore surface of activated carbon with the maximum porosity. Growing and opening of these carbon surface pores are expected to increase the adsorption capacity and efficiency of activated carbon so that it is more effective in heavy metal adsorption of the wastewater solution.

3.1 Characterization of activated carbon

The characterization results of the activated carbon of Screw-pine leaves are shown in table 1. The characterization including moisture content, ash content, volatile substance, bond carbon content, and capacity adsorption to I₂ were done to fulfill SNI 06-3730-1995 requirements. On the other hand, the characterization with porosimeter were completed the SNI measurement.

| Name                | Water content (%) | Ash content (%) | Volatile substance content (%) | Bond carbon content (%) | Capacity adsorption of I₂ (mg/g) | Single point surface area (m²/g) | BET surface area (m²/g) |
|---------------------|------------------|----------------|--------------------------------|------------------------|---------------------------------|---------------------------------|------------------------|
| Parameter according to SNI 06-3730-1995 | Max. 15 | Max. 10 | Max. 25 | Min. 65 | Min. 750 | - | - |
| Carbon              | 7.46             | 21.62          | 70.43                         | 0.49                   | 2157.5546                      | 3.7719                          | 3.5756                 |
| Activated carbon    | 1.02             | 6.44           | 65.58                         | 26.96                  | 2251.2530                      | 337.9532                        | 318.1830               |

Findings showed that water content before and after activation process have accordance with SNI requirement that were less than 10%. The purpose of this characterization was to know the hygroscopic nature of activated carbon. Low water levels of carbon indicate that the water content has evaporated much during the process of drying, carbonation and physical activation.

Ash content before activation process was more than 10% while ash content after activation process was less than 10%. It meets SNI 06-3730-1995 of activated carbon requirements. The purpose of characterization of ash content was to find the remaining minerals left behind in the carbon after the activation process. The results examined that the level of ash after activation was smaller than initially because the impurities and minerals that attach to the carbon were much lost during the activation process.
process. High ash content can reduce the adsorption capacity of activated carbon because the pores are blocked by minerals that still lag in carbon [10].

The volatile carbon content before and after the activation process were greater than 25% so it do not accordance SNI 06-3730-1995. The purpose of characterization of volatile substances was to determine the volatile compounds contained in activated carbon. The high levels of these volatile substances indicated that many non-carbon compounds such as H atoms and O atoms are still strongly bonded to carbon atoms. The amount of these non-carbon compounds can clog pores of the carbon surface so it reduces the adsorption capacity of activated carbon to heavy metals in waste water [11].

The adsorption capacity of activated carbon to iodine has fulfilled the quality of activated carbon of SNI 06-3730-1995 that is more than 750 mg/g. Determination of activated carbon adsorption to iodine was done by iodometric titration. This procedure aimed at investigating of adsorption ability of activated carbon to metal ion with a relatively small molecular weight. The larger the iodine number the greater the adsorption capacity of the active carbon will be achieved [6].

Because the characterization result of water content, ash content, volatile content of carbon before and after activation were under the SNI 06-3730-1995 standard, the resulting carbon content is not accordance with SNI 06-3730-1995 that is at least 65%. The carbon content bond before activation is 0.49% while after activation process is 26.96%. It is far less than SNI 06-3730-1995 requirements. It indicates the carbon shape tend to create single component than making amorphous structure that appropriates to adsorb molecules.

The characterization data was also completed by porosimeter measurement. Chemical and physical process applied on carbon of Screw-pine leaves will influence carbon surface structure. After carbonization, the raw carbon needed to increase the pore volume and to enlarge the pore diameter. The activation process causes the breakdown of the hydrocarbon bonds in the carbon structure so that the surface area of the pore will increase [12]. It is proved by this study of surface area comparison between before and after activation of raw carbon which became greater. The surface area of carbon prior to activation was 3.7719 m²/g. That area is classified into meso-pore carbon category with surface area in the range of 2-100 m²/g. The function of pore with meso-pore size will be meaningful for transportation purposes. However, for reducing liquid chemical pollution the meso-pore must be reduced to micro-pore level. This level requires surface area size of ≥91 m²/g. It was gained by treatment in combination of chemical and physical activations. The porosimeter output of surface area of activated carbon measurement is 337.9532 m²/g. This result is an evidence that the activated carbon belongs to a micro-pore of its surface area. The activation process alters the meso-pore structure of carbon into micro-pore structures with the helping of acidic chemical solutions and heating at high temperatures. Carbon with micro-pore size can adsorb small molecules on its surface [13].

3.2 Adsorption of wastewater solution properties
The heavy metal adsorption process wastewater in batch system. The ratio of activated carbon and the wastewater solution was 1:50 (gram/mL). The contact time between activated carbon and the wastewater solution was 24 hours [14].

This research purposes to find the efficiency, capacity, and adsorption isotherm patterns of activated carbon. The instrument to measure the concentration of Cu, Cd, Zn and Mg before and after adsorption process was Atomic Absorption Spectrophotometer (AAS).

Adsorption of Cd²⁺, Cu²⁺, Zn²⁺ and Fe⁺⁺ with activated carbon showed the various adsorption efficiency and capacity levels. All the adsorption efficiency measurement showed that the use of activated carbon is very significant to reduce the metal solutions content of samples due to higher efficiency than 90%. Additionally, levels of adsorption capacity are very randomly each other because of undefined relation between pore and ion particle size.
Table 2. Adsorption capacity and efficiency of activated carbon with 5% HNO\textsubscript{3}

| Type of ions | Adsorption capacity (mg/g) | Adsorption efficiency (%) |
|--------------|----------------------------|---------------------------|
| Cd\textsuperscript{2+} | 0.1170 | 92.5436 |
| Cu\textsuperscript{2+} | 0.6858 | 97.5707 |
| Zn\textsuperscript{2+} | 0.2471 | 97.9811 |
| Fe\textsuperscript{3+} | 0.5116 | 96.2066 |

Variations of concentrations of wastewater showed a linear relationship between the initial concentration and the adsorbed concentration. The results showed that the greater the concentration of metal ions in the wastewater, the greater amount of metal ions adsorbed as shown in table 2. This is consistent with the theory that the greater the solute concentration in the solution, the larger amount of solvated substances are adsorbed to reach a certain equilibrium.

To find the adsorption characteristics, two treatments were applied to activated carbon in the relation between log \(X_m/m\) vs log \(C_e\). \(X_m/m\) describes the adsorbed metal concentration every gram of activated carbon and \(C_e\) is the final concentration after adsorption process. These data will examine Langmuir and Freundlich models of adsorption isotherm. This differentiation is to find the pattern of mono or multi-layer of adsorption. The analysis of adsorption pattern of Cd, Cu, Fe and Zn can be concluded by looking at the determination coefficient of Freundlich and Langmuir adsorption isotherm curves at 5% significant level. Thus, it should be about 0.95 of \(R^2\) coefficient for each adsorption. Determination the adsorption isotherm graph of Freundlich and Langmuir were investigated by the data in table 3.

Table 3. The relation between Log \(X_m/m\) vs Log \(C_e\) of activated carbon by 5% HNO\textsubscript{3}

|        | Cd     | Cu     | Fe     | Zn     |
|--------|--------|--------|--------|--------|
| \(x\)  | \(y\)  | \(x\)  | \(y\)  | \(x\)  | \(y\)  | \(x\)  | \(y\)  |
| log \(X_m/m\) | log \(C_e\) | log \(X_m/m\) | log \(C_e\) | log \(X_m/m\) | log \(C_e\) | log \(X_m/m\) | log \(C_e\) |
| -0.4944 | -1.8182 | 0.5801 | -0.70509 | 0.43364 | -0.5439 | 0.04254 | - |
| -0.1848 | -1.2299 | 0.89244 | -0.71265 | 0.75581 | -0.5216 | 0.29747 | -1.7865 |
| 0.1019  | -0.7525 | 1.07148 | -0.67572 | 0.94098 | -0.5675 | 0.57346 | -0.5937 |
| 0.3109  | -0.449 | 1.19655 | -0.5583 | 1.06965 | -0.584 | 0.75396 | -0.4881 |
| 0.4023  | -0.4638 | 1.29354 | -0.4661 | 1.16863 | -0.5924 | 0.87422 | -0.2886 |
| 0.5173  | -0.239 | 1.37132 | -0.31283 | 1.24943 | -0.6191 | 0.98512 | -0.4727 |

By put the relation of log \(X_m/m\) and log \(C_e\), it resulted graph of Freundlich and Langmuir adsorption patterns. The graph of Freundlich model of Cd, Cu, Fe and Zn are shown in figure 1. Based on the figure 1, it is clearly seen that there were various linearity numbers. From the plotting of linearity formula, the \(R^2\) of determination coefficient are 0.9194, 0.6895, 0.7032 and 0.7647 for Cd, Cu, Fe, Zn respectively so that none of \(R^2\) measurement of Freundlich model at figure 1 exceed the linearity requirement at least 0.95.
Figure 1. Freundlich adsorption isotherm of Cd, Cu, Fe, Zn on activated carbon.

Figure 2. Langmuir adsorption isotherm of Cd, Cu, Fe, Zn on activated carbon.

On the other hand, plotting data of Langmuir model is given by figure 2. It is seen that the $R^2$ of determination coefficient are 0.7737, 0.1578, 0.7406, 0.5092 of Cd, Cu, Fe, Zn respectively. Compared to the previous isotherm models, the Langmuir are unacceptable to describe the adsorption pattern because of poorer determination coefficient than Freundlich. Hence, the adsorption pattern cannot be concluded to follow neither Langmuir nor Freundlich models.

All in all, the study of adsorption properties to wastewater solution only indicated the high efficiency of using activated carbon to reduce heavy metal level. Even though the capacity adsorption should be recalculated in further research, the efficiency adsorption gives high benefits in lowering level of Cd, Cu, Fe, and Zn in the wastewater.

4. Conclusion
The activated carbon produced from Screw-pine leaves remained a low quality of the properties of ash content, volatile content and carbon bond character of activated carbon based on SNI 06-3730-1995. However, water content, ash content, and absorption capacity of I$_2$ at activated carbon by 5% HNO$_3$ have accordance with the SNI standard. Additionally, the chemical and physical activation influence in making the surface area greater to 100 times porosity size of carbon pores. Thus, efficiency adsorptions
are satisfy at 92.5436%, 97.5707%, 97.9811% and 96.2066% while adsorption capacities are 0.1170mg/g, 0.6858mg/g, 0.2471mg/g, and 0.5116mg/g of Cd, Cu, Zn and Fe respectively.

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