Contribution of Activated Carbon Based on Cacao Peels (*Theobroma cacao L.*) to Improve the Well Water Quality (COLOR, BOD, and COD)

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Abstract. In this research, we have made activated carbon from the cacao peels (*Theobroma cacao L.*) for the purpose of water purification. The cacao peels activated using 50% H3PO4 at the temperature of 400 °C for 1 hour. Scanning Electron Microscopy was applied for a surface analysis of activated carbon, and the functional groups identified by Fourier Transform Infra-Red (FTIR). The adsorption process was carried out by a column method with a flow rate variation of 5 mL/min and 10 mL/min. The results showed that by using 2 grams of activated carbon with a flow rate of 5 mL/min is the optimum condition, with the obtained absorption efficiency of 91.8% BOD, 90.2% COD, and 96.5% color. Morphological analysis has determined the changes in pore on the surface of activated carbon. Analysis of functional groups showed that the produced activated carbon had a pattern of absorption with OH, CH, and CO type of bond. Based on the results, it can be concluded that the activated carbon of cacao peels can improve the quality of dirty well water, and make it consumable for the daily use.

1. Introduction

In line with the increasing population growth, industrial activity is also increased. However, industrial growth has adverse effects on society, because some of these industries dispose of their waste directly into sewers/water bodies without prior management. As a result, the water source can be polluted because of the exceeding use on its capacity to make it renewable [1].

To this day, many people still take well as their source for clean water supply. Nevertheless, at recent time, the water from the well has been contaminated, either organic or inorganic which causes the color of the water becoming unclear. The ideal clean water must have the characteristics of clear, colorless, tasteless, and odorless, does not contain chemical substances that can alter the function of the body, and harmless to human health, and others. It is noteworthy to prevent the occurrence and spread of water-borne disease [2].

To reduce the impact on the water, the well water must be purified in order to maintain the quality of the clean water so it can be consumed in the daily basis. To achieve the above mentioned objectives, the alternatives for natural and environmentally friendly water purification should be determined. Some studies on water purification have been carried out using the LMM (Layer Multi Media) method on local ingredients-basis. Taken as the example on the wastewater noodle industry, and peat water have been able to be used in constructing the pH value, Color, Chemical Oxygen Demand (COD), Biological Oxygen Demand (BOD), Total Suspended Solids (TSS), Total Dissolved Solids (TDS), to meet the Minister of Environment Regulation by utilizing the activated carbon [3]. Additionally it has done manufacture of activated carbon from bark peels to a solution of methylene
blue dyes and gumitir plant stems on water content, volatile matter, total ash content, carbon content, absorption of methylene blue, and absorption capacity of iodine [4], [5].

The price of commercialized activated carbon is very expensive, so it will cost a lot using it for water purification. Therefore, the alternative for activated carbon like the one derived from abundant natural ingredients should be made. One of natural resources which has not been maximally used is cacao peels. Some studies have utilized cacao peels for corrosion inhibitors [6], [7], [8], [9], mechanical properties repair [10], fodder [11], hydrophobic properties [12], thin layer [13], [14], and particle boards [15]. Using cacao peels directly is not good as an adsorbent for water purification due to many of cacao peels recently are attacked by pests so that they become rotten, and damage the environment [16]. While in Indonesia, cacao plants are widely grown by farmers, and generate solid waste which ruin the aesthetistics of environment.

Cacao peels produce 21.06% hemicellulose content, 20.15% cellulose, and 55.11% lignin. Such compounds are polymers of carbon elements so that the cacao peels can be used as activated carbon with a large porous, and deep surface to make its absorption capacity becoming high [17]. Therefore, to make the waste from cacao peels does not pollute the environment, it can be processed into activated carbon which can be used as an adsorbent to purify the water.

2. Materials And Methods

The tools used in this research is a glass column with a length of 25 cm, and 1.5 cm in diameter, standards, clamps, well water container, Front Laboratory Analytical Balance peristaltic pump (Kern & Sohn GmbH), Miyako Blender, Furnace Carbolute CWF 1200, pH meter (HANNA HI 98 127), mortar and pestle, FTIR (Mattson Unican 7000 Mod FTIR), SEM (HITACHI S-3400 N), UV-Vis Spectrophotometer (Thermo Scientific GENESYS 10S Series), a sieve with ≤ 160 µm particle size.

Preparation of Activated Carbon
Cacao peels washed with water, then wind dried, carbonized for 1 hour at 400°C. Cacao peels charcoal was then mixed with 50% H₃PO₄ with a ratio of 1:4, and allowed to stand for 24 hours. The mixture was washed with water until reaching neutral pH, and put in the oven at the temperature of 105 °C for 3 hours. Activated carbon was sifted until resulting ≤ 160 µm particle size, and it was ready to be used. At the end, obtained activated carbon was characterized by SEM and FTIR [18].

Treatments of Sample
The adsorbent was inserted into the column glass with mass variation of 1 gram, and 5 mL/minute and 10 mL/minute flow rates using a peristaltic pump. After obtaining the best flow rate, the treatment of 2 grams of perlite mass was performed. Sample of groundwater was channeled to the column, and the flowed sample volumes were calculated to see to what extent this material can still be used. The water that had been flowed through the adsorbent was then analyzed for its color, BOD, and COD values.

Determination of Color
The determination of the water color was carried out using a spectrophotometer with a spectrophotometric method by wavelength of 456 nm. The used standard solution is platinum-cobalt.

Determination of Biological Oxygen Demand (BOD)
The determination of the BOD value can be done by reducing the values of DO₀ with DO₅. Whereas, the determination of DO₀ was done by taking the sample that has been prepared. 1 mL of MnSO₄, and 1 mL of alkaline azide iodide were added by the tip of pipette right above the surface of the solution. Closed the solution immediately, and homogenized it until a perfect lump is formed. Next, left the lumps for 5 to 10 minutes. Afterward, added 1 mL of concentrated H₂SO₄, then covered and homogenized it until the deposits were completely dissolved. Then, took 50 mL by using pipette, and put into 150 mL of erlenmeyer. Titrated it with Na₂S₂O₃ by using the starch indicator until the
blue color disappeared. The determination on DO(5) was stored for 5 days, after 5 days it was titrated in the same way as the determination of DO(0).

Determination of Chemical Oxygen Demand (COD)
Organic and inorganic compounds, especially organic, in the sample test were oxidized by MnO_4^- in closed reflux for 1 hour producing Mn^{2+}. The excess of unreduced potassium dichromate was titrated with sodium thiosulfate solution using starch indicator. The amount of needed oxidant was stated in oxygen equivalent (O_2 mg/L).

The procedure in determining the COD was by pipetting 50 mL of the sample volume, adding ± 0.1 gram of HgSO_4, and 5 mL of KMnO_4 into erlenmeyer. Then closed and heated the erlenmeyer for ± 1 hour in a heater at the temperature of 70 °C. Let it slowly cooled down until it reached room temperature. After it was cold, 5 mL of potassium iodide and 10 mL of 4N H_2SO_4 were added. Then it was titrated with 0.025 N Na_2S_2O_3 until the color turned to light yellow, then 1 mL of starch indicator was added. Continued the titration until an obvious changed of color occured from blue to clear or until the blue color disappeared. Then, recorded the volume of 0.025 N Na_2S_2O_3 solution which was used. These steps were also done towards organic free water as blank. Likewise, the volume of Na_2S_2O_3 solution used was recorded as well.

3. Results And Discussion
Characterization of Activated Carbon
The activated carbon absorption on the iodine was set in order to determine the ability of activated carbon in absorbing colored solutions. The obtained value of iodine absorption in the study can be seen in Figure 1.

Notably, Iodine absorption value obtained in this research was 1012.662 mg/g, where the Iodine absorption capacity for commercial activated carbon was 1247.85 mg/g. To some extent, this obtained absorption capacity has met the SNI 06-3730-1995 standards (at least 750 mg/g). Hence, this Iodine absorption capacity was influenced by the activation and carbonization process. The immersed samples in H_3PO_4 produced samples with high iodine absorption, where the phosphoric acid cleansed the pores, expanded the carbon surface, provided active group in order to enlarge the absorption of activated carbon. The increase of activation temperature also raised the absorption capacity of activated carbon against iodine. It was due to the higher the temperature, the more the carbon plates were shifted that encouraged hydrocarbons, tar, other organic compounds to release during the activation time.

![Figure 1. Effect of Activated Carbon onto Iodine Absorption](image-url)

Characterization and FTIR analysis was conducted to determine the functional groups contained in the cacao peels so that it can be used as activated carbon in order to improve the water
quality. Shown in Figure 2 is carbon absorption band in the cacao peels before and after the adsorbed change. The main component of activated carbon from peels are cellulose, hemicellulose, and lignin [19].

FTIR analysis (Figure 2) shows the content of cellulose in the presence of hydroxyl OH bond at wave number 3347.13 cm\(^{-1}\) and shifted to a wave number 3232.33 cm\(^{-1}\) after the adsorption process - OH functional group on adsorbents experienced deprotonation, so the functional groups became negatively charged, which was very reactive in absorbing Ca\(^{2+}\) ions, and other metal cations [20].

![Figure 2. The FTIR spectrum Activated Carbon before absorption (a), and after absorption (b)](image)

At the early stage of activated carbon was seen a peak around a wavelength of 2346.79 cm\(^{-1}\) indicating the presence of C≡N group. The surface containing nitrogen group on the activated carbon surface increased the ability to absorb acid gases [21]. The carboxyl (Aliphatic C-O stretching) function at wave number 1235.96 cm\(^{-1}\) indicated the presence of hemicellulose content, and after adsorption there was a shift to the wave number 1236.01 cm\(^{-1}\). At wave number 1916.18 cm\(^{-1}\) showed lignin content, and undergone a shifting to wave number 1935.37 cm\(^{-1}\) marked by the presence of aromatic C-H group [22]. The hydroxyl and carboxyl groups took part in adsorbing metal cations. The produced activated carbon had an absorption pattern with O-H, C-H, and C-O bond types [19].

The SEM analysis results at 400\(^{\circ}\)C of combustion temperature is shown in Figure 3. Its shows that before experiencing the adsorption, activated carbon has a rough surface, and porous. Meanwhile, after the absorption, the pores are filled and becomes denser. It is due to the occurrence of metal ions adsorption, and other organic material containing in the well water into the activated carbon pores. The activation using acid phosphate at 50% concentration has made the pores becoming larger. The surface area and pore volume of activated carbon is increasing in line with the increase on the concentration of H\(_3\)PO\(_4\) solution as an activator. The increase in porosity is also caused by the amount of impregnating agent used, the more activator used the more pores formed on the activated carbon [23], [24], [4].

![Figure 3. Surface morphology of activated carbon (a) prior to adsorption, (b) after adsorption (magnification 2000x)](image)
Effect of BOD, COD, and Color Before and After Adsorption

The color of water is caused by the presence of organic and inorganic substances, plankton, humus and metal ions (iron and manganese), and other materials [25], [26], [27]. Colored water indicates that the quality of the water is low, so it is not consumable. The color concentration of well water before being flowed is 1.1718 TCU. The changes of the color concentration of this well water after being flowed can be seen in Figure 4.

![Figure 4. The Effect of Well Water Flow Rate and Adsorbent Mass on Changes in Color Values After Adsorption](image)

Figure 4 shows the effect of activated carbon mass on the color of well water. The well water that has been drained using the activated carbon went through a significant change in color concentration. Whereas the well water taken in this research was the water with yellow color as a consequence of the high level of iron in the water. After passing through the activated carbon, the cacao peels became clear. The decrease in color concentration occurred because the well water that had passed through the activated carbon received a filtration process so that the deposits in the water were lost, and the iron content was disappeared. Thus, the obtained well water after flowing it with activated carbon became colorless and in accordance with the water standards for daily consumption.

Color reduction efficiency using 1 gram activated carbon with a flow rate of 5 mL/minute and 10 mL/minute was 90.8%, whereas with 2 grams of activated carbon in the 5 mL/minute, the color reduction efficiency was 96.5%.

The analysis of Biochemical Oxygen Demand (BOD) in this research used the winkler method, and conducted at the Chemical Laboratory for Environmental Analysis. The whole measurement process was carried out in dark conditions, in order to avoid the occurrence of photosynthesis which produced oxygen. DO(0) was measured immediately right after sampling collected, then continued to measure the dissolved oxygen content in the sample that had been incubated for 5 days. Measurements for DO(5) were expected only set the occurrence of decomposition process by microorganisms, so only the use of oxygen ensued.

![Removal of BOD](image)
Figure 5. Effect of Well Water Flow Rate and Adsorbent Mass on Changes in BOD Values After Adsorption

The BOD concentration of the well water before flowing was 4.854 mg/L. The changes in BOD concentration from the water after being flowed can be seen in Figure 5. The data in Figure 5 points out that there is a significant decrease in BOD value. The decrease efficiency of BOD in activated carbon mass of 1 gram with a flow rate of 5 mL/min and 10 mL/min was 89.2%, while in 2 grams activated carbon mass, the decrease efficiency in BOD was 91.8%. The decrease in BOD value indicated that the number of microorganisms contained in the water was decreased as well. It was due to the reduced supply of food (organic matter) for microorganisms, so that it increased the dissolved oxygen, and reduced the levels of organic matter in the water [20].

BOD reduction efficiency is also affected by differences in flow rate. Where the higher the flow rate, the lesser the reduction efficiency. As a result of high flow rates, the contact time became shorter so it reduced the decomposition rate of organic substances in the water. Conversely, the efficiency of reduction increased when the flow rate decreased, by the reason of the contact time in the column lasted longer, and the decomposition rate by microorganisms occurred slowly, and ran more impeccable [28].

Chemical Oxygen Demand (COD) describes the total amount of the presented organic substances. The COD concentration of well water before being flowed was 9,114 mg/L. The changes in COD concentration of the well water after being flowed can be seen in Figure 6. Taken as a note, there is a significant decrease in COD value where the efficiency of COD reduction in activated carbon mass of 1 gram with a flow rate of 5 mL/min and 10 mL/min respectively was 88.0% and 77.1%, while on 2 grams activated carbon mass the efficiency of COD reduction was 90.2%.

COD reduction efficiency also represented that the lower the flow rate, the longer the contact time, therefore, the efficiency of COD reduction increased. The decrease in COD value was due to the solid material began to deposit, thus the organic substances within the water also decreased. In addition, the decrease made some organic materials being oxidized, whereas some others being absorbed by activated carbon reducing the value of COD [20]. The COD value is usually higher than the BOD value because many of waste material can be oxidized through a chemical process rather than through biological process. High COD values occured due to the presence of influencing environmental factors such as dissolved oxygen content in the well water which was sufficient to help the bacteria breaking down the pollutant compounds [29].

Figure 6. The Effect of Well Water Flow Rate and Adsorbent Mass on Changes in COD Values After Adsorption

4. Conclusion

Dirty water well can be purified by using activated carbon from cacao peels (Theobroma cacao L.) which is activated with 50% H₃PO₄ at 400 °C for 1 hour at 5 mL/ minute of flow rate optimum conditions, and 2 grams mass, with 96.5% decrease efficiency on the color value, 91.8% BOD, and
90.2% COD. The obtained analysis results determines that cacao peels are applicable to be used as activated carbon in the purification process on the dirty well water becoming clean water, in accordance with RI Minister of Health Regulation No. 492/Menkes/Per/IV/ 2010. Morphological analysis using scanning electron microscope (SEM) has indicated pore changes on the surface of activated carbon. Analysis of functional groups using FTIR spectroscopy shows that the produced activated carbon has an absorption pattern with O-H, C-H, and C-O bonds.

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