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Potential Activated Carbon of Theobroma cacao Shell for Pool Water Purification

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ABSTRACT

Research has been carried out to improve the quality of the yellow pool water. The water is used as a source of clean water for the academics of the Politeknik Negeri Padang, so it needs to be improved in accordance with the quality standards of clean water and is suitable for daily use. The adsorption process was carried out using activated carbon of Theobroma cacao shells which was carbonated at 400oC for 1 hour and activated with H3PO4. Characterization of functional groups using Frontier Transform Infra Red, and morphology of surface using Scanning Electron Microscopy. The quality of clean water standard analyzed is turbidity, Total Dissolved Solids, color, Total Suspended Solids, and Fe and Mn content. Functional group analysis exhibits that the activated carbon produced has a pattern of absorption with O-H, C-H, and C-O bond types. At the optimum condition of the activation process, a good adsorbent is absorbed in pool water purification at a flow rate of 5 mL/min with a mass of 2 grams. The efficiency value after the adsorption process showed 67% for turbidity, 71% for TDS, 97% for color, 86% for TSS, 38% for Fe content, and 66% for Mn content. The surface morphology of activated carbon showed the presence of pore cavities, and after the adsorption process, the cavities became saturated. This shows that there has been an absorption by activated carbon so that the water becomes clear. Cacao shell activated carbon is very effective in the process of purifying pool water into clean water and fulfilling clean water standards according to Permenkes 416/MENKES/PER/IX/1990, so it is suitable for being used.

1. INTRODUCTION

Water is one of the most important elements of human life. However, water pollution is still a serious problem in Indonesia at this time. Water pollution can be caused by human activities and by nature itself, such as the presence of organic and inorganic substances in water. One of the efforts to solve water pollution is by using the adsorption method (Rahmawati & Yuanita, 2013), (Yetri, Marantika, Alamsyah, Alif, & Zein, 2020). Clean water that meets health requirements must be free from pollution and meet the quality standards (Siti Munfiah & Anbariawan, 2015; Amin, et al., 2005). The pool water used by the Politeknik Negeri Padang academic community is slightly yellowish, so the quality is doubtful. This yellowish color is possible because of the large amount of Iron (Fe) dan Mangan (Mn) in it, or if this water is collected in the tub, it will give yellowish sediment and stains on the walls. For more details, the standard of clean water quality can be seen in Table 1. Fe in drinking water will accumulate in the body and attack organs such as damage to the intestinal wall and other organs (Amin, et al., 2005). In addition, the presence of suspended substances in the pool

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Table 1. Clean Water Quality Standards According Permenkes RI No.416 / MENKES / PER / IX / 1990

Parametes	Units	Quality Standards	Method Standards
pH	-	6.5 – 8.5	-
Color	TCU	15	SNI 3554:2015
BOD	mg/L	2	SNI 06-6989. 14-2004
COD	mg/L	10	-
TSS	mg/L	50	SNI 06-6989.3-2004
TDS	mg/L	500	SNI 3554:2015
Turbidity	NTU	5	SNI 3554:2015
Fe	mg/L	1	-
Mn	mg/L	0.5	-

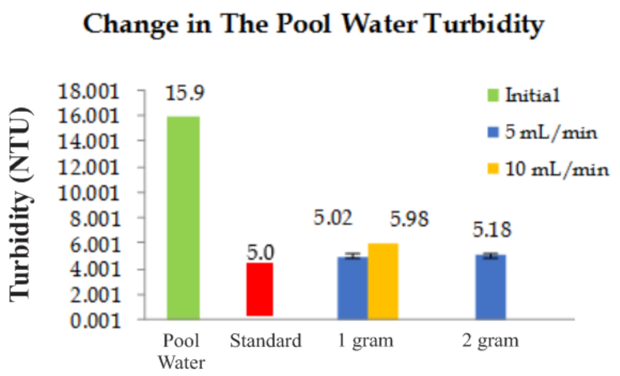

Figure 1. The Influence of Flow Rate and Mass of Activated Carbon on Turbidity Value Changes After Adsorption

water also causes color changes in the water. Therefore, a process is needed to improve the quality of pool water so that it can be used to meet daily needs.

Previous research has carried out water purification methods using activated carbon from coconut shells (Budiono, Suhartana, & Gunawan, 2008; Surest, Kasih, & Wisanti, 2008), super activated carbon from coal and coconut shells (Surest et al., 2008). In this research, the use of cacao shells activated carbon will be carried out for purifying pool water at Politeknik Negeri Padang. Activated carbon was chosen because it has a large surface area, large adsorption ability, is easy to apply, and the cost required is relatively cheap (Dąbrowski, Podkościelny, Hubicki, & Barczak, 2005; Gupta, Sharma, Yadav, & Mohan, 1998). Previous research suggested that functional group analysis and surface morphology of activated carbon from cacao shells had better absorption processes than coconut shells (Mozammel, H.M., Masahiro, O., Bhattacharya SC, 2002). The activation process is carried out using H3PO4. Previous research, when compared to the activation process of coconut shell charcoal with sulfuric acid and phosphoric acid for phenol adsorption, showed better results when activated using phosphoric acid (Budiono et al., 2008). The activated carbon consists of 87%-97% carbon and the rest in the form of hydrogen, oxygen, sulfur, nitrogen and other compounds shaped from the manufacturing process (Arsad, 2010; France, 1991, Lelifajri, 2010). A required material for making activated carbon is the presence of cellulose or hemicellulose in the material. The content of cacao shells consists of 21.06% hemicellulose, 20.15% cellulose, and 55.11% lignin, and coconut shells containing 34% cellulose, 21% hemicellulose, and 27% lignin (Mozammel, H.M., et al, 2002, Yetri Y et al, 2017). The high lignin content in the skin of the cacao is very promising for a higher percentage of efficiency. (Bledzki, A.K., Mamuna, A.A., Volk, J, 2010). So it has the potential to be used as an adsorbent in the adsorption process (Wijaya.M & Wiharto, 2017). The parameters analyzed were pH, color, TSS, TDS, turbidity and iron by using AAS and looking for the optimum flow rate and mass conditions (Gupta et al., 1998; Misran, 2009; Siti Munfiah, 2015).

2. METHODS

2.1. Materials and Tools

The materials used were pool water, cacao shells, paper of filter, glass woll, aquadest, concentrated H_3PO_4 (Merck), K_2PtCl_6 (Merck), $CoCl_2.6H_2O$ (Merck), pH 4.7 and 9 buffer solutions (Merck).

The tools used were a column of glass with a length of 25 cm and diameter of 1.5 cm, standard, clamp, container of well water, Front Lab peristaltic pump, Analytical Balance (Kern & Sohn GmbH), Miyako Blender, Furnace Carbolite CWF 1200, pH meter (HANNA HI 98127), mortar and pestle, Frontier Transform Infra Red (FTIR) (Unican Mattson Mod 7000 FTIR), Scanning Electron Microscopy by HITACHI S-3400 N, UV-Vis Spectrophotometer with

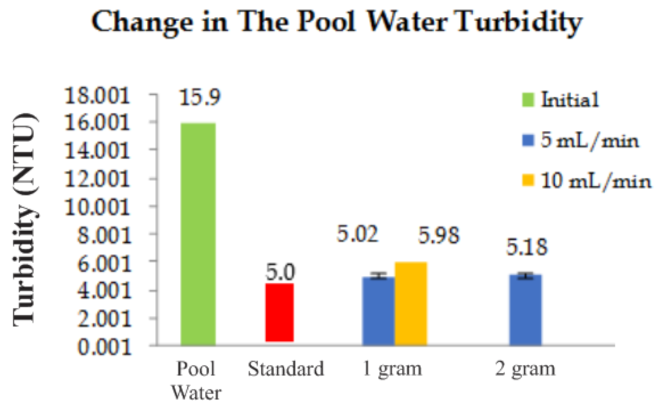

Figure 1. The Influence of Flow Rate and Mass of Activated Carbon on Turbidity Value Changes After Adsorption

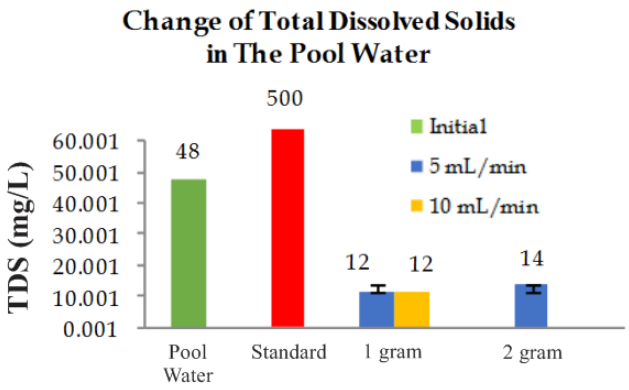

Figure 2. The Influence of Flow Rate and Mass of Activated Carbon on the Change in the Value of Total Disolved Solids (TDS) after Adsorption

Thermo Scientific GENESYS 10S Series, sieve with size particles ≤ 160 μm.

2.2. Activated Carbon Preparation

The cacao shells were washed with water, dried, and then carbonized at 400 oC for 1 hour to form charcoal. The charcoal was then mixed with 50% H3PO4 in a ratio of 1:4 and left for 24 hours. Then the mixture was washed with distilled water until the pH was neutral, then oven at 105 ^{o}C for 3 hours. The resulting activated carbon was sieved to produce a particle size of ≤ 160 μm to be used. SEM and FTIR are used to characterize the activated carbon produced (Purnamawati & Utami, 2014; Wijaya.M & Wiharto, 2017).

2.3. Treatment of Samples

The method of purifying pool water uses a glass column measuring 1.5 cm in diameter and 25 cm in height. Activated carbon was put into the column as much as 1 gram with a variation of flow rate of 5 mL/minute and 10 mL/minute using a pump of peristaltic. After obtaining the best flow rate, 2 grams of adsorbent was treated. The resulting filtrate was analyzed for color, pH, Total Dissolved Solids (TDS), Total Suspended Solids (TSS), turbidity and metal content of Fe and Mn.

Determination of the water color was carried out by a spectrophotometer using the method of spectrophotometric at 456 nm of wavelength with the standard solution used was platinum-cobalt. Quotation of turbidity values using a turbidimeter. TDS is carried out by SNI 01-3554-2015. Determination of TSS value according to SNI 19-7119.3-2005 with gravimetric method, and determination of iron content according to SNI 6989.4: 2009. Meanwhile, for the characterization of activated carbon produced, were used SEM and FTIR.

3. RESULT AND DISCUSSION

Turbidity in pool water samples possibly caused by the presence of suspended and dissolved organic and inorganic materials, such as mud, fine sand, and soil. Turbidity can also be caused by the presence of plankton and microorganisms that are present in large quantities in water. The turbidity value is directly proportional to suspended solids, however, the high dissolved solids turbidity does not always occur (Arsad, 2010; Siti Munfiah, 2015). The results of the initial turbidity analysis of pool water were 15.9 NTU. The value of turbidity in pool water after adsorption can be seen in Figure 1.

Figure 1 tends the effect of the mass of activated carbon on the pool water turbidity. Based on these data, it can be shown that the turbidity of the pond water has decreased after passing through the activated carbon of the cocoa shells. This decrease in turbidity value occurred because the number of particles is well adsorbed by the activated carbon used. The activation process can enlarge carbon pores by breaking hydrocarbon bonds or by oxidizing surface molecules so that the surface area increases and affects the adsorption power (Arsad, 2010; Guo et al., 2007). Adsorption occurs because of the weak Vander Waals forces between particles (Edward Tandy, Ismail Fahmi Hasibuan, & Hamidah Harahap, 2012; Siti Munfiah, 2015).

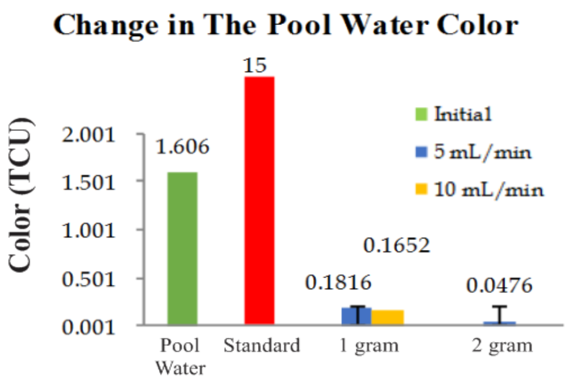

Figure 3. The Influence of Flow Rate and Mass of Activated Carbon on Changes in the Value of Color After Adsorption

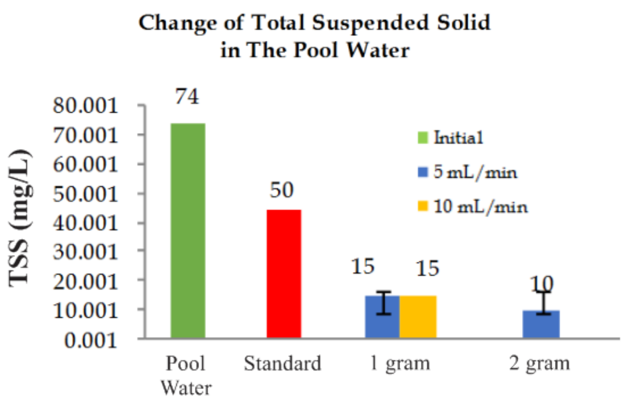

Figure 4. The Influence of Flow Rate and Mass of Cacao Shell Activated Carbon on Changes in Total Suspended Solids (TSS) Value After Adsorption

The efficiency of reducing the turbidity value using 1 gram of activated carbon with flow rates of 5 mL/minute and 10 mL/minute was 68% and 62%. Meanwhile, using the mass of 2 grams of activated carbon, the reduction efficiency was 67%. The results above indicate that the turbidity value of pool water after surpassing activated carbon is according to the clean water quality standards Permenkes 416/MENKES/PER/IX/ 1990.

Total Disolved Solids (TDS) contains various solutes (organic, inorganic, or other materials) in a solution (Guo et al., 2007). The TDS value is one of the chemical parameters in determining the quality of a water, because it represents the number of ions in the water.

Based on Figure 2, it can be seen that the TDS value of the pond water has decreased after surpassing the activated carbon. The efficiency of reducing the TDS value on the mass of 1 gram activated carbon with a flow rate of 5 mL/minute and 10 mL/minute was 75%, and with a mass of 2 grams was 71%. The large percentage of TDS indicates that the solid particles dissolved in the pool water have been adsorbed into the pores of cocoa activated carbon so that the pool water becomes colorless.

Color can be one of the parameters for determining water quality. The water color possibly caused by the presence of organic and inorganic materials, plankton, ions, humus, and other materials in water (Surest et al., 2008; Effendi & Hefni, 2003).

Drinking water must be clear and colorless. Previous research has carried out a reduction in color content analysis using activated carbon from wood and coconut shell of 69.21% and 93.57%, respectively (Budiono et al., 2008). While the analysis of results of pool water after adsorption by activated carbon from cacao shells showed better results, where the color change from yellow to colorless with a reduction in mass efficiency of 1 gram, flow rate of 5 mL/minute and 10 mL/minute was 89% and 90%, while the mass of 2 grams was 97%, as shown in Figure 3. It means that the more mass of activated carbon, the surface area becomes larger so that its absorption capacity will increase. The pool water that has passed through the activated carbon of cacao shells has met the quality of clean water. The yellow color in the water is also caused by the presence of Fe metal, which was 0.842 mg/L in the initial sample of pool water. After the adsorption process, the Fe concentration decreased from 0.842 mg/L to 0.522 mg/L for a flow rate of 5 mL/minute and a mass of 2 grams by 38% efficiency. Meanwhile, Mn decreased from 0.375 mg/L to 0.127 mg/L after adsorption, as shown in Figure 5. This is because the smaller flow rate gives the more dissolved Fe ions in the pool water are adsorbed into the activated carbon (Wieber, J. F., Kuick, B., Zuman, P. 1988).

Water quality is also influenced by the amount of suspended substances in the water. Water quality standards based on PP. 82 of 2001, the TSS threshold is 50 mg/L as measured by the gravimetric method. This regulation was issued to strengthen the Republic of Indonesia Minister of Permenkes No. 416/MENKES/PER/IX/1990 concerning the importance of clean water management for the benefit of the public, as well as to prevent people from hazardous substances

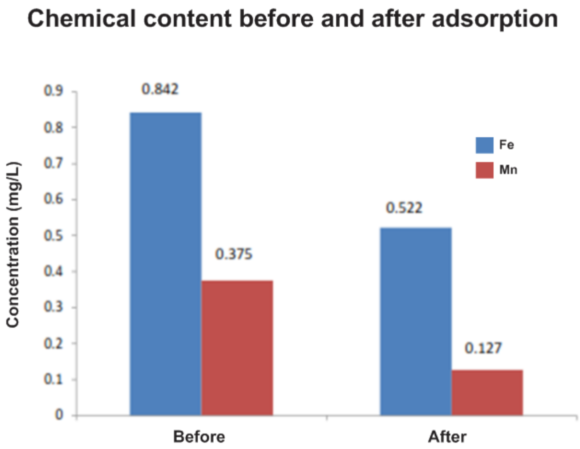

Figure 5. Chemical Content Before and After Adsorption

Table 2. Quality standard of each parameter

Parametes	Units	Quality Standards	Method Standards
pH	-	6.5 – 8.5	-
Color	TCU	15	SNI 3554:2015
BOD	mg/L	2	SNI 06-6989. 14-2004
COD	mg/L	10	-
TSS	mg/L	50	SNI 06-6989.3-2004
TDS	mg/L	500	SNI 3554:2015
Turbidity	NTU	5	SNI 3554:2015
Fe	mg/L	1	-
Mn	mg/L	0.5	-

contained in water. Suspended material consists of mud and microorganisms originating from soil erosion or erosion that is carried into the water (Hendra & Darmawan, 2007; Siti Munfiah, 2015).

The efficiency of TSS reduction on the mass of 1 gram of cacao shell activated carbon with a flow rate of 5 mL/minute and 10 mL/minute was 80%, while 2 grams of activated carbon was 86%. The TSS value after adsorption can be seen in Figure 4. When the flow rate of 5 mL/minute and a mass of 2 grams, the optimum absorption conditions are where the adsorbent contact with water is longer. The longer the contact time, the more chance the activated carbon particles will come into contact with the ions that are bound to the pores of the activated carbon (Lu & Chung, 2001; Misran, 2009). For more details, the comparison between initial, quality standard, and adsorption results can be seen in Table 2.

3.1 Characterization of Activated Carbon

The results of characterization by FTIR are shown in Figure 6 to see the absorption of functional groups contained in the sample.

There was a change in the absorption band on the carbon of the cacao shells before and after adsorption. The main components of it are cellulose, hemicellulose and lignin (Purnamawati & Utami, 2014; Rahmadani & Kurniawati, 2017). Figure 6 shows the cellulose content in the presence of O-H hydroxyl bonds at wave number 3347.13 cm^{-1} and experiencing a shift to wave number 3232.33 cm^{-1} after processing of adsorption. The functional group of –OH on the adsorbent undergoes deprotonation, so that the group of functional becomes negatively charged, which is very reactive in adsorbing ions of Ca^{2+}, and other cations of metal (Rahmadani & Kurniawati, 2017). This Ca^{2+} ion will bind with OH^- from the adsorbent to form a base. This condition will accelerate the adsorption by the adsorbent. At the initial activated carbon, a peak was seen around the wavelength of 2346.79 cm-1 which indicates the appearance of the group of C≡N. The surface containing the group of nitrogen on the surface of the activated carbon increases the ability to adsorb acid gases. The functional group of carboxyl (Aliphatic C-O stretching) at wavenumber 1235.96 cm^{-1} shows the presence of hemicellulose content and after adsorption, there is a shift to wavenumber 1236.01 cm^{-1}. The wavenumber 1916.18 cm^{-1} shows the lignin content and undergoes a shift to the wavenumber 1935.37 cm^{-1} which is indicated by the presence of aromatic C-H groups (Wijaya.M & Wiharto, 2017). Carboxyl and hydroxyl groups play a role in adsorbing cations of metal. The resulting activated carbon has an adsorption pattern with the types of C-H, C-O, and O-H bonds (Rahmadani & Kurniawati, 2017).

The results of surface analysis by SEM at 400°C can be seen in Figure 7. Cacao shells activated carbon with H_3PO_4 has a porous surface because the activator used is water-binding. Water will be firmly bound to the carbon pore and then the activator will enter the pore and open the active surface which is still closed so that its adsorption capacity will

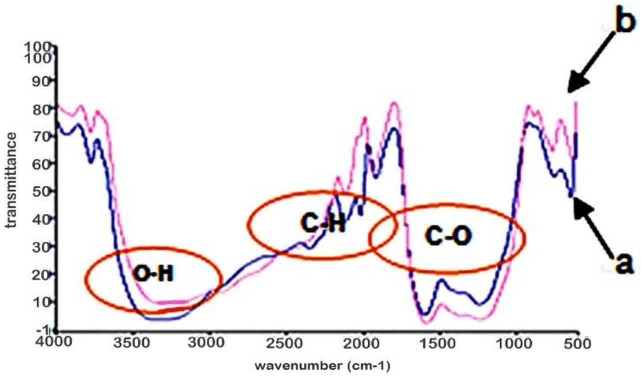

Figure 6. FTIR Spectrum of Cacao Shell Activated Carbon Absorption, (a) Before and (b) After

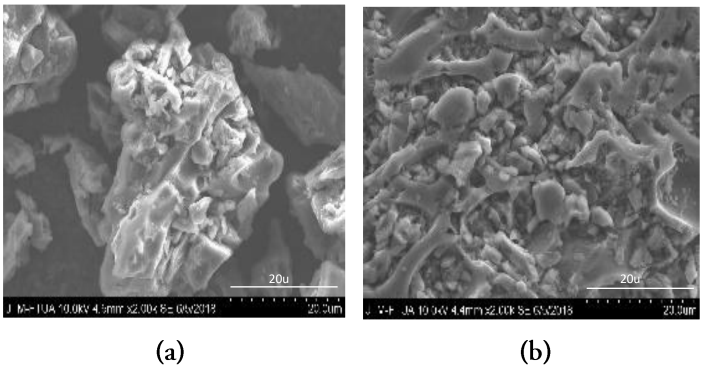

Figure 7. Morphology of surface of activated carbon adsorption with magnification 2000X, (a). before, (b). after

be better (Dąbrowski et al., 2005). The more activators used will increase pore formation on activated carbon (Rahmadani & Kurniawati, 2017). In Figure 6a, the pores are clean, clear and still open, because adsorption has not occurred. Meanwhile, Figure 6b shows that adsorption of activated carbon has occurred, the pores have closed and become denser. This is because the interaction between the adsorbate and the adsorbent only occurs on the surface of the adsorbent (Edward Tandy et al., 2012).

CONCLUSION

Activated carbon of cacao shells obtained from carbonation at 400°C for 1 hour which was activated with H_3PO_4 showed good adsorption in pond water purification. The optimum condition is obtained at a mass of 2 grams with a flow rate of 5 mL / minute. The analysis showed that the efficiency of decreasing the turbidity value was 67%, TDS 71%, color 97%, TSS 86%, Fe 38%, and Mn 66%. Characterization of surface and groups of functional shows that the morphology of activated carbon greatly influences the adsorption process. These results indicate that the activated carbon of cacao shells is very effective in the process of purifying pool water into clean water and meets the requirements of Permenkes 416/MENKES/PER/IX/1990.

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