THE APPLICATION OF GOAT BONE WASTE ACTIVATED CHARCOAL AS MANGANESE HEAVY METAL ABSORBENT IN BOREHOLE WATER

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Received : May 17, 2021           Accepted : December 6, 2021         Published : December 31, 2021

Abstract: Bone is a waste from livestock that contains both organic and inorganic components. It consists of 69% organic compounds used as raw materials for activated charcoal manufacturing. The research aimed to process goat bone waste into activated charcoal products to absorb manganese-heavy metals in borehole water. This research was conducted through carbonization, activation, and characterization. The goat bone waste was carbonized and heated at 700°C for 1 hour, followed by activation. The absorption of manganese-heavy metal was determined by varying the weight of goat bone activated charcoal in 5 g, 10 g, 15 g with a contact time of 15 and 30 minutes. The goat bone waste charcoal obtained was characterized by proximate test, Fourier Transform Infrared Spectroscopy (FT-IR), and Scanning Electron Microscopy (SEM). The results showed that goat bone activated charcoal has a water content value of 2%, ash content of 7%, volatile matter of 10%, fixed carbon 87%, and iodine absorption of 968 mg/g. These values still meet the requirement specified in SNI 06-3730-1995 and SNI 06-4253-1996. The Fourier Transform Infrared Spectroscopy (FTIR) analysis produced functions groups of C–H, C=C, C=H, C≡C, N-H dan O–H. The Scanning Electron Microscopy (SEM) test results found an active charcoal pore diameter of 5,200 μm x 12,952 μm. The efficiency of manganese heavy metals absorption in borehole water ranges from 99.707% - 99.821%.

Keywords: goat bone activated charcoal, manganese-heavy metals, borehole water
Sari Wardani, Savitri, Firda Mawardah, Muhammad Adham, & Lindawati: The Application of Goat Bone Waste Activated Charcoal as Manganese Heavy Metal Absorbent In Borehole Water

Introduction

Goat meat and milk are two of the most popular livestock products in the world today, particularly in Aceh Province. In 2020, the goat population increased by 18,413 heads, totaling 632,282 goats, up from 613,869 in 2019 (Badan Pusat Statistik, 2020). The population of goats will continue to increase along with the increasing demand for meat and milk in the community. Instead, livestock businesses contribute to producing a large amount of waste, including livestock manure, urine, blood, food scraps, feathers, rumen contents, bones, and others (Yaman, 2019). In general, one goat produces 35% meat and 30% bone waste based on its live weight. As a result, the bone waste produced by a 30 kg goat is estimated to be around 9 kilograms. (Azmi et al., 2015). However, bone waste has not been optimally utilized.

Agricultural waste, when processed properly, can yield items with a high resale value. Coconut shells, palm kernel shells, wood, animal bones, maize cobs, rice husks, and other materials containing many organic compounds can all be used to make activated charcoal. (Arsad & Hamdi, 2010; Mohammed et al., 2012). Bone is a waste product resulting from livestock containing organic and inorganic components. It comprises 69% inorganic compounds, 22% organic compounds, and 9% water (Euw et al., 2019). Inorganic compounds consist of 90% collagen, which is a source of raw material for making bone charcoal. Activated charcoal contains 85-95% carbon produced from carbonized materials with high-temperature processing. The demand for activated charcoal is increasing every year. Activated charcoal has been widely used in various industries including the pharmaceutical, food and beverage, and petroleum sector through the adsorption process and as a catalyst in the fertilizer processing process applications. In addition, it can be used for agricultural waste residues remover through the amelioration method, vapor absorbent, and heavy metals absorbent material (Arsad & Hamdi, 2010).

Animal bones can be utilized as raw material for making charcoal, commonly known as black charcoal or abaiser. Animal bones are part of composites that shape and support the skeletal system of the animal body.
Compounds in animal bones consist of 10% carbon, 80% magnesium and calcium, and 10% other organic compounds (Mohammed et al., 2012). Activated charcoal can be applied in the absorption process of certain compounds. It can absorb heavy metal levels of Cu, Pb, Mn, Hg, and Fe (Jamiatun & Setyawan, 2014). Activated charcoal is composed of layers that stack each other to form pores. Generally, the pores in activated charcoal contain impurity compounds in inorganic minerals and metal oxides (Sembiring & Sinaga, 2003).

Clean water is a basic human need for daily life activities. Gradually, it is becoming difficult to obtain. Most springs have been polluted by waste resulting from industry, household, agricultural, and others. For regularly consuming, clean water used for daily needs must be free of all contaminants that endanger health. The soil's mineral and other material content significantly impact groundwater quality. Water consists of minerals that are required by the body. On the other hand, some minerals are harmful to the body. For long-term consumption, the water used must meet the requirements of physical, chemical, microbiological, and radioactive parameters stated by the World Health Organization (WHO) (Trisetyani & Sutrisno, 2014).

Iron and manganese are chemical substances contained in groundwater. High concentrations of iron content can cause brownish-yellow spots, while high manganese concentrations can cause blackness. It is very detrimental to human health if used for daily purposes. Manganese is naturally contained in surface water as a result of rock erosion. High concentrations of manganese, above 0.1 mg/l, can cause a pleasant taste in water and cause blackish stains on pipes and clothing. This compound will precipitate and cause scale when it is oxidized. Consuming water that contains high levels of manganese will cause manganese syndrome, which symptoms are similar to those of Parkinson's syndrome, including weakness, muscle pain, apathy, slow communication, and clumsy limb movements (WHO, 2004). The quality standard for manganese levels for sanitation hygiene purposes is 0.5 mg/l according to PERMENKES No. 32 of 2017, and the quality standard for manganese levels for drinking water is 0.4 mg/l PERMENKES No. 492 in 2010.

Several previous studies on the utilization of goat bone waste into activated charcoal using chemical activation, namely sulfuric acid with concentrations of 1N, 2N, and 3 N, reported were able to absorb iod of 983 mg/g (Wardani & Rosa, 2018). Physically activated charcoal for 3 hours at 500°C, 600°C, and 700°C was able to absorb iodine at 926 mg/g, 806 mg/g, and 768 mg/g (Wardani & Mirdayanti, 2019). Physically, bones have pores that can be used as activated charcoal because the pores found in goat bones can adsorb other substances to the surface of the bone pores and contain calcium hydroxyapatite (Euw et al., 2019). So far, goat bones have only been utilized to make a bone meal. (Fitryani et al., 2014). Bone flour is used as a mixture in animal feed, but the addition of bone meal in animal feed is very low. The goat bone waste has not been optimally
utilized. The novelty of this study is to produce goat bone waste-based activated charcoal by using a physical activation process. Hopefully, it can be applied as an absorbent material for the manganese-heavy metal in borehole water. Besides increasing the income of goat farmers, it can improve public health status by using water free from manganese-heavy metals. The water used by the community for daily needs come from bore wells. According to the Health Laboratory of the Aceh Government Health Service, the manganese content in borehole water reached 8,497 mg/l. This concentration is far above the quality standard set by the Indonesia Minister of Health, so it is harmful to human health for a long time-consuming. This research aims to process goat bone waste into activated charcoal to reduce manganese levels in borehole water. This research will contribute to goat farming in reducing waste accumulation by utilizing goat bone waste as a new alternative to activated charcoal.

Materials and Method

Materials

The materials used in this study are goat bone waste, aquadest, Whatman filter paper, 0.1 N iodine (Merck), 0.1 N sodium thiosulfate (Merck), 1% starch indicator (Merck), and borehole water. The goat bone waste was collected from a Slaughterhouse located in Lambaro, Ingin Jaya, Aceh Besar District. The borehole water with identified manganese content was taken from the bore well located in Tengku Malem Muda street, Kampung Mulia, Kuta Alam, Banda Aceh City at coordinates 5°33'52.1" N and 95°19'21.7" E.

Research Equipment

The equipment used in this research is oven, dropper, furnace, desiccator, analytical balance, ball mill, glass funnel, spatula, mesh sieve, mask, gloves, measuring cup, beaker, measuring flask, pH meter, centrifuge, burette, stative, metal plate, Fourier Transform-Infra Red (FTIR) Agilent Technologies Cary 630 FT-IR, Scanning Electron Microscopy (SEM) JEOL JSM-6510 LA, and Atomic Absorption Spectrophotometry (AAS) Shimadzu AA 6200.

Research Stages

Carbonization process

The collected goat bone waste is washed and dried for ± seven days using sunlight. For the carbonization process, the dried goat bone waste is then crushed into a size of ± 3 cm using a ball mill. Organic cellulosic materials contained in the bone are broken through the carbonization process. The carbonization process to produce charcoal can be carried out at a temperature of 600 °C – 800 °C (Arsad & Hamdi, 2010; Meisrilestari et al., 2013). The carbonization process uses a furnace at 700 °C for 20 minutes. The goat bone charcoal produced cannot be used as an absorbent medium because the pores of the charcoal are still closed with impurities.
Activation Process
The resulting charcoal was then pulverized to a size of 100 mesh. The next step is the activation of goat bone charcoal using the physical activation method at a temperature of 700 °C for 1 hour. Activated goat bone charcoal products can already be applied as a medium for absorbing manganese-heavy metal in borehole water.

Characterization
Absorption Process of Manganese Heavy Metal in Borehole Water
The absorption process of manganese heavy metal was determined follows the steps: activated charcoal of goat bone waste is weighed as much as 5, 10, and 15 grams, then each is put into 100 mL of borehole water with known manganese metal content then stirred using a magnetic stirrer for 15 and 20 minutes with a stirring speed of 50 rpm. The mixture was then filtered and separated for testing the manganese levels using the Atomic Absorption Spectrophotometer (AAS) tool.

Quality Analysis of Goat Bone Activated Charcoal
The quality of activated charcoal was characterized based on comparative tests, namely water content, ash content, iodine absorption, volatile matter, fixed carbon. The procedure for analyzing the characteristics of activated charcoal was conducted under SNI 06-4253-1996 on the mechanism for testing activated charcoal for drinking water. The functions group of goat bone waste-activated charcoal was analyzed using Fourier Transform Infrared Spectroscopy (FT-IR). Furthermore, the surface morphology of activated charcoal was characterized using Scanning Electron Microscope (SEM).

The effectiveness of Manganese Heavy Metal Absorption in Borehole Water
The effectiveness of heavy metal absorption was determined using the following equation:

\[
\text{Decrease Effectiveness } (E_f) = \frac{(Y_i - Y_f)}{Y_i} \times 100 \% 
\]

Where \(E_f\) is the reduction effectiveness, \(Y_i\) is the initial heavy metal content, and \(Y_f\) is the final heavy metal content (Larasati et al., 2015)

Results and Discussion
Making activated charcoal from goat bones was carried out in two stages: the carbonization and activation process. The carbonization process removes volatile substances, decomposes organic cellulose into carbon elements, and remove non-carbon compounds (Adikusuma et al., 2018; Imammuddin et al., 2018; Lempang, 2014). The carbonization process was carried out at a temperature of 700 °C for 20 minutes. This is based on the fact that the quality of carbonized charcoal at an activation temperature of 700°C gave the best results for
the proximate test and ultimate analysis when compared to the activation temperatures of 400 °C, 500 °C, 600 °C, and 800 °C (Adikusuma et al., 2018; Agustin, 2020).

The activation process of charcoal produced activated charcoal. The activation process used a temperature of 700 °C for 1 hour. The function of the activation process is to open, increase, and expand the volume and diameter of the charcoal pores. Carbon chains in organic compounds within the bone structure can be broken down into carbon elements using heat, steam, and carbon dioxide (CO₂) through an activation process (Sembiring & Sinaga, 2003). The higher the activation temperature, the more minerals are evaporated so that the surface area of the activated charcoal pores increases.

The quality of goat bone waste-activated charcoal is tabulated in table 1. It includes the results of water content, ash content, volatile matter, fixed carbon, iodine absorption ability, functional groups, and morphology testing.

| Characteristics      | Goat Bone Charcoal | Goat Bone Activated Charcoal | Quality standards SNI 06-3730-1995 | Quality standards SNI 06-4253-1996 |
|----------------------|--------------------|------------------------------|-----------------------------------|-----------------------------------|
| Water Content (%)    | 0.959              | 1.566                        | Max 15                            | Max 15                            |
| Ash content (%)      | 15.411             | 6.757                        | Max 10                            | Max 10                            |
| Volatile Matter (%)  | 14.626             | 9.619                        | Max 25                            | Max 25                            |
| Fixed Carbon (%)     | 82.454             | 87.391                       | Min 65                            | Min 65                            |
| Iodine Absorption(mg/g) | 920                | 968                          | Min 750                           | Min 750                           |
| Functional groups    | O-H; C-H; O-N; C-O; C-C; C=; C=; NO₂ | O-H; C-H; C=C; C=C; N-H | - | - |
| Morphology           | 0.825 μm – 1.811 μm | 5.200 μm – 12.952 μm         | -                                 | -                                 |

The water content test is used to determine the hygroscopic nature of activated charcoal. The activation process of charcoal can increase the pore size and surface area of the charcoal. Consequently, it can increase the ability of activated charcoal as absorbent material (Prasetyo et al., 2013). Data in table 1 shows that the water content of charcoal was 0.959%, and activated charcoal was 1.566%. The less water content percentage of the sample might be affected by the activated charcoal surface. It is due to the fewer polar functional groups so that the interaction between polar water vapor is also less (Prasetyo et al., 2013). Ash content testing aims to calculate the mineral content contained in activated charcoal (Agustin, 2020). The results showed that bone charcoal still contains a very high ash content exceeding the specified quality standard of 15.411%. This is
because the metal oxide content contained in the charcoal cannot evaporate in the ashing process. However, the ash content in activated charcoal meets the specified quality standard, which is 6.757%.

The volatile matter test aimed to calculate non-carbon compounds in charcoal and activated charcoals. The results showed that the volatile matter levels for charcoal and activated charcoals were 14.626% and 9.619%, respectively. The volatile matter content of charcoal is higher than that of activated charcoal, and this is because the content of organic compounds in charcoal is more significant, and the carbonization time is relatively short. The high levels of volatile matter are influenced by carbonization time and temperature. The longer the time and the higher the carbonization temperature, the more volatile matter is lost (Agustin, 2020).

An Iodine absorption test was used to assess the ability of activated charcoal as an absorbent medium. This study used the iodometric titration method to analyze the ability of charcoal and activated charcoal to absorb iodine. The results showed that the iodine absorption capacity of activated charcoal was greater than that of charcoal, which was 968. The better the quality of activated charcoal absorbs dissolved substances or pollutants (Adikusuma et al., 2018). Overall, the quality of goat bone activated charcoal meets the requirement stated by SNI Number 06-3730-1995 regarding technical activated charcoal and SNI 06-4253-1996 regarding activated charcoal for drinking water.

For FT-IR analysis, it showed the FT-IR spectrum on charcoal containing the OH functional group at 3205 cm\(^{-1}\), functional group C-H aliphatic at 2917 cm\(^{-1}\) and 2851 cm\(^{-1}\), functional group C-C at 2141 cm\(^{-1}\), functional group C=C at 1637 cm\(^{-1}\), functional group NO\(_2\) at 1541 cm\(^{-1}\) dan 1508 cm\(^{-1}\), functional group C-H at 960 cm\(^{-1}\) and 871 cm\(^{-1}\), functional group C-N at 717 cm\(^{-1}\) and functional group C-O at 1197 cm\(^{-1}\) and 1178 cm\(^{-1}\). Whereas, the functional groups produced by activated charcoal consist of the functional group in the N-N at 3394.72 cm\(^{-1}\), functional group C=C at 2202.71 cm\(^{-1}\), functional group O-H at 2011.76 cm\(^{-1}\), functional group C=C at 1654.92 cm\(^{-1}\), functional group C-H at 1463.97 cm\(^{-1}\) and 1411.89 cm\(^{-1}\) and functional group C=H at 960.55 cm\(^{-1}\) and 873.75 cm\(^{-1}\). Based on the results, it can be seen that activated charcoal has functional groups that are in accordance with the structure of activated charcoal in general, which contains O-H, C=C, C=H aromatics, and C-H groups, which indicates that the activated charcoal produced tends to be more polar. Thus the activated charcoal produced can be used as an adsorbent for substances that tend to be polar such as for purifying water, sugar, alcohol, or as an absorbent for formaldehyde emissions (Setiawan et al., 2017; Waluyo et al., 2020). The results of testing the functional groups of charcoal and activated charcoal of goat bone waste are presented in figure 1.
The Scanning Electron Microscope (SEM) characterization aimed to determine the morphology of charcoal and activated charcoal. The result showed that the diameter of the pore size of activated charcoal was larger than the diameter of the pore size of the charcoal. Samples of goat bone charcoal analyzed at 1000 x magnification have not shown the pore diameter size. The pore diameter size can be seen clearly by using a magnification of 2000 x. The pore diameter size was revealed at 0.825 µm -1.811 µm. Meanwhile, activated charcoal from goat bones at 1000 x magnification has seen the pores. The pore size of activated charcoal depends on the type of raw material, temperature and carbonization conditions, and the activation process (Lempang, 2014). The activation process can reduce the hydrocarbon compounds attached to the surface of the charcoal. Based on IUPAC (International Union of Pure and Applied Chemistry), the pore particle sizes are grouped into three groups, namely micropores (< 2 m), mesopores (2 – 50 m), and macropores (> 50 m) (Budi et al., 2012). Based on its structure, goat bone-activated charcoal can be categorized in the mesopore structure because it has a diameter ranging from 1.018 m - 5.284 m (Wardani & Rosa, 2018). The pore size of goat bone charcoal resulted in this study was 1.811 m x 1.811 m, while the pore diameter size of activated goat bone charcoal was 5.200 m x 12.952 m which belongs to the mesopore structure. The morphological surface of goat bone waste charcoal and activated charcoal are presented in figure 2 and figure 3.
The Efficiency of Absorption of Manganese Levels in Borehole Water

Figure 4 presents the efficiency of absorption of manganese levels in borehole water using activated charcoal from goat bones using variations in the weight of activated charcoal and absorption time. The results indicate that high absorption efficiency resulted from the high amount of activated charcoal used and longer the absorption time. The higher the amount of activated charcoal used and the longer the absorption time, the higher the absorption efficiency. A sample with the weight of activated charcoal of 15 g and an absorption time of 30 minutes was able to absorb Manganese content of 99.821% compared to manganese absorption efficiency at 15 minutes which is only 99.766%. Overall, the absorption of activated charcoal from goat bones to manganese levels in borehole water was 99.707% - 99.821%. It is due to the manganese content in the borehole water absorbed into the pores of the activated charcoal.
Figure 4. The efficiency of Absorption of Manganese Levels in Well Water

The results of this study are in line with research on the absorption of manganese levels using activated carbon from corn cobs. The more amount of activated charcoal added the more manganese levels are absorbed with the absorption efficiency of manganese levels at 3 grams of activated charcoal weight of 98.40% compared to the weight of activated charcoal 1 gram and 2 grams that are equal to 80.46% and 92.32% (Antika et al., 2019). The results of other studies also state that the longer the contact time, the higher the absorption efficiency of manganese levels. The best manganese absorption efficiency was found at 120 minutes with an absorption efficiency of 52.12% compared to manganese absorption efficiency at 30 minutes which is only 9.44% (Viena et al., 2020).

Conclusion

Based on the result, it can be concluded that goat bone waste can become a physically activated charcoal product. It is appropriate to be applied as an alternative medium for absorbing manganese in borehole water, with the absorption efficiency of activated charcoal reaching 99.707% - 99.821%. The quality of the activated charcoal has complied with the requirement of the Indonesian Nasional Standard, SNI 06-3730-1995 and SNI 06-4253-1996, concerning technical activated charcoal.

Acknowledgement

The research was supported and funded by Abulyatama University Foundation through program Hibah Yayasan Abulyatama-Hj.Rosnati is governed by Research and Community Service Institute (LPPM) Abulyatama University with contract number 44/KONTRAK/LPPM/XII/2020.
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