



The Utilization of Corn Stalks as Biochar to Adsorb BOD and COD in Hospital Wastewater

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<https://doi.org/10.18280/ijdne.170114>

ABSTRACT

Received: 24 November 2021

Accepted: 14 January 2022

Keywords:

biochar, COD, BOD, SEM-EDS, corn stalks, adsorption, pyrolysis

Biochar preparation from biomass and organic materials such as fruit peels, livestock manure, wood chips, and other agricultural residues has been studied. Those materials are prepared through a pyrolysis process, heating at a specific temperature, then utilized for adsorption waste pollution such as heavy metal ions. This study aimed to produce activated biochar from corn stalks (ABCS) as an adsorbent of BOD and COD in hospital wastewater. Activation of the biochar was carried out with an activator agent, namely ZnCl₂. The moisture and ash content of activated biochar with a pyrolysis temperature of 400°C and 500°C meet SNI. SEM-EDS determined the pore and elements analysis. ABCS consist of 44.88 % and 60.56% of the carbon produced with different temperature of 400°C and 500°C, respectively. One gram of ABCS reduced COD up to 71.4% in 4.5 hours and a maximum of 56.83% of BOD in 3 hours. While in an hour, a maximum of 2.5 g ABCS decreased COD 62.5% and 71.1% of BOD with the most of 1.5 g ABCS.

1. INTRODUCTION

Central Sulawesi is one of the centers of corn production in Indonesia, with total corn production in 2018 of 380.650 tons [1]. Waste from corn in the form of cobs, stems, husk, and leaves is the main source of biomass for the manufacture of activated carbon. Usually, these wastes have not been used properly and are only left to rot which can pollute the surrounding environment. Activated carbon is defined as pure charcoal that is chemically or physically treated to produce a micropore product, increasing its adsorptive surface area [2]. The large surface area (between 500 and 1500 m²/g) and the electric charge adsorb various polar compounds, mainly phenols, and derivatives [3].

Some research results on biochar derived from agricultural plant biomass, especially from fruit peels such as banana peels [4], cocoa [5], durian [6], salak fruit seeds [7], coconut husk [8], has been published in various reputable journals both nationally and internationally. Generally, the research carried out is applied as an adsorbent for metal ions such as Chromium, Cadmium, Lead, and others metals contained in the solution. These research experiences can be developed to increase biochar's capacity or adsorption capacity for mass production, which can improve water quality or wastewater treatment.

Wastewater contains a lot of hazardous substances such as BOD and COD. Chemical oxygen demand (COD) is the amount of oxygen needed to oxidize organic waste in water through chemical reactions. Organic waste will be corrupted by potassium dichromate (K₂Cr₂O₄) as a source of Oxygen into CO₂ and H₂O gas and some chromium ions. COD value is a measure of the level of pollution by organic matter. Biological Oxygen Demand (BOD) is the amount of Oxygen needed to overhaul organic matter in water by microorganisms

at a specific temperature and volume. The greater the BOD value of water, the less oxygen is available to organisms in the water. BOD is closely related to DO (Dissolved Oxygen) or dissolved oxygen. The higher the BOD level of water, the less the amount of dissolved oxygen. So, the higher the BOD level, the higher the level of pollution [9].

Water treatment can be done physically by using a sand filter with a silica size adjusted to the size of the suspended materials to be filtered. Meanwhile, chemical wastewater treatment is usually carried out to remove non-precipitating particles (colloids), heavy metals, phosphorus compounds, and toxic organic substances by affixing certain required chemicals [10]. The removal of these materials in principle takes place through changes in the properties of these materials, namely from non-precipitation (flocculation-coagulation), either with or without an oxidation-reduction reaction, and also takes place as a result of an oxidation reaction [11]. Biological wastewater treatment is one of the treatment methods directed at reducing or eliminating specific substrates contained in wastewater by utilizing the activity of microorganisms to remodel the substrate. Physical water treatment with filter media, namely activated carbon, can reduce pollutant levels, namely BOD and COD in water. Activated charcoal is defined as a by-product obtained by the thermochemical conversion of biomass into heat, energy, fuel, and chemicals in a limited oxygen environment [8]. Activated biochar from corn stalks is made to be used to improve water quality by reducing BOD and COD levels in hospital wastewater. The utilization of corn stalks as materials for the manufacture of activated carbon strongly supports the zero-waste principle and prevents environmental damage due to waste.

2. RESEARCH METHODS

The raw material, corn stalks, is cut into pieces and dried in the sun, then converted biomass material, staking corn into charcoal (biochar). ABCS is produced using pyrolysis, in which the biomass is heated in the absence of Oxygen to two various temperatures; 400°C and 500°C. The product made through the pyrolysis process is in the form of solid black powder. The principle of the carbonization process is the burning of biomass in the absence of oxygen. So that only the volatile matter is released, while the carbon remains in it. The carbonization temperature will affect the biochar produced so that the determination of the right temperature will determine the quality of the biochar. The following process is the activation process with Calcium Chloride (CaCl₂). This process takes place by immersion the biochar in a beaker filled with CaCl₂ for 24 hours. Activation is a process in the manufacture of activated carbon or biochar which aims to increase and expand the pore volume, as well as enlarge the pore diameter. Through the activation process, usually biochar will have an increasing adsorption power. The activating agent (CaCl₂) functions to degrade or hydrate organic molecules during the carbonization process, limit the formation of tar, assist in the decomposition of organic compounds on subsequent activation, dehydrate water trapped in carbon cavities, help remove hydrocarbon deposits produced during the carbonization process and protect carbon surface so that the possibility of oxidation can be reduced. After then, the activated charcoal was filtered, then placed in a furnace to dried. The drying process is by placing ABCS in a porcelain cup, then leave it in the Laboratory Furnace for 2 hours at a temperature of 500°C. Drying is the final stage of the production of ABCS, reducing the water content and removing the remaining activator solution in the material. ABCS was then sieved with 80 mesh size according to PAC Powder Active Carbon standard. The purpose of this sieving is so that the surface area of ABCS has the right pores as an adsorbent. The smaller the particle diameter, the larger the surface area so that it has a greater adsorption ability.

The ABCS then analyze and characterize their (a) pore analysis, (b) moisture content, (c) ash content, and (d) determination of carbon and other elements. The activated carbon pore characterization takes place with SEM-EDS.

3. RESULT AND DISCUSSION

3.1 Biochar characterization

ABCS was analyzed water and ash content to ensure the quality fit the Indonesia National Standard, as shown in Table 1. Determination of water, and ash content is carried out by the gravimetric method, namely the drying method (with an ordinary oven). The weight of the ABCS calculated after being removed from the oven must be obtained constant weight, namely the weight of ABCS that will not decrease or remain after being put in the oven. The sample weight after constant means that the water contained in the sample has evaporated and what is left is only solids and water that are really strongly bound in the sample, after which calculations can be made to determine the percent water content in ABCS. The measurement results show that the water content of ABCS produced from pyrolysis at a temperature of 400°C contains more water (12.67%) than ABCS produced from pyrolysis at

a temperature of 500°C (5.90%). The higher the pyrolysis temperature, the more water content evaporates, making the sample more hygroscopic [12]. In contrast, the ash content increases with the increase in pyrolysis temperature. The ash content of biochar produced at a temperature of 400°C contains was 8.89% and increased to 12.96% with an increase in the pyrolysis temperature to 500°C. The condition is caused by the rise in temperature, causing more material to burn and become ash [13].

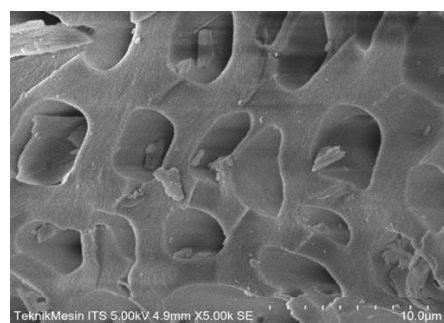
Table 1. Water and ash content of biochar

Pyrolysis Temperature (°C)	Water Content (%)	Ash Content (%)
400	12.67	8.89
500	5.90	12.96

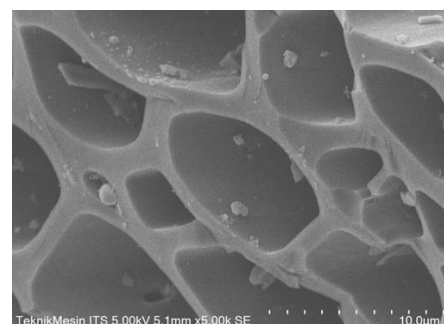
The ABCS produced has met the Indonesian National Standard SNI 06-3730-1995 for moisture, ash, and the content of the amount of bound carbon in the biochar. Scanning electronic microscopy (SEM) analysis was conducted to see the microstructure originating of ABCS. Because adsorption is the process of entering molecules into the pores, the carbon adsorption process depends on the physical characteristics of the activated carbon and the size of the adsorbate molecule [14].

3.1.1 Pore morphology

Molecular size is an essential part of adsorption because the molecule must enter the micropore of the carbon particles to be adsorbed. The adsorption rate usually increases as the molecular size of the adsorbate increases [15]. Most waste consists of mixed materials, so that the molecular size is different. In this situation, the filtering of the molecules will worsen because the larger molecules will close the pores, thereby preventing the passage of the smaller molecules [16].



(a) Pyrolysis Temperature 400°C



(b) Pyrolysis Temperature 500°C

Figure 1. ABCS pore morphology resulting from pyrolysis at a temperature of 400°C (a), and corn stalk pore morphology resulting from pyrolysis at a temperature 500°C (b)

SEM results of ABCS pyrolyzed at 400°C and 500°C (Figure 1) showed different pore sizes when scanned under the same conditions measurement, namely Magnification 5000×, Working Distance 5000 m, Emission Current = 122000 nA, with Photo size 1000. ABCS produced with a pyrolysis temperature of 500°C showed a larger pore size than the one created with a pyrolysis temperature of 400°C. Coordinate horizontal are the pore's cross-sections in the (x, y) plane are of compact irregular form, and vertical are the cross-sections of the pores in (y, z) plane are of elliptic form with the major and minor axes ordered in parallel to the y and z coordinate axes. The results of this study follow those produced by researchers on the effect of temperature on the pore characteristics of rice straw and canola stalk biochar. The pyrolysis temperature of 450°C is the optimal temperature to produce biochar with greater porosity, the pore size is 1~3 mm [17, 18].

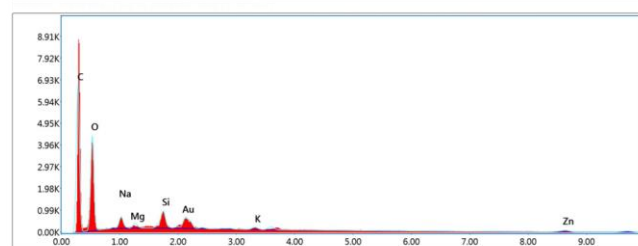
Particle size and surface area are essential in activated carbon. The particle size of activated carbon affects the adsorption rate but does not affect the adsorption capacity related to the carbon surface area [14]. So, the adsorption speed using powdered activated carbon is more significant than granular activated carbon [17]. The total surface area affects the full adsorption capacity, thereby increasing the effectiveness of activated carbon in the removal of organic compounds in wastewater. Particle size does not affect the total surface area, mainly covering the pores of the carbon particles. The pore structure of activated carbon affects the ratio between surface area and particle size. The main factor in the adsorption process is the pore structure determines the distribution of molecules that enter the carbon particles for adsorption [18]. Large molecules can block the entrance to the micropore, thereby making the surface area available for adsorption wasted. Due to the irregular shape of the molecules and the constant movement of the molecules, smaller molecules can penetrate the smaller capillaries [19].

3.1.2 Element content

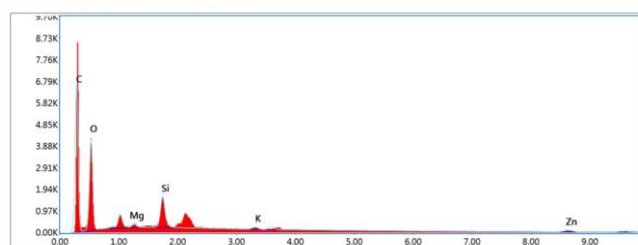
The results of the Energy Dispersive X-Ray Spectroscopy (EDS) analysis showed that the element carbon (C) was the dominant element in corn stalk charcoal. Graph 1 shows the composition of ABCS produced at different pyrolysis temperatures, namely 400°C (a) and 500°C (b). The carbon content in ABCS with a higher pyrolysis temperature was also higher. The result is in line with the research that has been done by previous researchers on pruned apple tree branches, where the resulting conditions were determined to be appropriate for the carbonization at the temperature of 500°C. The impacts of the most factors influencing abdicate diminished within the arranged temperature > holding time > heating rate, though that on the settled carbon substance was temperature > heating rate > holding [20].

The EDS data (Figure 2) shows the levels of carbon and other elements that are still present in the activated biochar. In the biochar produced at a carbonation temperature of 400°C (Table 2), the percentage of atomic carbon was 44.88%, Oxygen (35.82%), Silicon (9.73%), and Zinc (6.33%). Other elements with levels between 0-1% are Magnesium (0.5%), Aluminum (0.32%), Phosphorus (1.1%), Potassium (0.22%), and Calcium (1.12%). There are still elements such as Aluminum, Phosphorus, and Calcium in the biochar, most likely due to the low carbonation temperature (400°C). This composition comes from the energy produced by X-rays. In the spectrum produced by EDS, the X-axis shows the X-ray

energy produced by each atom in units, while the Y-axis shows the intensity of the absorbed light proportional to the percent (%) mass of the element present in the sample. In qualitative analysis, this EDS method provides information on the types of elements contained in the material. The result can be compared to the examination of the impact of generation conditions such as pyrolysis temperature and residence time on the fundamental properties and the wholesome characteristics of biochar determined from distinctive feedstocks; corn stalk, assault straw, wheat stalk, and shelled nutshell, where appeared that pyrolysis temperature was a basic parameter influencing biochar properties [21]. For carbonation temperature 500°C, straw biochar contained a high level of Potassium but limited amounts of Nitrogen and Phosphorus [21].



(a) Pyrolysis Temperature 400°C



(b) Pyrolysis Temperature 500°C

Figure 2. EDS analysis of ABCS with a pyrolysis temperature of 400°C (a) and 500°C (b), and the activation of ZnCl₂ agents

Table 2. Elemental composition of activated carbon from corn stalks at a pyrolysis temperature of 400°C

Element	Weight (%)	Atomic (%)
C	28.26	44.88
O	30.04	35.81
Mg	0.64	0.50
Al	0.45	0.32
Si	14.31	9.72
P	1.79	1.10
K	0.44	0.22
Ca	2.36	1.12
Zn	21.71	6.33

Table 3. Elemental composition of ABCS at a pyrolysis temperature of 500°C

Element	Weight (%)	Atomic (%)
C	49.31	60.56
O	37.45	34.53
Mg	0.86	0.52
Si	4.90	2.57
K	0.84	0.32
Zn	6.63	1.50

In contrast to ABCS produced with a carbonation temperature of 400°C, at a pyrolysis temperature of 500°C, the carbon content reaches 60.56%. Other elements contained in it are Oxygen (34.53%), Magnesium (0.52%), Silicon (2.57%), potassium (0.32%), and Zinc (1.50%) (Table 3). Other elements found in biochar due to carbonation at 400°C are no longer visible in biochar with a carbonation temperature of 500°C. That means that the increase in the pyrolysis temperature causes some elements such as Aluminum, Phosphorus, and Calcium to evaporate. The tendency to increase elemental content in biochar is an increase in heavy metals in biochar produced from cow manure. The part of heavy metals was changed into a stable portion with increasing carbonation temperature. Moreover, biochar's potential danger and ecotoxicity were decreased, hence improving environmental security [22].

Although both products met the quality requirements of ABCS according to SNI 06-3730-1995 for moisture and ash content, the ABCS from the pyrolysis process temperature of 500°C was chosen for further study. The choice of ABCS with the temperature of 500°C refers to the percentage of the atomic carbon of SEM-EDS in the sample, which is more extensive than the one created with the temperature of 400°C. The second consideration was the pore morphology. It has shown that the pore size of ABCS produced at higher temperature has the bigger pore size; hence, only the ABCS produced by pyrolysis at a temperature of 500°C will be tested as an adsorbent for BOD and COD of wastewater.

3.2 ABCS testing on hospital wastewater

The results of ABCS testing on COD and BOD levels in hospital waste showed a decrease with increasing contact time (Table 4). Before treatment with biochar, the samples' amount of COD and BOD were 56.0 mg/L and 46.8 mg/L, respectively. With a contact time of 3 hours, the levels of COD and BOD decreased by more than 50%, to 24.0 mg/L (COD) and 20.2 mg/L (BOD). After 4.5 hours of contact time, COD in the sample decreased to 16.0 mg/L, but this was not the case with BOD levels. It increased by 6.6 mg/L. Likewise, when the time was raised twice, namely to 6 hours of contact time, the BOD level rose to 40.2 mg/L, while the COD level was stagnant and did not change. Thus, the optimum contact time for reducing COD levels in hospital waste is 4.5 hours, while BOD is 3.0 hours, with the amount of ABCS used being 1.0 grams. The difference from BOD is that COD indicates an organic compound that cannot be degraded biologically. COD in waste is usually greater than its BOD value because more chemical compounds can be oxidized chemically than biological oxidation. The decrease in COD was caused by partially adsorbed organic materials and bound by ABCS. The amount of organic matter present in wastewater would automatically decrease the need for Oxygen to oxidize organic matter chemically. The reduced oxygen demand will result in a decrease in the COD value in wastewater. So as in the reduction of BOD, the reduction in COD is also proportional to the amount of ABCS added and the contact time of ABCS with wastewater. Experiments using activated biochar from corn husks and used as an adsorbent to reduce BOD and COD levels in dug well water [23]. Biochar from corn husk, can reduce 15.83 mg/L COD, and 12.24 mg/L with a contact time of 10 hours. While ABCS can reduce COD and BOD in hospital wastewater by more than 50% within 5 hours. This shows that ABCS is more advantage to use as an adsorbent to

reduce COD and BOD levels. The decrease in COD also occurs in produced water by utilizing the biochar dregs as an adsorbent with a particular contact time [24].

In addition to conducting trials at varying times, the treatment was also carried out with various weights of ABCS. COD and BOD levels based on differences in sample weight are shown in Table 5 below. The COD level decreased by 16.0 mg/L with a weight of 1.5 g of biochar and 2.5 g with a contact time of 1 hour. However, with biochar as much as 3.5 g, the COD level in hospital waste increased by eight mg/L. This means that an increase of 1 gram of ABCS increases the amount of COD by eight mg/L. Thus, the optimum weight of ABCS that can reduce COD levels within 1 hour is 2.5 g. Meanwhile, the maximum decrease in BOD levels was 1.5 grams with a contact time of 1 hour, reducing 33.3 mg/L. The removal of COD and BOD showed an increase with the increment of gravel size and pavement thickness which can remove up to 54% and 68%, respectively [25].

Table 4. COD and BOD levels in the hospital wastewater before and after treatment with various contact time

Time (hours)	COD (mg/L)	BOD (mg/L)
0.0	56.0	46.8
3.0	24.0	20.2
4.5	16.0	26.8
6.0	16.0	40.2

Table 5. COD and BOD levels in the hospital wastewater before and after treatment with various biochar weights

Weight (g)	COD (mg/L)	BOD (mg/L)
0	56.0	46.8
1.5	40.0	13.5
2.5	24.0	33.5
3.5	32.0	40.2

Differences in levels of COD and BOD in hospital waste can be caused by the type of waste studied. In addition to general rubbish, there are also pathological wastes, chemical wastes, infectious wastes, sharps waste, and pharmaceutical wastes. In this study, the sample hospital waste was general and chemical waste, from washing and other activities that do not harm human health and the environment and from research or diagnostic work, cleaning, or disinfection procedures. There have been many treatments for hospital wastewater, including therapy for laundry wastewater [26], antibiotics [27], fluoroquinolones [28], and this research that focused on general waste.

4. CONCLUSION

The ABCS was prepared at pyrolysis temperatures of 400°C, 500°C, resulting in the moisture content of 12.67% and 5.90% while ash content was 8.89% and 12.96%. The pore characteristics and the elemental composition for a temperature of 500°C were analyzed with Scanning Electron microscopy- Energy Disperse Spectrophotometry (SEM)-EDS at various magnifications with C elements dominated by 44.88% and 60.56%. The concentration of COD and BOD adsorbed by the biochar at a temperature of 500°C was 32 mg/L and 26.6 ml/L. Adsorption of COD and BOD at various weights indicates that increasing the weight of biochar and the contact time will reduce the concentration of COD and BOD

in the wastewater.

The process of making ABCS greatly influences the surface (pore) condition of the product. The pyrolysis temperature and the type of furnace used also affect the quality of the biochar. A furnace modification can be done to see the difference in ABCS produced. The activation also affects pore size. ABCS is a form of charcoal that has been started with open pores morphology. Its absorption power is high—ABCS functions as a filter to reduce COD and BOD in wastewater. Temperature is a crucial parameter in the preparation of biochar. The utilization of other agricultural waste as biochar and analysis of biochar's pore morphology produced at temperatures of 500°C and 600°C needs to be done.

Furthermore, its adsorption power to metal ions measurement is also needed. Because the corn plant consists of cob fruit and leaved, it is essential to carry out further research to make activated biochar leaves and test its adsorption power against COD and BOD or as an adsorbent of heavy metal. Activated biochar is a source of carbon, an alternative energy source that can be used for multiple fields of application.

ACKNOWLEDGMENT

The research support by the grant from the Postgraduate Studies, Tadulako University.

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