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The Conversion of Sorghum (Sorghum bicolor (L.) Moench) Stem Waste into Activated Carbon by the Pyrolysis Method Using $ZnCl_2$ Activator

Natasya Dian Andini[1,2], Yuliana Prasetiyani[1,2], Fisafillah Al Mumtahinah[1,2], Bintari Astika and Cornelius Satria Yudha[2,*]

[1]*Chemical Engineering Department, Vocational School, Sebelas Maret University*
Jl. Colonel Sutarto no 150 K, Surakarta 57126
[2]*Center of Excellence for Science and Technology for Electrical Energy Storage Technology, UNS*
Jl. Slamet Riyadi no 435, Surakarta 57146

[*]Corresponding Authors: corneliussyudha@staff.uns.ac.id

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ABSTRACT. The use of activated carbon in Indonesia is expanding along with the increasing demand for activated carbon. Therefore, it is necessary to continue to search for raw materials and methods for producing activated carbon to produce high-quality activated carbon. Sorghum stalk (Sorghum bicolor (L.) Moench) is used as a new precursor for the formation of activated carbon by utilizing a $ZnCl_2$ activator followed by pyrolysis in a furnace with a temperature of 800°C. This study aims to determine the effect of drying and the concentration of activator agents on activated carbon production. The $ZnCl_2$ activator concentrations used were 15% and 30%. The results showed that the activated carbon obtained through the withdrawal process with a $ZnCl_2$ concentration of 30% had the highest carbon content, namely 100%. Test results with FTIR spectroscopy showed that the activated carbon samples had groups (C-H), (O-H), (C≡C), (C=O), (C=C), and (C-O). In addition, the SEM test results showed that the surface of the activated carbon formed had many pores. With the presence of activated carbon from sorghum stem waste, it is hoped that this product can reduce the contaminants contained in wastewater.

1. INTRODUCTION

Activated carbon is a solid material with pores containing approximately 90-99% carbon compounds. Activated carbon is widely used in separation processes, gas purification, cooling, electrocatalysts food and beverages, pharmaceutical, and water purification industries. Activated carbon is a very effective adsorbent for many harmful organic and inorganic species. Activated carbon is usually made from carbon-based materials, such as coal, lignin, lignocellulosic materials, synthetic polymers, and carbon waste.[1]. Various renewable raw materials have been used as activated carbon precursors in the last decade. The most important new resource is agricultural residues, especially non-food or non-feed by-product materials, available at very low prices or is invaluable in many cases. In addition, converting agricultural residues into carbon-containing materials reduces CO_2 accumulation in the atmosphere, eliminates agricultural residues, and helps to mitigate climate change.

Several previous studies have used lignocellulosic biomass of various types as a raw material for activated carbon for multiple applications with various activators. Some of them are pomegranate peel for the adsorption of Remazol brilliant blue-R (RBBR), with an optimum adsorption value of 94.36% [2], cassava peel waste for crystal violet adsorption [3], apple peel waste for adsorption of methyl red [4], and bagasse waste for basic violet 10 cationic adsorption [5]. Another raw material that is also used is kenaf (Hibiscus cannabinus, L) with H_3PO_4 activator [6] and mango seeds with 40% H_3PO_4 activator for maximum adsorption of Cr (VI) of 7.8 mg/g [7]. Other activated carbon applications include fertilizers and plant media, supercapacitor materials, electrochemistry, and catalysts [8].

Sorghum plants have broad adaptability, are tolerant to drought, can produce on marginal land, and are relatively more resistant to pests and diseases, so they are suitable for development in dry climate areas [9]. Yields of sorghum seeds can average up to 4-5 tons/ha, and sorghum stalks around 15 tons/ha, which so far is still considered waste and has not been optimally utilized [10].The production of activated carbon from residues of sorghum stems, which are agricultural residues, is rarely used in the literature as activated carbon precursor.

Sorghum stalks are one of the agricultural wastes that contain lignocellulose, and their amount is the most widely available [11]... Therefore, sorghum stalk is a strong candidate precursor for the formation of activated carbon, which meets the requirements for industrial production.

This study aims to determine the process of making activated carbon from sorghum stem waste and the effect of drying and the concentration of activating agents in the manufacture of activated carbon. The $ZnCl_2$ activator concentration used was between 15% and 30%.. $ZnCl_2$ was chosen as an acidic activating agent for this method because this activator is better suited for lignocellulosic materials, such as sorghum stalks, compared to alkaline activators, such as KOH. Lignocellulosic material has a high oxygen content, and the acidic activator reacts with oxygen-containing functional groups. The use of $ZnCl_2$ also beneficial due to its recoverability and availability. Overall, the utilization of sorghum-based waste as activated carbon opens opportunity for various carbon technology without sacrificing the economic and environmental aspect of the preparation process [12].

2. MATERIALS AND METHODS

2.1 Materials and tools

The materials used were chopped sorghum stems, $ZnCl_2$ (Merck, Germany), HCl (Merck, Germany), distilled water, filter paper, and pH indicators. N_2 gas (PT Aneka Gas, Indonesia) was used as the inert gas during the pyrolysis of sorghum stalk. The equipment used in this study was a tubular furnace (MTI, USA), electric oven (MTI, USA), measuring cup, Erlenmeyer, glass funnel, desiccator, glass stirrer, filter, porcelain cup, digital balance.

2.2 Preparation of the activated carbon

The process of making activated carbon from sorghum stalk waste can be seen in Figure 1. Activated carbon is obtained through a pyrolysis process, namely a decomposition process carried out in the absence of oxygen or under inert gas conditions [13]. The first step in making activated carbon from waste sorghum stalks is to cut the stalks into small pieces. Then four samples of sorghum were prepared with a weight of 20 grams each. The samples were separated into two parts, namely, two samples with drying and two samples without drying. Samples with drying were dried in an oven for 2 hours at 50°C. After 2 hours, the samples were cooled in a desiccator for 15 minutes. The next step is to make a $ZnCl_2$ solution with a concentration between 15% and 30%. The preparation of 15% $ZnCl_2$ solution was carried out by dissolving 20 grams of $ZnCl_2$ in 113.33 mL of distilled water. Preparing a 30% $ZnCl_2$ solution is done by dissolving 20 grams of $ZnCl_2$ in 46.67 mL of distilled water. Furthermore, each sorghum sample was immersed in a $ZnCl_2$ solution with different concentrations for 2 hours. After 2 hours, each sorghum sample was filtered and then dried in an oven for two days at 80°C. The dried sorghum is then pyrolyzed at 800°C for 60 minutes to form carbon. After that, the carbon was washed with 1 N HCl. 1 N HCl was prepared by dissolving 20.72 mL of concentrated HCl with distilled water in a 250 mL volumetric flask. The acid-treated carbon was washed using distilled water until neutral pH of the filtrate was reached. Next, the carbon was dried in a vacuum oven overnight at 90°C. The activated carbon samples were ground and sieved using 100-mesh stainless steel filter. After drying, the formed carbon was ready to be characterized.

2.3. Activated carbon characterization

The functional group in the activated carbon was analyzed using Fourier Transformed Infra-Red spectroscopy or FTIR (IR-Spirit, Shimadzu) at the wavenumber range of 400-4000/cm. The morphology and elemental composition of the activated carbon is examined by Scanning Electron Microscope – Energy Dispersive X-Ray (SEM-EDX) spectroscopy (SEM, JCM7000, JEOL). The sample was undergoing Au-sputtering or coating prior to SEM-EDX analysis.

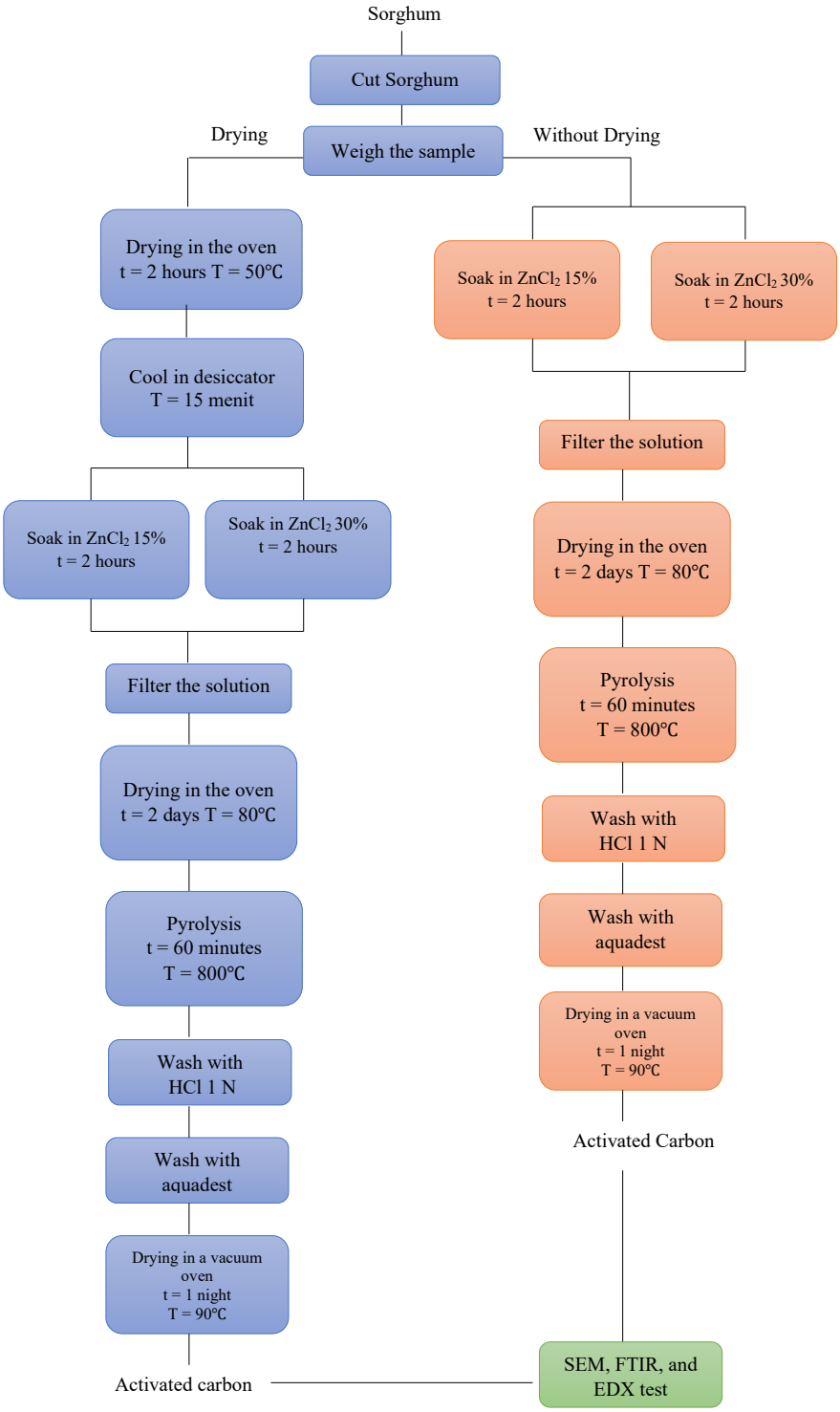

Figure 1. Activated Carbon Preparation from Sorghum Stems using $ZnCl_2$ as activator

3.1 RESULTS AND DISCUSSION

3.1 Activated Carbon Surface Morphology Analysis

Surface morphology analysis of activated carbon was carried out using a Scanning Electron Microscope (SEM) with 2500x magnification for each sample. The results obtained from the SEM analysis are shown in Figure 2.

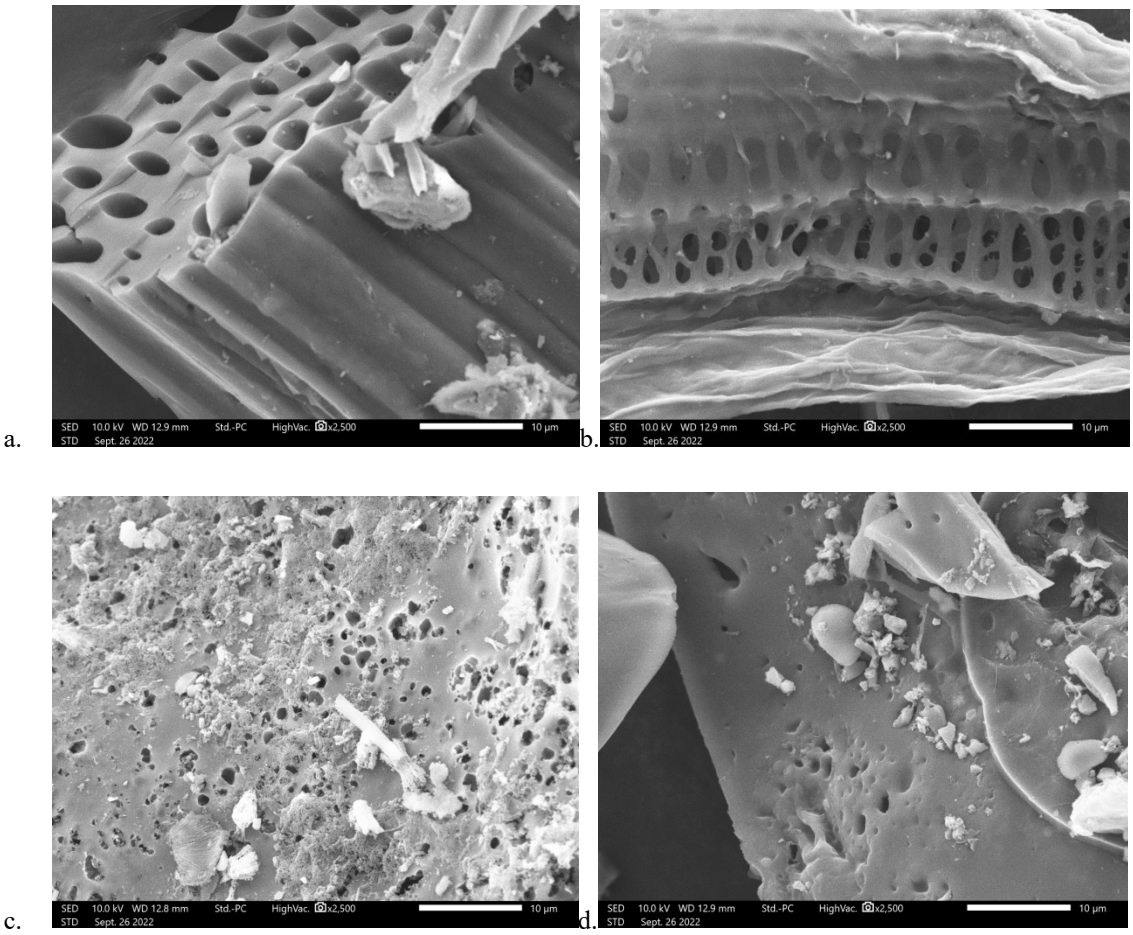

Figure 2. Results of Morphological Analysis Using SEM (a) Activated Carbon $ZnCl_2$ 15% Without Drying; (b) Activated Carbon $ZnCl_2$ 15% with Drying; (c) Activated Carbon $ZnCl_2$30% Without Drying; (d) Activated Carbon $ZnCl_2$ 30% with Drying

SEM analysis aimed to determine the differences in the pore surface shape of sorghum-activated carbon. The shape of the pore surface is one of the factors that play a role in the ability of an adsorbent to adsorb. The pores contained in activated charcoal can increase the ability to adsorb adsorbate because these pores are gaps that expand the surface area of activated charcoal [14]. The formation and enlargement of pores are due to the evaporation of degraded cellulose components. Reduction of the hydrocarbon compounds results in the surface of the activated carbon being seen more clearly. The activation process aims to enlarge the pore by breaking the hydrocarbon bonds or oxidizing the surface molecules so that the carbon undergoes a change; namely, the surface area increases and affects the adsorption power. The pore structure that is formed comes from the evaporation and dissolution of non-carbon compounds contained in the raw material caused by the pyrolysis process, which can leave some empty space that forms pores [15].

In Figure (a) Activated carbon $ZnCl_2$ 15% without drying, it can be seen that the activated carbon has various pore sizes and a large pore wall thickness. In Figure (b), Activated carbon $ZnCl_2$ 15% with drying has a more regular distribution of pores with large pore sizes and a large number of pores. Meanwhile in figure (c), Activated carbon $ZnCl_2$ 30% without drying, it appears that it has a smaller pore size with thick pore walls and a fairly even pore distribution. However, it can be seen that some of the pores are still covered by impurities. Meanwhile, in figure (d), Activated carbon $ZnCl_2$ 30% with drying has a small pore size and fewer pores than the other three samples. It can be predicted that viewer pores detected is the result of micropores formation. Sample with higher activating agent content has a tendency to form a smaller pore which also indicates the formation of large surface area. However, further analysis on surface area using surface area analyzer equipment is necessary to assure the exact pore size and surface area using BET Method[14]. This pore structure is closely related to carbon absorption, where the larger the pores, the surface area of activated carbon increases. The more pores on the surface of

activated carbon, the the more adsorption capacity is achieved [16]. Analysis using SAA is recommended for the future research.

3.2 Functional Group Analysis of Activated Carbon (contains FTIR analysis)

Functional group analysis of activated carbon was carried out using a tool called Fourier Transform Infrared Spectroscopy (FTIR) refined by 30 pts SG for each activated carbon sample. The results of the FTIR analysis obtained are shown in Figure 3.

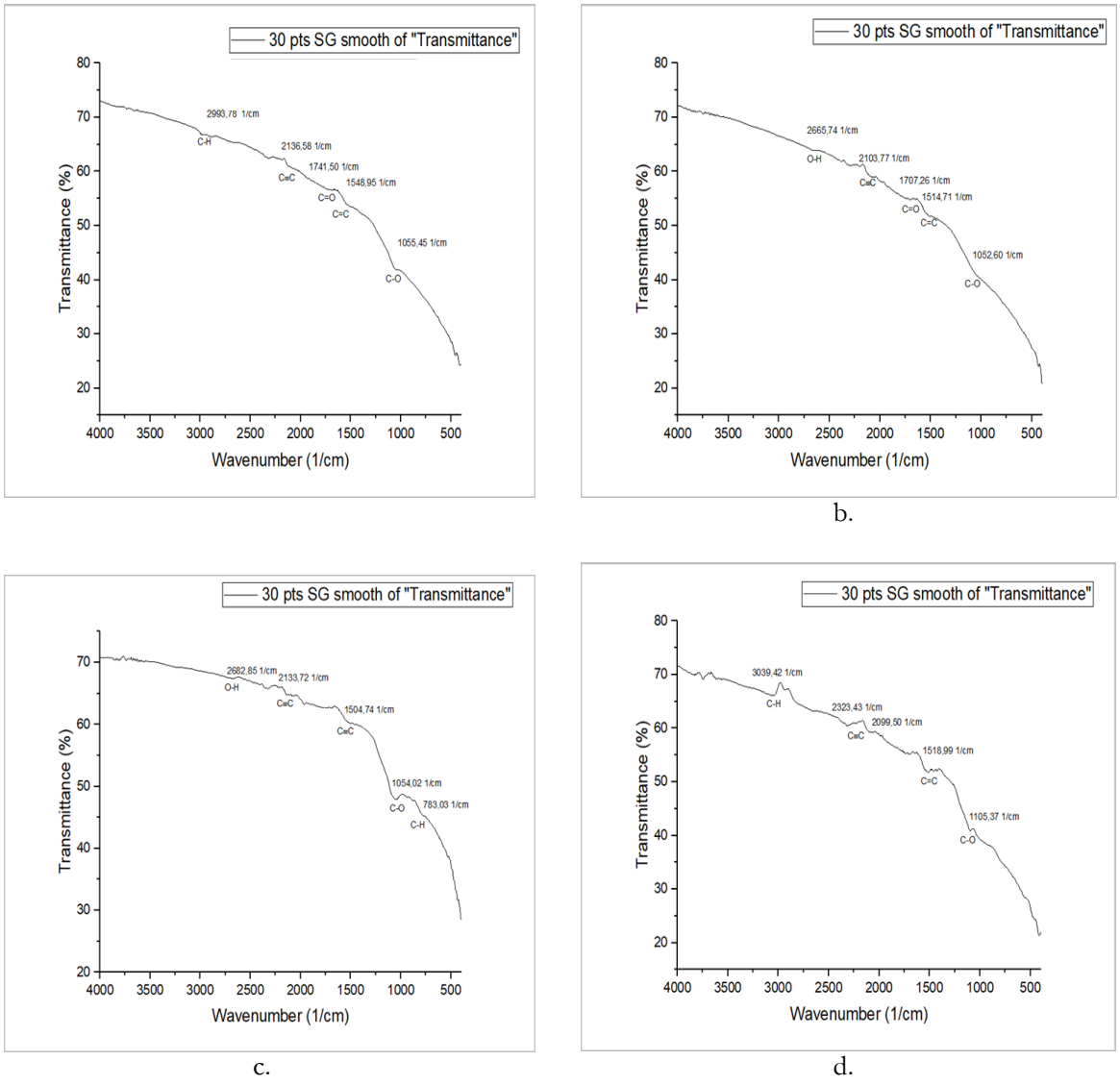

Figure 3. Results of analysis of functional groups of activated carbon using FTIR (a) Activated Carbon $ZnCl_2$ 15% Without Drying (b) Activated Carbon $ZnCl_2$15% with Drying (c) Activated Carbon $ZnCl_2$ 30% Without Drying (d) Activated Carbon $ZnCl_2$ 30% Drying, after washing with HCl solution.

Fourier Transform Infrared Spectroscopy (FTIR) is a method that observes the interaction of molecules with electromagnetic radiation that is in the wavelength region of 0.75 – 1,000 µm or at Wave Numbers 13,000 - 10 cm-1. Electromagnetic radiation was first put forward by James Clark Maxwell, who stated that light is physically an electromagnetic wave, meaning that it has an electric vector and a magnetic vector which are both perpendicular to the direction of propagation [15]. The infrared spectrum in FTIR is generated from the transmission of light passing through the sample, measured with a detector, and compared to the intensity without the sample as a function of wavelength. The infrared spectrum obtained is then plotted as the intensity of the energy function,

wavelength (μm), or wave number (cm-1) [18]. FTIR analysis aims to clarify the types of compounds contained in each sorghum sample.

Figure (a) sorghum stem carbon without 15% drying and figure (b) with 15% drying shows that there has been a change in the absorption band due to the $ZnCl_2$ activator so that a shift occurs based on the chemical environment. In Figure (a), activated carbon without 15% drying shows a peak in the absorption area of 2993.78 1/cm which is an alkane (C-H) group, whereas in Figure (b), with 15% drying, no alkane groups appear. However, in Figure (b), with 15% drying, there is a phenol group (O-H) in the absorption area of 2665.74 1/cm. In Figure (a) and Figure (b), the alkyne group (C≡C) also appears in the absorption area of 2136.58 1/cm and 2103.77 1/cm. Then, in Figure(a) and Figure(b) the aldehyde group (C=O) also appears in the absorption areas of 1741.50 1/cm and 1707.26 1/cm. In figure (a) and figure (b) aromatic ring clusters (C=C) also appear in the absorption areas of 1548.45 1/cm and 1514.71 1/cm. In addition, in figure (a) and figure (b) alcohol groups (C-O) also appear in the absorption areas of 1055.45 1/cm and 1052.60 1/cm. The main groups identified in figure (a) of sorghum stem carbon without 15% drying and figure (b) with 15% drying according to their spectra are (C-H), (O-H), (C≡C), (C=O), (C= C), and (C-O).

In figure (c) activated carbon without 30% drying shows a peak in the absorption area of 2682.85 1/cm which is a phenol (O-H) group, whereas in figure (d) with 30% drying no phenol groups appear. However, in figure (d) there is an aromatic ring group (C-H) in the absorption area of 3039.42 1/cm. In figure (c) the alkyne group (C≡C) also appears in the absorption area, namely 2133.72 1/cm, and in figure (d) there are two absorption areas, namely 2323.43 1/cm and 2099.50 l/cm. In figure (c) the aromatic ring group (C=C) also appears in the absorption area of 1504.74 1/cm, while in figure (d) it appears in the absorption area of 1518.99 1/cm. Then, in figure (c) and figure (d) the alcohol group (C-O) also appears in the absorption areas of 1054.02 1/cm and 1105.37 1/cm. In figure (c) there is also an alkene group (C-H) in the absorption area of 783.03 1/cm. The main groups identified in figure (c) activated carbon without 30% drying and (d) with 30% drying according to the spectrum are (C-H), (O-H), (C≡C), (C=C), and (C-O).

Characterization of activated carbon using FTIR showed that the functional groups detected in activated carbon at concentrations of 15% and 30% with or without drying were the (C-O) and (C≡C) groups. The (C-O) group indicates that the activated carbon produced tends to be more polar. Thus, the resulting activated carbon can be an adsorbent [16]. Meanwhile, the (C≡C) group proves that carbonization and activation into activated charcoal will increase aromatic compounds. These compounds are the constituents of the hexagonal structure of charcoal and activated charcoal[17].

3.3 Activated Carbon Material Composition Analysis

Energy Dispersive X-Ray (EDX) analysis of activated carbon from sorghum shows the elemental composition of the activated carbon.

Table 1. Sorghum activated carbon composition

Element	Without Drying				With Drying			
	Activated Carbon $ZnCl_2$ 15%		Activated Carbon $ZnCl_2$ 30%		Activated Carbon $ZnCl_2$ 15%		Activated Carbon $ZnCl_2$ 30%	
	Mass, %	Atoms, %	Mass, %	Atoms, %	Mass, %	Atoms, %	Mass, %	Atoms, %
C	85.56	94.21	67.53	85.25	94.64	98.12	100.00	100.00
Si	4.10	1.93	7.75	4.18	-	-	-	-
Cl	10.34	3.86	24.72	10.57	5.36	1.88	-	-

Table 1 shows that the carbon atoms contained in 30% $ZnCl_2$ activated carbon with the drying process have the highest percentage, namely 100%. At the same time, the smallest carbon content is in 30% $ZnCl_2$ activated carbon without a drying process. Carbon elements dominate the elemental content of activated carbon. The presence of elements contained in activated carbon in the form of Si and Cl is due to the washing process using HCl, the inorganic substances contained in activated carbon have not been completely dissolved. 30% $ZnCl_2$ activated carbon with the drying process only contains carbon elements. This is because the EDX analysis can only scan the surface of activated carbon exposed to X-Ray light, so the overall elemental composition contained in activated carbon is unknown.

3.4. Adsorption of Co ions

Based on FTIR and SEM-EDX data, we can conclude that carbon with the best characteristic is exhibited by Activated Carbon 15/30% with drying samples. The samples were used as adsorbent of 7.7 ppm Co^{2+} containing solution. The batch adsorption were conducted under room temperature and adsorbent to Co^{2+} solution ratio of 1 g : 300 ml. Atomic Adsorption Spectroscopy or AAS was used to detect the concentration of cobalt (II) after being adsorbed using activated carbon from sorghum with a 15% and 30% concentration of $ZnCl_2$ activator. Based on the research results using the AAS instrument, it can be expressed through the relationship between the concentration of heavy metal cobalt (II) (Co(II)) in Cobalt Sulfate solution ($CoSO_4.7H_2O$) and adsorption time as shown in Table 2 and Figure 4. After 1 hour, the adsorption efficiency of Co^{2+} ion for Activated Carbon $ZnCl_2$ 15% and Activated Carbon $ZnCl_2$ 30% are 95.75% and 96.28%, respectively. Based on this findings, activated carbon is successfully synthesized using $ZnCl_2$ and sorghum stalks as the activating agent and carbon source, respectively. Since the behavior is almost identical, a concentration of 15% is preferred.

Tabel 3. Co^{2+} adsorption behaviour of activated carbon samples

Time (min)	Co^{2+} concentration (ppm)	
	Activated Carbon $ZnCl_2$ 15% with drying	Activated carbon $ZnCl_2$ 30% without drying
0	7.714286	7.714286
5	3.414575	2.500965
10	1.072635	0.609073
20	0.517616	0.363900
30	0.454875	0.360039
40	0.444015	0.351351
50	0.363176	0.340734
60	0.328185	0.286680

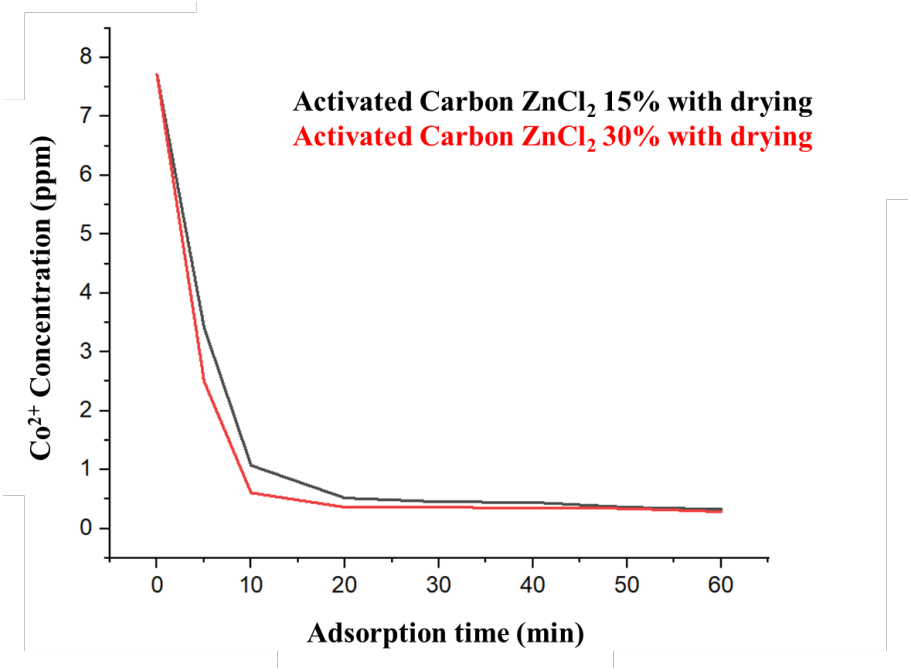

Figure 4. Adsorption behavior of Co^{2+} ion on the activated carbon samples

4. CONCLUSION

The results obtained from the study showed that 30% $ZnCl_2$ activated carbon obtained by the drying process had the highest carbon content compared to other samples, namely as much as 100%. Test results with FTIR spectroscopy showed that the activated carbon samples had groups (C-H), (O-H), (C≡C), (C=O), (C=C), and (C-O). This group will play an important role in the adsorption process, making the activated carbon surface more chemically reactive and affecting the adsorption properties. In addition, the SEM test results showed that the surface of the activated carbon formed had many pores. The pores contained in activated carbon can increase the ability to adsorb adsorbate because these pores are gaps that expand the surface of activated carbon. Based on the adsorption performance, the best activated carbon is obtained from pre-dried sorghum stalks using 15% of $ZnCl_2$ as activating agent.

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