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Research Article

Synthesis of Carbon from Rice Groats at Various Pyrolysis Temperatures and Its Application for the Recovery of Chromium Wastewater from the Tannery Industry

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Abstract: The research on synthesis of carbon from rice groats at various pyrolysis temperatures and its application for the recovery of chromium wastewater from the tannery industry by varying pyrolysis temperatures at 300, 400, and 500 °C. The results of carbon synthesis are analyzed in the form of determination of yield, water content, ash content, and iodine number. The best pyrolysis condition with the quality requirement of carbon is at a pyrolysis temperature of 500 °C with 760 $mg.g^{-1}$ (iodine number). Adsorption kinetics was also carried out to determine the adsorption kinetics of chromium ions from tannery wastewater. Adsorption kinetics model of chromium wastewater from the tannery industry corresponds to the pseudo-second-order kinetics model with R^2 is 0.9857, k_2 is 0.0093 $g.mg^{-1}.min^{-1}$, and qe is 28.5714 $mg.g^{-1}$.

Keywords: Pirolysis, carbon, rice groat, chromium, tannery industry

Introduction

Activated carbon is a carbon that has good absorption ability against anions, cation, and molecules in the form of organic and inorganic compounds, both in the form of solutions and gases [1,2]. Activated carbon consists of a variety of minerals that are distinguished based on their adsorption ability and characteristics. Some materials that contain a lot of carbon and especially those that have pores can be used as raw materials to make activated carbon [3, 4, 5].

Industrial progress in Indonesia is growing very rapidly at this time, this can certainly boost the economy in Indonesia, especially the world industry has entered the industrial revolution 4.0. In every industry there must always be product failures that can actually be utilized for other industries. For example, in the agricultural sector, rice that is damaged or even unfit for food is still widely sold in Indonesia. Rice like this usually does not pass the quality control process so it is cheap. However, rice that is not food worthy (rice groats) can be used into other products such as carbon.

Rice is dominated by starch (about 80-85%). Rice also contains protein, vitamins (especially in the aleuron), minerals, and water [6,7]. Rice starch is composed of two carbohydrate polymers, namely amylose is a starch with a non-branching structure and amylopectin which is starch with a branching structure and tends to be sticky [8,9,10].

The synthesis of carbon is usually through the process of pyrolysis which is the process of chemical decomposition of substances or biomass where heating is carried out in the absence of oxidizing agents

[11,12,13,14]. Pyrolysis is commonly used for organic compounds. Pyrolysis process occurs mass reduction due to the release of H_2, CH_4, H_2O, CO and CO_2 gases [15,16,17,18]. In this research, carbon synthesis from rice groats will be carried out with pyrolysis temperature variations to determine the temperature effect of the characteristics of carbon (yield, water content, ash content, and iodine number). The tannery industry usually produces chromium waste from the tanning process [19]. The process usually uses chromium salts such as $CrSO_4$ [19,20]. If the waste is not treated, it can have a negative impact on the environment and health [21]. Therefore, this research will also carry out the application of the use of synthesized carbon to reduce the chromium content of wastewater from the tannery industry and study its kinetics.

Materials and Methods

Materials

The chemicals used in this research are rice is not suitable for consumption (menir), I_2 (0.1 N), amylase, sodium thiosulfate, aquadest, and chemicals others that are in accordance with work procedures.

Synthesis of Carbon from Rice Groats

The first process is to separate dirt (gravel, lime, plastic, or other objects) from rice that will make the process of making carbon inhibited. Then the rice is burned in the furnace at 300, 400, and 500 °C for 5 hours. Furthermore, the pyrolysis results are referred to as carbon A, B, and C respectively. Carbon is removed and cooled to be calculated and analyzed yield,water content, ash content, and absorption of I_2 solution (iodine number) (eq. 1-4).

Calculation of yield:

$$\text{Yield (\%)} = \frac{\text{mass of activated carbon}}{\text{mass of sample}} \times 100\% \tag{1}$$

Calculation of water content:

$$\text{Water content (\%)} = \frac{A-B}{A} \times 100\% \tag{2}$$

A: Weight of carbon before heating 103±2 °C

B: Weight of carbon after heating 103±2 °C

Calculation of ash content:

Heating a carbon sample of 800 °C for 2 hours.

$$\text{Ash content(\%)} = \frac{\text{Mass of ash}}{\text{Mass of activated carbon}} \times 100\% \tag{3}$$

Calculation of absorption of I_2:

A sample of 0.25 grams of carbon was soaked in a 25 mL Iodine (I_2) solution of 0.1 N then sorted for 15 minutes. Then the filtered mixture and filtrate is taken 10 mL then titrated with sodium thiosulfate 0.1 N, if the yellow color in the solution is faint, added a 1% amylase solution to the solution as an indicator. The solution is retitred with the dark blue color gone.

$$\text{Iod number } \left(\frac{\text{mg}}{\text{g}}\right) = \frac{V_{thio}\ (\text{mL}) \times N_{thio} \left(\frac{\text{meK}}{\text{mL}}\right)}{\text{mass of sample (g)}} \tag{4}$$

Adsorption kinetic study of chromium using the carbon

Adsorption kinetics studies were carried out by adding 1.0 gram of carbon (adsorbent) to chromium wastewater from a tannery industry (the initial concentration of chromium was analyzed by Atomic Absobtion Spectrophotometer (AAS)). The mixture was stirred at 200 rpm with variations in contact time (0, 10, 20, 30, 40, 50, and 60 minutes) at pH 5 and room temperature (±28 °C). The filtrate was then analyzed with AAS.

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Results and Discussions

Based on Table 1, carbon produced from synthesis through pyrolysis process in the form of powder then the requirements that must be met are maximum water content of 15%, ash content of 10%, absorption of solution I_2 at least 750 mg/g, and carbon (yield) at least 65%. The process of pyrolysis carried out to make carbon from rice that is not suitable for consumption occurs at variations in pyrolysis temperature. The temperature variation is done to find out its effect on the results of carbon synthesized.

Table 1. Active Carbon Quality Requirements (SNI. 06-3730-1995)

No.	Description	Unit	Requirement	
			Grain	**Powder**
1	The missing part of the heating 500 °C	%	Max 15	Max 25
2	Water content	%	Max 4.5	Max 15
3	Ash content	%	Max 2.5	Max 10
4	Iodine number	mg/gram	Min 750	Min 750
5	Absorption of Pure carbon I_2	%	Min 80	Min 65

Table 2. Data from carbon powder analysis from synthesis

No.	Description	Unit	Pirolysis temperature (°C)		
			300	**400**	**500**
1	Yied	%	85.3	79.0	76.5
2	Water content	%	14.3	9.4	7.7
3	Ash content	%	9.1	7.3	4.9
4	Iodine number	mg/gram	605	710	760

Based on Table 2 it is known that the yield or level of carbon produced through pyrolysis at a temperature of 300 °C has the highest carbon content of 85.3%. The higher the pyrolysis temperature, the less carbon is produced. At low temperatures there are still many organic compounds and other impurities that are not fully evaporated so that it will increase the weight (mass) of the carbon produced.

The water content produced at a pyrolysis temperature of 300 °C has the highest water content. This is because at a high pyrolysis temperature will be able to stretch the sample and make the sample small, so that the water will be liberated easily after the sample is well-affected and the surface area becomes large after experiencing pyrolysis at a high temperature. Wystalska and Kwarciak-Kozlowska (2021) found that the higher pyrolysis temperature will make the surface area of the sample greater [22].

Ash content in carbon resulting from pyrolysis of 300 °C have the highest ash levels. At low temperatures there are still many inorganic compounds that are not fully prepared so that it will increase the ash content in the sample. Absorption of solution I_2 indicates that the carbon resulting from pyrolysis at a temperature of 500 °C has the highest absorption and in accordance with the quality requirement of carbon which is 760 mg/g. The absorption of the I_2 solution indicates the number of microporous structures formed in carbon. The higher the pyrolysis temperature, the more active carbon pores are formed. So that the higher the pyrolysis temperature will increase the specific surface area of carbon [23]. Based on the three pyrolysis temperatures it is known that only at a pyrolysis temperature of 500 °C is able to produce absorption against I_2 solution in accordance with the quality requirement of carbon which is at least 750 mg/g.

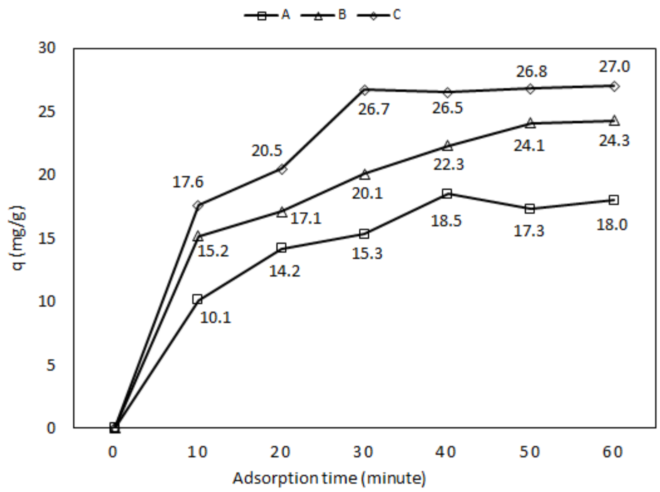

Figure 1. Adsorption of chromium wastewater using different types of carbon at pH 5 and room temperature.

Synthesized carbon with variations in the pyrolysis temperature (carbon A=300 °C, B=400 °C, C=500 °C) was then carried out by adsorption of chromium wastewater with the conditions according to Figure 1. Based on Figure 1, it is known that carbon synthesized at a pyrolysis temperature of 500 °C (Carbon C) is able to adsorb 26.7 $mg.g^{-1}$ of chromium in wastewater (optimum conditions) at 30 minutes. After 30 minutes, the adsorption was in equilibrium because the chromium adsorption did not increase significantly. This is because at the time of adsorption equilibrium, the adsorbate that has been adsorbed will be desorbed simultaneously with a constant value [24]. Carbon C was determined for its adsorption kinetics with variations in adsorption time (0, 10, 20, 30, 40, 50, and 60 minutes) to determine the adsorption kinetics. The kinetic models used in the adsorption of chromium wastewater from the tannery industry are pseudo-first-order, pseudo-second-order and intra-particle diffusion (eq. 5-11) [25,26].

Pseudo-first-order:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{5}$$

$$\log(q_e - q_t) \text{ vs } t \tag{6}$$

Pseudo-second-order:

$$q_t = \frac{q_e^2 k_2 t}{1 + k_2 q_e t} \tag{7}$$

$$\frac{t}{q_t} = \frac{1}{q_e}t + \frac{1}{h} = \frac{1}{q_e}t + \frac{1}{k_2 q_e^2} \tag{8}$$

$$\frac{t}{q_t} \text{ vs } t \tag{9}$$

Intra-particle diffusion:

$$q_t = k_3 t^{1/2} + c \tag{10}$$

$$q_t \text{ vs } t^{1/2} \tag{11}$$

Where q_e and q_t amount of adsorbate adsorbed at equilibrium and time t ($mg.g^{-1}$). k_1 is the pseudo-first-order rate constant (min^{-1}). k_2 is the pseudo-second-order rate constant ($g.mg^{-1}.min^{-1}$). K_3 is intra-particle diffusion rate constant ($mg.g^{-1}.min^{-1}$).

Tabel 3. Adsorption kinetic models for adsorption chromium wastewater using carbon as adsorbent.

No.	Adsorption kinetic models	Parameter			
		R^2	k	qe	h
1.	Pseudo-first-order	0.6612	-0.0633 min^{-1}	15.0812 $mg.g^{-1}$	-
2.	Pseudo-second-order	0.9857	0.0093 $g.mg^{-1}.min^{-1}$	28.5714 $mg.g^{-1}$	7.6219 $mg.g^{-1}.min^{-1}$
3.	Intra-particle diffusion	0.9055	3.5341 $mg.g^{-1}.min^{-1/2}$	-	-

Based on Table 3 it is known that the adsorption kinetics model of chromium wastewater from the tannery industry corresponds to the pseudo-second-order kinetics model. The R^2 value of the pseudo-second-order is close to 1, which is 0.9857, 0.0093 $g.mg^{-1}.min^{-1}$ for the rate constant and 28.5714 $mg.g^{-1}$ for the adsorption capacity at the equilibrium. It can be assumed that the adsorption process of chromium wastewater from the tannery industry occurs through chemical interactions. This is due to the presence of functional groups on carbon which is synthesized at a temperature of 500 °C. This could be due to the interaction of the positive charge of the metal ion with the functional group of the adsorbent [27].

Conclusion

Based on the results of the study, it can be concluded that pyrolysis temperature affects the characteristic results of the carbon synthesized. Pyrolysis temperature of 500 °C is the best temperature for the synthesis of carbon from rice groats in accordance with the quality requirements of carbon. The yield of carbon yield of pyrolysis at a temperature of 500 °C is 76.5%, water content is 7.7%, ash content is 4.9%, and iodine number is 760 $mg.g^{-1}$. Adsorption equilibrium time occurs at t=30 minutes. Adsorption kinetics model of chromium wastewater from the tannery industry corresponds to the pseudo-second-order kinetics model with R^2 is 0.9857, k_2 is 0.0093 $g.mg^{-1}.min^{-1}$, and q_e is 28.5714 $mg.g^{-1}$.

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