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Water Quality

# Application of Eco-Friendly Activated Carbon from Organic Waste for Polluted River Water Treatment: Kinetic Study and Water Quality Evaluation

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# ABSTRACT

River water pollution in Cilacap Regency is caused by industrial activities related to oil refining and river crossing traffic, which generate wastewater containing Total Suspended Solids (TSS), Total Dissolved Solids (TDS), Biological Oxygen Demand (BOD), Chemical Oxygen Demand (COD), and heavy metals such as lead. This study aims to evaluate the performance of biomass-based activated carbon-derived from coconut fronds and laban wood sawdust-in river water purification through physicochemical characterization and adsorption kinetics approaches. The activated carbon was characterized according to the Indonesian National Standard (SNI) 06-3730-1995, and its surface area was analyzed using the Brunauer-Emmett-Teller (BET) method. Characterization results for AC-PK 1(100) showed a moisture content of 0.1085%, ash content of 3.05%, iodine adsorption capacity of 571 mg/g, and a surface area of 110.595 m<sup>2</sup>/g. The adsorption process after 15 minutes demonstrated that the activated carbon was effective in reducing water quality parameters, with the pH reaching neutral (7) and TSS decreasing to 212 mg/L, meeting Class III standards based on Government Regulation No. 82 of 2001. However, the TDS value of 4690 mg/L did not meet the quality standard. Kinetic studies indicated that the first-order reaction model best described the adsorption mechanism, with R<sup>2</sup> values approaching 1. The adsorption rate constants were 0.0041 min<sup>-1</sup> for TSS and 0.0686 min<sup>-1</sup> for TDS. These findings suggest the potential application of biomass waste as a raw material for activated carbon in environmentally friendly river water purification technologies.

# 1. INTRODUCTION

A river is a natural water body that stores water and has a network of channels extending from its source to its mouth. The direction of river flow, from upstream to downstream, is determined by the slope of the riverbed and the force of Earth's gravity [1]. According to data from the Ministry of Environment in 2014, approximately 70–75% of rivers in Indonesia have been polluted [2]. One example is the Donan estuary river located in Cilacap Regency, where water pollution is caused by oil refining industry activities and ferry crossing routes. Previous studies have shown that the waters of the Donan estuary contain an average Total Suspended Solids (TSS) level of 301 mg/L, an

average Total Dissolved Solids (TDS) level of 24,713 mg/L, a Biological Oxygen Demand (BOD) of 3.679 mg/L, a Chemical Oxygen Demand (COD) of 31 mg/L, and a lead (Pb) concentration of 0.0418 mg/L. These conditions do not meet Class III water quality standards as stipulated in Government Regulation No. 82 of 2001 [3]. One method that can be used to reduce pollutant levels to meet the required standards is the adsorption method. This process involves the accumulation of dissolved substances in a solution onto the surface of an adsorbing material, known as adsorption. The use of additional absorbent materials with porous structures to trap contaminants is a key part of this process. Due to its large surface area of pores, activated carbon is highly effective as an adsorbent [4]. Activated carbon also has a large specific surface area, is tasteless, non-toxic, renewable, and possesses low adsorption energy [5].

Wood chips, wood shavings, and sawdust are waste products from the wood industry that have the potential to pollute water bodies [6]. Sawdust, which is rich in carbon, can serve as an effective pollutant adsorbent. However, the utilization and management of sawdust waste in several industries remain limited. The potential of sawdust as a source of activated carbon lies in its lignin, cellulose, and hemicellulose content. In addition, coconut fronds contain 31.95% cellulose and 73.49% holocellulose, which are higher than other parts such as coconut fiber and husk [7]. This activated carbon can be used as an adsorbent to capture heavy metals such as Mn, Fe, Co, Cu, Zn, Ni, and others.

Phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) solutions at concentrations of 1 M and 2 M can be used in the chemical activation process to activate carbon from coconut fronds and laban wood sawdust. Subsequently, characterization of the activated carbon is conducted, along with adsorption applications for pollutants in water samples from the Donan estuary river, with attention to adsorption kinetics. The aim of this study is to characterize the activated carbon, including a maximum moisture content of 15%, a maximum ash content of 10%, and an iodine adsorption capacity of at least 750 mg/L, in accordance with the Indonesian National Standard (SNI 06-3730-1995). The study also seeks to determine the surface area of the activated carbon pores and the adsorption kinetics of Donan estuary river water samples based on reaction order values approaching 1 (first-order kinetics).

# 2. LITERATURE REVIEW

#### 2.1. Activated Carbon

Activated carbon is widely known as an effective adsorbent in water purification due to its ability to adsorb various contaminants. However, the use of commercial activated carbon is often limited by high production costs and raw material availability. As an alternative, biomass from agricultural and forestry waste has been explored as a raw material for activated carbon production. A study by Rofikoh et al. showed that biomass-based activated carbon is effective in removing heavy metals from wastewater, achieving removal efficiencies of 84–99% for Pb<sup>2+</sup> and 55–92% for Cd<sup>2+</sup> ions [8]. Moreover, utilizing biomass waste for activated carbon production supports circular economy principles and sustainable waste management practices.

# 2.2. Chemical Activation and Characteristics of Activated Carbon

Chemical activation, particularly using phosphoric acid (H<sub>3</sub>PO<sub>4</sub>), has been proven to enhance the porosity and surface area of activated carbon, contributing to higher adsorption capacity. Chemically activated carbon derived from biomass showed high adsorption capacity for Fe(III) and Mn(II) ions in aqueous solutions. Key characteristics such as moisture content, ash content, and iodine adsorption capacity are critical in evaluating activated carbon quality. Activated carbon with low moisture and ash content and high iodine value indicates good quality, meeting the Indonesian National Standard (SNI) 06-3730-1995) [9].

# 3. Adsorption Kinetics and Water Purification Efficiency

Understanding adsorption kinetics is essential for optimizing the water purification process using activated carbon. First- and second-order kinetic models are commonly used to describe adsorption mechanisms. A study demonstrated that biosorbents derived from *Phragmites australis* followed a pseudo-secondorder kinetic model with an R<sup>2</sup> value of 0.984, indicating high efficiency in removing COD, BOD, TSS, and TDS from wastewater [9]. Furthermore, its emphasized the importance of the surface area of activated carbon, where materials with larger surface areas exhibited superior adsorption performance in water treatment applications.

## 4. METHODOLOGY

The methodological stages of this study consist of a series of steps beginning with carbonization, carbon activation, activated carbon characterization, surface area analysis of the activated carbon, and application of the activated carbon to water samples from the Donan estuary river. The equipment used in this research includes an analytical balance, furnace, oven, desiccator, magnetic stirrer, hot plate, beaker glass, funnel, filter paper, and crucibles. The materials used include coconut fronds, laban wood sawdust, H<sub>3</sub>PO<sub>4</sub>, distilled water, 0.1N sodium thiosulfate solution, 1% starch solution, 0.1N iodine solution, and water samples from the Donan estuary river.

The characterization tests of the activated carbon involve measuring moisture content, ash content, and iodine adsorption capacity. Furthermore, the surface area of the activated carbon is analyzed using the Brunauer, Emmett, and Teller (BET) method at the Integrated Laboratory of Universitas Pembangunan Nasional Veteran Yogyakarta. In addition, the adsorption kinetics test for the Donan estuary river water sample includes parameters such as Total Suspended Solids (TSS) and Total Dissolved Solids (TDS), analyzed based on reaction order. The detailed methodological steps are as follows:

#### 4.1. Stages of Carbon Production

The raw materials, namely coconut fronds and laban wood sawdust, are burned in a furnace at a temperature of 350°C for 1.5 hours to produce charcoal. The charcoal is then crushed and ground using a porcelain mortar and pestle, and sieved using a 100 mesh sieve. The carbon yield (%) can be calculated using the following formula:

$$Yield (\%) = \frac{Weight of activated carbon (W2)}{Initial weight of the raw material (W1)} x100$$

#### 4.2. Stages of Chemical Activation of Carbon

Next, 40 grams of carbon from coconut fronds and laban wood sawdust are soaked in 500 mL of  $H_3PO_4$  solution with concentrations of 1 M and 2 M for 24 hours. Afterward, the resulting carbon paste is filtered using distilled water until the pH

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returns to neutral. The activated carbon is then dried in an oven at 110°C until the weight of the activated carbon stabilizes.

# 4.3. Stages of Characterization of Activated Carbon

Next, 1 gram of activated carbon (W1) is weighed and then dried in an oven for 1 hour at 115°C, after which it is placed in a desiccator for 15 minutes. The weight of the dried activated carbon (W2) is then measured, and the drying process is repeated until the weight of the activated carbon becomes constant.

The moisture content is calculated based on the Indonesian National Standard (SNI) for activated charcoal 06-3730-1995 as follows:

Moisture content (%) =  $(W1 - W2)/W1 \times 100$ 

where:

W1 = Initial weight of the activated carbon before drying (grams) W2 = Weight of the activated carbon after drying (grams)

Two grams of activated carbon are weighed in a crucible, heated for 2 hours in a furnace at 800°C, and then the remaining ash is cooled in a desiccator for 15 minutes. The weight is measured until it becomes constant.

The ash content is calculated using the following formula [10]:

Ash content (%) = 
$$\frac{W1 - W2}{weight sample} x100$$

Where:

W1 = Initial weight of the activated carbon before heating

W2 = Weight of the activated carbon after heating and cooling (remaining ash)

Sample weight = The initial weight of the sample before the heating process

Next, 0.5 grams of activated carbon are heated for 1 hour at 115°C. Then, 50 mL of 0.1 N iodine solution is added to the activated carbon in an Erlenmeyer flask. The mixture is stirred using a magnetic stirrer at 150 rpm for 15 minutes before being placed in a centrifuge tube. Next, 10 mL of the 0.1 N iodine solution is taken and transferred to an Erlenmeyer flask to be titrated using 0.1 N Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution until the color almost fades. Then, 1% starch solution is added as an indicator. The titration continues until the blue color disappears, and the volume of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution used is recorded.

The iodine number [10] is calculated using the following formula:

$$Iodin \ \left(\frac{mg}{g}\right) = 10 - (VxN(Na_2 S_2 O_3)/0, 1)x12, 69x5/w$$

where:

V	=	Volume of $Na_2S_2O_3$ solution used in	
		the titration (mL)	

$$N = Normality of Na_2S_2O_3 solution (0.1 N)$$

10 = Volume fitrat iod yang dititrasi dengan $Na_2S_2O_3 (mL)$ 

 $\begin{array}{rl} 12{,}69 & = & \mbox{The amount of iodine per 1 mL of 0.1} \\ & & \mbox{N} \mbox{N} \mbox{a} \mbox{S}_2 \mbox{O}_3 \mbox{ solution} \end{array}$ 

# 4.4. Stages of Pore Surface Area Testing of H<sub>3</sub>PO<sub>4</sub> Activated Carbon

The pore surface area of activated carbon is tested using a surface area analyzer with the BET method (Brunauer-Emmett-Teller method).

# 4.5. Stages of Activated Carbon Application in River Water Purification Process

A 2000 mL river water sample is poured into a beaker, and then 2 grams of activated carbon are added. The mixture is stirred using a magnetic stirrer at a stirring speed of 200 rpm for varying contact times of 3, 6, 9, 12, and 15 minutes until it is thoroughly mixed. River water samples are taken every minute to test the parameters of TDS and TSS. Then, the adsorption kinetics are calculated based on the time function for each TDS and TSS parameter in the river water samples.

# 5. RESULT AND DISCUSSION

The yield of carbon from coconut fronds and laban wood powder was obtained at 28.95% and 21.55%, respectively. The breakdown of the lignocellulosic structure due to the combustion process on these materials results in the carbon chains breaking into more complex compounds, which in turn causes the carbon pores to expand. The formation of pores in the carbon occurs because of the release of complex compounds in the gas phase. The carbonization process produces solid materials that remain in the carbon, causing the carbon pores to become narrower. Therefore, a carbon activation process is needed to optimize its performance [11]. In this process, phosphoric acid ( $H_3PO_4$ ) solution with concentrations of 1M and 2M is used as an activating agent. Activated carbon is essential to improve the effectiveness of adsorbate absorption. The purpose of this process is to increase and expand the pores within the carbon [12].

## 5.1. Characterization Test of Activated Carbon

The characterization analysis of activated carbon derived from coconut fronds and laban wood powder is conducted by measuring the moisture content, ash content, and iodine absorption capacity. Meanwhile, the surface area analysis of the activated carbon is performed using the Brunauer, Emmett, and Teller (BET) method. Below is Table 1 showing the results of the characterization of the activated carbon.

Sample	Moisture content (%)	Standard quality of moisture content * (%)	Ash content (%)	Standard quality of Ash content * (%)	Iodine absorption capacity (mg/g)	Standard quality of Iodine absorption capacity* (mg/g)	Surface area of activated carbon (m²/g)
KA-PK 1 M	0,11	Max 15	3,05	Max 10	571,1	Min 750	110.595
KA-SK 2 M	0,05	Max 15	2,55	Max 10	380,1	Min 750	35.574

Table 1 shows the moisture content and ash content of the activated carbon samples that meet the SNI quality standards [10]. The decrease in moisture content in the samples is influenced by the increase in temperature. The phase change of water in the activated carbon to water vapor requires a temperature of 100°C, which is its boiling point. As the carbonization temperature increases, the amount of water vapor produced also increases, causing the moisture content in the samples to decrease [13]. In addition, the moisture content can also be affected by the hygroscopic properties of the activated carbon can be analyzed through the ash content [14]. The quality of activated carbon is greatly influenced by the ash content, as the presence of ash can lead to pore blockages, which in turn reduces the surface area of the pores [15].

According to the quality standards set by [10], the iodine absorption capacity of activated carbon must reach at least 750 mg/g. However, the results of the iodine absorption test on the KA-PK 1 M and KA-SK 2 M samples showed values below this standard, namely 571.05 mg/g and 380.07 mg/g, respectively. This decrease is caused by the residual activating solution of H<sub>3</sub>PO<sub>4</sub> that remains after the washing process, causing the pores in the activated carbon to become blocked [16]. Additionally, the surface area results showed that the pore surface area of the activated carbon from coconut fronds reached 110.595 m<sup>2</sup>/g, while the laban wood powder was only 35.574 m<sup>2</sup>/g. To produce better activated carbon, variations in activation concentration should be tested. However, the results actually decreased due to the differences in material properties and incomplete elimination of minerals in the activator, which impacted the reduction in the surface area of the activated carbon pores formed [17].

# 5.2. River Water Sample Testing

The results of the river water sample testing using a combination of activated carbon with a 1:1 ratio can be seen in Table 2. Furthermore, these results are adjusted to the water quality standards and water pollution control regulations based on Government Regulation No. 82 of 2021, which includes Class III standards. Class III water is suitable for use in freshwater fish farming, livestock, and irrigation for plants.

The shorter the stirring time, the more acidic the pH value obtained. The washing process of activated carbon with  $H_3PO_4$  solution is carried out until the acidity level reaches neutral, because activated carbon is acidic in nature. This acidic property of activated carbon can lower the pH of the river water sample [18]. The decrease in the river water pH to an acidic level may be caused by an incorrect contact time. The  $H^+$  ions contained in the coconut frond and laban wood powder activated carbon, with  $H_3PO_4$  activator, indicate that the contact time intervals of 3 and 6 minutes are not optimal for the adsorption process. This is due to the presence of  $H_3PO_4$ , which increases the acidic pH in the river water sample [19].

Table 2. Results of the Donan River Mouth Water Sample Test							
Sample	<b>Temperature</b> (°C)	рН	Quality Standard pH	TSS (mg/L)	Quality StandardTSS (mg/L)	TDS (mg/L)	Quality Standard TDS (mg/L)
Before	36	8	6-9	546	400	5170	1000
K3	28	5,5	6-9	459	400	4910	1000
K6	26	5,5	6-9	456	400	4910	1000
K9	27	6,6	6-9	378	400	4910	1000
K12	26	7,5	6-9	273	400	4760	1000
K15	26	7,0	6-9	212	400	4690	1000

All solid particles present in water are referred to as Total Suspended Solids (TSS). TSS contaminants can form sediments and hinder the production of organic matter in water. The presence of TSS contaminants can also block sunlight, thereby inhibiting the photosynthesis process [20]. The results from the variation in contact time show that the TSS value decreases with increasing time. This is due to the high adsorption capacity of activated carbon, which effectively binds dissolved particles in the river water, thus reducing the TSS value.

As contact time increases, the TDS value from adsorption shows a decrease. This indicates that metals, organic compounds, minerals, and salts in the Donan River water sample are absorbed through the adsorption process [21]. However, the adsorption results show that the TDS value has not yet reached the quality standard, as the performance of the adsorbent is still not optimal in the adsorption process of river water.

## 5.3. Adsorption Kinetics

One way to evaluate the characteristics of adsorbents in environmental rehabilitation is through the adsorption kinetics equation. This adsorption kinetics model serves as a mathematical equation that helps estimate the adsorption rate or the sorption of adsorbates onto a particular adsorbent [22]. A factor that influences the sorption process is the variation in contact time. Adsorption equilibrium is a measure of the adsorption rate that requires contact time [23]. The adsorption kinetics on the river water samples, related to TDS and TSS parameters, can be seen in the reaction order 1 and 2 graphs attached in Table 3 below:

Table 3. Adsorption Kinetics					
Parameter	Reaction	K (minute <sup>-1</sup> )	R <sup>2</sup>		
	Order				
TDS -	1	0,0041	0,8734		
105 -	2	9x10 <sup>7</sup>	0,8722		
TSS -	1	0,0686	0,9232		
155 -	2	0,0002	0,8915		

The adsorption kinetics model, which shows a coefficient of determination ( $R^2$ ) approaching 1, can be seen in the adsorption kinetics data listed in Table 3. For the first-order reaction, the  $R^2$  values for each parameter were obtained as 0.8734 and 0.9232. Meanwhile, for the second-order reaction, the  $R^2$  values for each parameter were 0.8722 and 0.8915, which are still slightly lower than 1. This indicates that the value of K (min<sup>-1</sup>) provides an overview of the adsorption rate occurring [24]. The results obtained indicate that the adsorption rate for adsorbing the TSS and TDS parameters were 0.0041 min<sup>-1</sup> and 0.0686 min<sup>-1</sup>, respectively.

# 6. CONCLUSION

The analysis results of the characteristics of moisture content, ash content, and iodine adsorption capacity on the activated carbon samples KA-PK 1M and KA-SK 2M show that both meet the requirements of the SNI 06-3730-1995 standard. The iodine adsorption capacity for the KA-PK 1M sample was recorded as 571.05 mg/g, while the KA-SK 2M sample was 380.07 mg/g, both meeting the established quality standards. Additionally, the pore surface area test showed the best results for the KA-PK 1M sample with a value of 110,595 m<sup>2</sup>/g. In the adsorption kinetics test, the R<sup>2</sup> value approaching 1 indicates that this process follows a first-order reaction.

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